Preparation and Properties of the σ-Picolyl Complexes of Palladium(II), [{PdCl(C_5H_4N-2-CH_2)$PPh_{3-n}Me_n$}$_2$] (n=0, 1, and 2)

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The oxidative addition of 2-(chloromethyl)pyridine to tetrakis(triphenylphosphine)palladium(0) in toluene at 100 °C gave [{PdCl(C_5H_4N-2-CH_2)PPh_3}$_2$] (**1a**), which was characterized by analytical, molecular-weight, and IR data as well as ^1H, ^{31}P, and ^{13}C NMR spectroscopy. The chloride ligand was readily replaced by other halides, whereas tertiary phosphines such as diphenylmethyl-, phenyldimethyl-, and triethylphosphines cleaved the bridge after substitution of triphenylphosphine to result in the monomeric *trans*-[PdCl(C_5H_4N-2-CH_2)(PR_3)$_2$] complexes. Reactions of **1a** with carbon monoxide and other reagents are also reported. The corresponding 3-picolyl complex [{PdCl(C_5H_4N-3-CH_2)PPh_3}$_n$] was also prepared, but could not be well characterized because of lower stability and solubility.

Organopalladium complexes have been investigated extensively,[1] since they play important parts in organic synthesis as catalysts and/or intermediates.[2] The benzylpalladium(II) complexes prepared by oxidative addition of benzyl halides to palladium(0)[3] have attracted special attention of many workers. Thus Stille and his collaborators revealed the S_N2 nature of the oxidative addition of benzyl chloride and related compounds to $Pd(PPh_3)_4$ and $PdCO(PPh_3)_3$ based on the stereochemical investigations.[4] Carbon monoxide is readily inserted into the Pd-C bond,[5] leading to synthesis of ketones[6] and esters.[7] Oxidative addition of benzyl chloride to palladium atoms yielded dimeric η^3-benzylchloropalladium(II),[8] and the same η^3-benzylpalladium(II) structure was also realized by the reaction of *trans*-benzylchlorobis(triethylphosphine)palladium(II) with sodium tetraphenylborate in ethanol.[9]

The benzylpalladium(II) complexes have thus been studied extensively, but investigation of the picolylpalladium(II) complexes are rather few, although several papers have appeared in reporting the picolyl complexes of Cr,[10] Co,[11] and other metals such as Mn, Mo, and Fe,[12] and their reactions with various electrophiles.[13] Roberts and Klabunde[8] obtained a picolylpalladium(II) complex by cocondensation of 2-(chloromethyl)pyridine with palladium vapors, but the exact structure has not been clarified. Recently Hiraki and his collaborators reported several 2-picolylpalladium(II) complexes.[14] As an extension of our studies on the σ-pyridyl complexes,[15-17] this paper reports on the properties and structures of some picolyl-palladium(II) complexes. A preliminary account and X-ray molecular structure of the 2-picolylpalladium(II) complex have previously been reported.[18]

Experimental

Air-sensitive compounds were handled in an atmosphere of nitrogen using solvents and reagents which had been redistilled under and purged with nitrogen, respectively. Tetrakis(triphenylphosphine)palladium(0), $Pd(PPh_3)_4$, was prepared according to literature.[19] 3-(Chloromethyl)-pyridine was prepared by treating the hydrochloride commercially available with triethylamine in diethyl ether. Tertiary phosphines and other reagents were purchased and used without further purification.

Preparation of the [Chloro(2- and 3-picolyl)(triphenylphosphine)palladium(II)] Complexes, [{PdCl(C_5H_4N-2-CH_2)PPh_3}$_2$] (1a) and [{PdCl(C_5H_4N-3-CH_2)PPh_3}$_n$] (4). To a solution of $Pd(PPh_3)_4$ (3.15 g, 2.73 mmol) in toluene (50 cm^3) was added 2- or 3-(chloromethyl)pyridine (3.48 g, 27.3 mmol) and the mixture was heated to 100 °C for 30 min. The mixture was then left standing at room temperature for 4 h to deposit a yellow-green precipitate, which was filtered and dissolved in dichloromethane (50 cm^3). After filtration, the solvent was distilled away under reduced pressure to obtain a yellow solid of **1a** or **4** in 73 and 15% yields, respectively, which was recrystallized from a mixture of dichloromethane and methanol (1 : 5 by volume).

Preparation of the Bis[chloro(2-picolyl)(diphenylmethyl- and phenyldimethylphosphine)palladium(II)] Complexes, [{PdCl(C_5H_4N-2-CH_2)PPh_2Me}$_2$] (1b) and [{PdCl(C_5H_4N-2-CH_2)$PPhMe_2$}$_2$] (1c). To a solution of **1a** (0.28 g, 0.28 mmol) in dichloromethane (10 cm^3) was added PPh_2Me (0.43 g, 2.2 mmol) or $PPhMe_2$ (0.30 g, 2.2 mmol) to change the color of solution from yellow to pale orange-yellow. After the reaction at room temperature for 3 h, the solution was concentrated to ca. 3 cm^3 by evaporation under reduced pressure. The concentrate was charged onto a column (30 cm×1.5 cm d) of Aluminiumoxid 60 PF_{254} (Type E, Merck). Petroleum ether (150 cm^3) was passed through the column to elute the excess phosphine, and dichloromethane (70 cm^3) was used as the developing solvent. The eluate was concentrated to 10 cm^3 again, and petroleum ether (50 cm^3) was added to the concentrate to precipitate yellow crystals of **1b** or **1c** in 62 and 45% yields, respectively, which were recrystallized from a mixture of dichloromethane and diethyl ether (1 : 6 by volume).

Preparation of the Bis[bromo- and iodo(2-picolyl)-(triphenylphosphine)palladium(II)] Complexes, [{PdX-(C_5H_4N-2-CH_2)PPh_3}$_2$], X=Br (1d) and I (1e). A methanol

solution (15 cm^3) of sodium bromide (0.309 g, 3.00 mmol) or iodide (0.450 g, 3.00 mmol) was added to a dichloromethane solution (30 cm^3) of **1a** (0.15 g, 0.15 mmol). The mixture was allowed to react at room temperature for 3 h and then concentrated to ca. 20 cm^3 by evaporation under reduced pressure to deposit a yellow (**1d**) or deep yellow (**1e**) precipitate in 80 and 65% yields, respectively. They were recrystallized from a mixture of dichloromethane and methanol (1 : 5 by volume).

Preparation of the *trans*-Chloro(2-picolyl)bis(triethylphosphine and phenyldimethylphosphine)palladium(II) Complexes, *trans*-[PdCl(C_5H_4N-2-CH_2)(PR_3)$_2$], PR_3= PEt_3 (2a) and $PPhMe_2$ (2b). To a solution of **1a** (0.35 g, 0.35 mmol) in dichloromethane (10 cm^3) was added PEt_3 (0.50 g, 4.2 mmol) or $PPhMe_2$ (0.59 g, 4.3 mmol), when color of the solution changed from yellow to pale orange-yellow. After the reaction at room temperature for 3 h, the solution was concentrated to ca. 1 cm^3 by evaporation under reduced pressure. Diethyl ether (30 cm^3) was added to the concentrate and the mixture was cooled to −78 °C to precipitate white to pale yellow crystals in 15 (**2a**) and 62% (**2b**) yields, respectively. They were recrystallized at the Dry Ice-methanol temperature from a mixture of dichloromethane and diethyl ether (1 : 10 by volume) containing a small amount of free phosphine.

Preparation of Chloro(2-pyridylacetyl-*C,N*)(triphenylphosphine)palladium(II), [PdCl(C_5H_4N-2-CH_2CO-*C,N*)PPh_3] (3). Carbon monoxide was bubbled at ambient temperature and pressure for 8 h through a suspension of **1a** (0.15 g, 0.15 mmol) in tetrahydrofuran (THF) (50 cm^3) to result in a pale yellow clear solution. Then the vessel was stoppered and the reaction was allowed to continue for further 4 h. Then the slightly reddish solution was concentrated to ca. 10 cm^3 by evaporation under reduced pressure to precipitate white crystals in a 47% yield. A mixture of dichloromethane and diethyl ether (1 : 5 by volume) was used for recrystallization.

Reaction of 1a with Phenyldimethylphosphine. Four different quantities of phenyldimethylphosphine (0.009 g (0.065 mmol), 0.027 g (0.0195 mmol), 0.032 g (0.23 mmol), and 0.054 g (0.39 mmol)) were added to four tubes of which each contained a solution of **1a** (0.065 g, 0.065 mmol) in CD_2Cl_2 (0.3 cm^3). Concentrations of $PPhMe_2$ were 0.22, 0.65, 0.77, and 1.3 mol dm^{-3}, respectively, **1a** being 0.217 mol dm^{-3} in each solution. These solutions were subjected to ^1H NMR assay of **1c** and **2b** formed.

Reaction of 1a with Hydrogen Chloride. A dichloromethane solution (15 cm^3) of hydrogen chloride (0.07 mol dm^{-3}) was added dropwise to a solution of **1a** (0.23 g, 0.23 mmol) in dichloromethane (20 cm^3) and the mixture was stirred at room temperature for 2 h. The solvent was then evaporated to dryness under reduced pressure and the residue was extracted with CD_3OD (0.7 cm^3). The solution was subjected to ^1H NMR measurement to identify 2-methylpyridine hydrochloride. No other organic compounds except triphenylphosphine were detected. The residue was further extracted with chloroform. The extract was evaporated to dryness to leave an orange solid, which was identified to be trans-[$PdCl_2(PPh_3)_2$] by IR spectroscopy[20] and elemental analysis (Found: C, 60.93; H, 4.08%. Calcd for $C_{36}H_{30}Cl_2P_2Pd$: C, 61.60; H, 4.31%) and the yield was 36%.

Reaction of 1a with Silver Acetate. Silver acetate (0.12 g, 0.72 mmol) was added to a suspension of 1a (0.29 g, 0.29 mmol) in benzene (20 cm^3) and the mixture was allowed to react at 40 °C for 3 h. The solvent was evaporated to dryness under reduced pressure. The residue was treated with dichloromethane (20 cm^3), and silver chloride and remaining silver acetate were filtered off. The yellow filtrate was again evaporated to dryness and the residue was extracted with diethyl ether (20 cm^3). The solvent was vaporized and the residue was dissolved in $CDCl_3$ (0.5 cm^3). A small amount of 2-picolyl acetate was identified on the ^1H NMR spectrum (CH_3, 2.16 s; CH_2, 5.27 s; H^6 of pyridine, δ 8.66 d). On the other hand the IR spectrum of residue suggests the presence of triphenylphosphine, picolyl and acetoxyl groups, and the elemental analysis (C, 52.03; H, 4.10; N, 2.47%) is near the values calculated for [{$PdOCOCH_3(C_5H_4N$-$CH_2)PPh_3$}$_2$] (C, 60.07; H, 4.65; N, 2.69%). The yield was 43%. Purification was not successful.

Reaction of 1a with Phenylacetyl Chloride. To a solution of **1a** (0.32 g, 0.32 mmol) in CD_2Cl_2 (0.5 cm^3) were added C_6D_6 (4 cm^3) and phenylacetyl chloride (0.10 g, 0.65 mmol), and the mixture was heated to 80 °C for 3 h, color of the solution changing from yellow to red. Then the solution was cooled and evaporated to ca. 2 cm^3 under reduced pressure. Red-orange crystals were filtered and the filtrate was subjected to ^1H NMR spectrometry. The organic compound giving proton signals at 3.83 d and 4.17 s ppm could not be identified. The crystals were identified as $Pd_2Cl_4(PPh_3)_2$ by elemental analysis (Found: C, 48.76; H, 3.29%. Calcd for $C_{36}H_{30}P_2Cl_4Pd_2$: C, 49.18; H, 3.44%) and comparison of the IR spectrum with that of an authentic sample and literature.[21] The yield of the dinuclear complex in the present reaction was 73%.

Derivation of Methyl 2-Pyridylacetate from 1a. Carbon monoxide was passed slowly through a suspension of **1a** (0.18 g, 0.18 mmol) in THF (30 cm^3) for 7 h. A methanol solution (5 cm^3) of sodium methoxide (0.023 g, 0.43 mmol) was added to the reaction mixture and CO bubbling was continued for further 2 h. The solvent was evaporated to dryness under reduced pressure and the residue was extracted with diethyl ether (20 cm^3), which was again vaporized. The residue was dissolved in $CDCl_3$ (0.5 cm^3) and shown by ^1H NMR assay to contain a small amount of methyl 2-pyridylacetate (CH_3 and CH_2 overlapping, 3.77 broad: H^6 of pyridine, δ 8.40).

Measurements. Infrared spectra were recorded in Nujol on a JASCO DS-701G spectrophotometer. A JEOL JNM MH-100 instrument was used to obtain ^1H NMR spectra at 100 MHz with tetramethylsilane as internal reference. ^{13}C NMR spectra were taken at 25.0 MHz on a JEOL JNM FX-100 spectrometer with tetramethylsilane as external reference and ^{31}P NMR spectra were recorded at 40.25 MHz on the same instrument with phosphoric acid as external reference. The molecular weight was determined in dichloromethane at 25 °C by vapor pressure osmometry with an instrument manufactured by Knauer in West Berlin, West Germany.

Results and Discussion

Although $Ni(PPh_3)_4$ reacted readily with 2-, 3-, and 4-(chloromethyl)pyridines, the expected picolylnickel(II) complexes could not be isolated, On the other hand, the reactions of $Pd(PPh_3)_4$ with these pyridine

Table 1. Analytical Data for the Picolyl Palladium(II) Complexes

Complex		Found (Calcd)			
		C/%	H/%	N/%	Mol wt
[{PdCl(C_5H_4N-2-CH_2)PPh_3}$_2$]	**1a**	58.01 (58.09)	4.30 (4.29)	2.94 (2.82)	924 (993)
[{PdCl(C_5H_4N-2-CH_2)PPh_2Me}$_2$]	**1b**	52.71 (52.56)	4.42 (4.41)	3.11 (3.23)	851 (868)
[{PdCl(C_5H_4N-2-CH_2)$PPhMe_2$}$_2$]	**1c**	45.17 (45.19)	4.58 (4.61)	3.65 (3.76)	733 (744)
[{PdBr(C_5H_4N-2-CH_2)PPh_3}$_2$]	**1d**	52.70 (53.31)	4.02 (3.91)	2.50 (2.59)	1065 (1081)
[{PdI(C_5H_4N-2-CH_2)PPh_3}$_2$]	**1e**	48.23 (49.05)	3.51 (3.60)	2.24 (2.38)	1083 (1175)
[PdCl(C_5H_4N-2-CH_2)(PEt_3)$_2$]	**2a**	45.77 (45.97)	7.42 (7.72)	2.75 (2.98)	447 (470)
[PdCl(C_5H_4N-2-CH_2)($PPhMe_2$)$_2$]	**2b**	51.88 (51.78)	5.57 (5.53)	2.46 (2.74)	501 (510)
[PdCl(C_5H_4N-2-CH_2CO)PPh_3]	**3**	57.09 (57.28)	4.14 (4.04)	2.70 (2.67)	518 (524)
[{PdCl(C_5H_4N-3-CH_2)PPh_3}$_n$]	**4**	57.41 (58.09)	4.11 (4.27)	2.61 (2.82)	

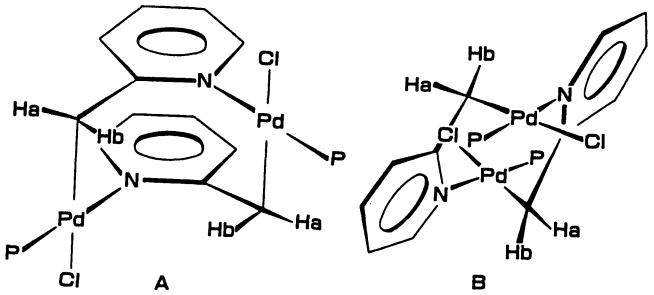


Fig. 1. Two possible dinuclear structures for [{PdCl(C_5H_4N-2-CH_2)PPh_3}$_2$] (**1a**).

Table 2. Some Far IR Data in cm^{-1}

Complex	ν(Pd-X)	ν(Pd-P)
1a	284m	420m
1b	280m	430m
1c	268m	420m
1d	181m	420m
1e	153m	420w
2b	278m	415m
3	292w	427m
4	265w	420w

derivatives did not take place at room temperature, but occurred at 100 °C to finish after 30 min. The 2- and 3-picolylpalladium(II) complexes were isolated, but stability and solubility of the latter were not enough to allow full characterization. The 4-picolyl complex was not even isolated. Thus the stability of the picolylpalladium(II) complexes varies remarkably with the site of substitution on the pyridine ring.

Characterization of the Dinuclear Picolyl Complexes. The analytical and molecular-weight data in Table 1 indicate that complexes **1a** and **1b—1e** which were derived from **1a** by the ligand substitution reactions are dinuclear. As a dinuclear structure for the palladium(II) complexes the di-μ-chloro structure is most common.[21] However, X-ray analysis revealed that [{PdBr(C_5H_4N-C^2)PPh_3}$_2$] has the pyridyl(C^2, N)-bridged structure.[22] If the picolyl ligand in the present dinuclear complexes also functions as a similar bridging ligand, the two structures depicted in Fig. 1 are conceivable. Structure A has a C_2 axis, while B being shown in the 2-litiomethyl-6-methylpyridine-tetramethylethylenediamine dimer[23] has a center of inversion. Hiraki and his co-workers proposed structure B,[14] but molecular models indicate that A is more favorable, since the bulky triphenylphosphine ligands experience a serious steric interference by the picolyl ligand in structure B. In fact X-ray analysis has confirmed that compound **1a** has structure A.[18]

The ν(Pd-Cl) frequencies observed for **1a—1c** (Table 2) are rather low for the terminal chloride, but are reasonable when located at the coordination site trans to carbon.[5] Table 3 lists ^1H NMR data for complexes **1a—1c**. The pyridyl ring protons are readily assigned by reference to the data for free 2-picoline[24] except the H^6 atoms of **1a** and **1b** of which signals are indiscernible because of overlapping with those for the phenyl-ring protons. Thus, the triplet signal at about δ 6.5 is assigned to H^5 and the doublet in the δ 6.7—7.0 region to H^3 which resonates at lower field than H^5 because of the anisotropic effect of the (PPh_3)ClPdCH$_2$ substituent.[25,17] The remaining triplet in the δ 7.0—7.3 region is attributed to H^4, H^6 of **1c** appearing as a doublet at δ 7.84.

Each of the pyridyl-ring protons except H^4 of the picolyl ligands resonates at a remarkably higher field than that of 2-(chloromethyl)pyridine (H^3 and H^5, around δ 7.6; H^4, 7.13; H^6, 8.56).[12a] In the case of Fe(C_5H_4N-2-CH_2)(η^5-C_5H_5)(CO)$_2$, the pyridyl-ring

protons show similar upfield shifts (H^3 and H^5, δ 6.90; H^4, 7.32; H^6, 8.28),[12a] which were considered to be caused by the electron-donating effect of the CH_2ML_n moiety.[11,12b] The phenyl-ring protons in **1a**, **1b**, and **1c** exhibit two multiplets at about δ 7.5 and 7.9, the former being assigned to the meta and para protons and the latter to the ortho protons.[26] The methyl protons of the phosphine in **1b** resonate as a doublet at δ 2.22 with ^2J(P-H)=ca. 12.5 Hz, but those in **1c** exhibit two doublets at δ 1.88 and 1.91 both with ^2J(P-H)=ca. 11 Hz (Fig. 2), showing that the two methyl groups of phenyldimethylphosphine in **1c** differ in their time-averaged magnetic environments. This indicates that there is no plane of symmetry through the Pd-P bond[27] in accordance with the dinuclear structure A in Fig. 1.

The methylene protons of the picolyl ligand in **1a**—**1c** are not equivalent as is seen in Fig. 1, but exhibit two separate signals in the δ 2.42—2.52 and 3.72—3.81 regions, respectively (Fig. 2 and Table 3). The higher-field signal is a triplet and the lower-field one doublet, both having the same coupling constant of about 9 Hz. Irradiation at the frequency of the triplet reduced the lower-field doublet to a singlet, and irradiation at the latter frequency reduced the triplet to a doublet, confirming the geminal coupling (J=ca. 9 Hz) of the methylene protons. The ^{31}P NMR spectrum of **1a** exhibits a signal at δ 36.06 downfield from H_3PO_4. Irradiation only at the region for the phenyl-ring protons gave a doublet shown in Fig. 3. The coupling constant is ca. 9 Hz, indicating that the phosphorus atom couples to one of the methylene protons which resonates as a triplet. As is seen in Fig. 2, the low-field doublet for **1c** splits due to ca. 3 Hz coupling to phosphorus. Thus one of the methylene protons in **1c** strongly couples to ^{31}P with J=ca. 9 Hz, while the other weakly with J=ca. 3 Hz.

Table 4 lists the ^{13}C chemical shifts and J(P-C) values for complex **1a** together with the corresponding data for uncoordinated triphenylphosphine[28] and 2-ethylpyridine[29] for comparison. Assignment for the phenyl carbons in **1a** was made on the basis of J(P-C)

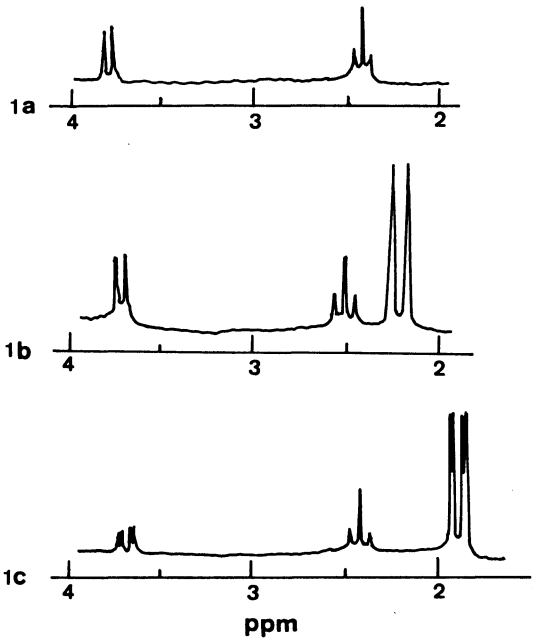


Fig. 2. Methyl and methylene signals in ^{1}H NMR spectra of [{PdCl(C$_5$H$_4$N-2-CH$_2$)L}$_2$] with PPh_3 (**1a**), PPh_2Me (**1b**) and $PPhMe_2$ (**1c**) as L.

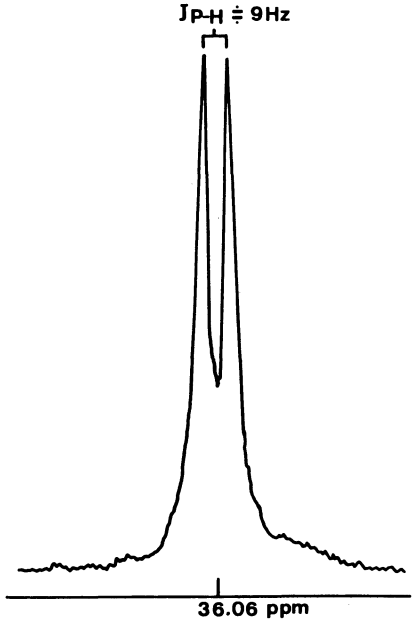


Fig. 3. ^{31}P NMR signal from [{PdCl(C$_5$H$_4$N-2-CH$_2$)PPh$_3$)$_2$] (**1a**) under irradiation at the phenyl-ring proton resonances.

Table 3. Proton Chemical Shifts in ppm from Internal Tetramethylsilane at Room Temperature

Complex	Solvent	Pyridyl-ring proton				CH_2	Phenyl-ring proton		CH_3
		H^3	H^4	H^5	H^6		meta and para	ortho	
1a	CD_2Cl_2	6.95d	7.26t	6.53t	a)	2.44t 3.81d	7.55m	7.89m	
1b	$CDCl_3$	6.80d	7.15t	6.47t	a)	2.52t 3.72d	7.51m	7.85m	2.22d
1c	$CDCl_3$	6.74d	7.09t	6.46t	7.84d	2.42t 3.75dd	7.53m	7.97m	1.88d, 1.91d
2b	CD_2Cl_2	7.13d	6.77t	6.53br	8.15d	2.78s,br	7.43m	7.65m	1.80s
3	$CDCl_3$	a)	a)	a)	9.57d	4.11s	7.45m	7.75m	

a) Indiscernible because of overlapping with signals from the phenyl-ring proton.
s: singlet, d: doublet, t: triplet, dd: doublet of doublets, m: multiplet, br: broad.

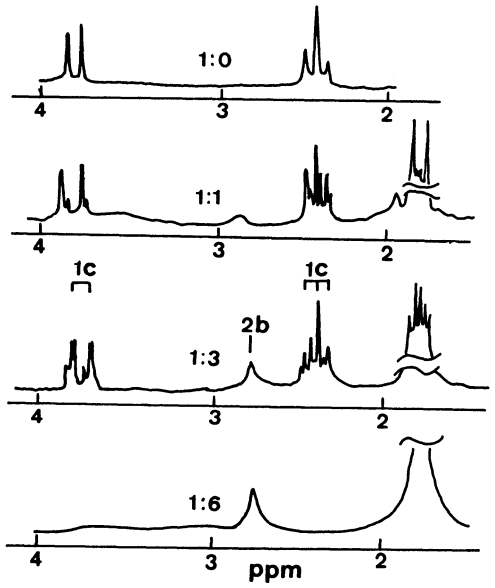
values and by reference to uncoordinated PPh_3 and $[\{PdBr(C_5H_4\text{-}C^2)PPh_3\}_2]$.[16] The methylene carbon of the picolyl ligand in **1a** resonates at δ 28.47 and appears as a triplet of doublets under the off-resonance condition, ^2J(P-C) being ca. 7 Hz. The small coupling constant suggests that the methylene and phosphine ligands are mutually cis. Assignments for the pyridyl-ring carbons were made based on the off-resonance data and referring to $[\{PdBr(C_5H_4N\text{-}C^2)PPh_3\}_2]$.[16] As is shown by Table 4, the shielding of each carbon is quite similar to that of the corresponding ring carbon in 2-ethylpyridine, indicating that the $(PPh_3)ClPdCH_2$ moiety is functioning as an electron-donating group, but the effect is weaker than that of the $(PPh_3)BrPd$ group directly attached to the pyridyl ring in $[\{PPdBr(C_5H_4N\text{-}C^2)PPh_3\}_2]$.[16]

Table 4. ^{13}C Chemical Shifts δ (in ppm from external Me_4Si) and Coupling Constants J (in Hz) in CD_2Cl_2 at Room Temperature

Phenyl carbon in **1a**			Phenyl carbon in free PPh_3		
	δ	J(P-C)		δ	J(P-C)
C^1	130.98	51.5	C^1	138.3	21
C^2	135.13	11.8	C^2	134.4	20
C^3	128.60	11.8	C^3	129.2	7
C^4	131.01	0	C^4	129.3	<1
Picolyl carbon in **1a**			2-Ethylpyridine		
	δ	J(P-C)		δ	
CH_2	28.47	ca. 7	CH_2	32.0	
C^2	169.83		C^2	163.9	
C^3	123.48		C^3	121.9	
C^4	136.01		C^4	136.3	
C^5	117.7		C^5	121.9	
C^6	151.72		C^6	149.8	

Although the 3-picolyl complex **4** was prepared and isolated, it is less stable and less soluble in organic solvents than the 2-picolyl complex **1a** and its characterization has not been enough to allow the structure assignment. Results of the elemental analysis indicate that the complex is not mononuclear but may be polynuclear, since a dinuclear structure seems difficult.

Characterization of the Mononuclear Picolyl Complexes. The mononuclear picolyl complexes **2a** and **2b** were prepared by the reactions of **1a** with excess amounts of PEt_3 and $PPhMe_2$, respectively and isolated at low temperature. The analytical and molecular-weight data in Table 1 indicate that they are mononuclear and the ν(Pd-Cl) frequency of **2b** in Table 2 is quite similar to that recorded for *trans*-$[PdCl(CH_2Ph)(PPh_3)_2]$.[3] The ^1H NMR data for **2b** are included in Table 3. Contrary to the case of **1c**, the methyl protons of the phosphine ligands in **2b**



$$[\{PdClR(PPh_3\}_2] + 2PPhMe_2 \rightleftharpoons [\{PdClR(PPhMe_2)\}_2] + 2PPh_3$$

1a **1c**

$+2PPhMe_2$ $-2PPhMe_2$

$2[PdClR(PPhMe_2)_2]$

2b

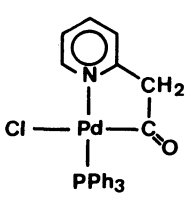
Fig. 4. The methylene-proton signals from $[\{PdCl(C_5H_4N\text{-}2\text{-}CH_2)PPh_3\}_2]$ (**1a**) in CD_2Cl_2 at room temperature in the absence and in the presence of one equivalent, three times, and six times molar amount of phenyldimethylphosphine. In the reaction scheme R represents the 2-picolyl ligand.

resonate as a singlet at δ 1.80 with no coupling to phosphorus, and the picolylic protons also exhibit a broad singlet at δ 2.78. The benzylic protons in *trans*-[PdCl(CH_2Ph)(PPh_3)$_2$] also lack coupling to phosphorus and the behavior was rationalized by the rapid phosphine exchange between the mononuclear complex and PPh_3 freed by the equilibrium $2[PdCl(CH_2Ph)(PPh_3)_2] \rightleftarrows [\{PdCl(CH_2Ph)PPh_3\}_2]+2PPh_3$.[3] Similar situation seems to be realized for **2b**. In fact the ^{1}H NMR spectrum of **2b** in CD_2Cl_2 at −40 °C exhibits two triplets at δ 1.83 and 2.74 assignable to the phosphine methyl (J=ca. 3 Hz) and picolyl methylene (J=ca. 8 Hz) protons, respectively, indicating that the rapid phosphine exchange is prohibited at lower temperature and that **2b** has the trans structure.[30]

The Phosphine Substitution and Bridge Cleavage Reactions of 1a with Phenyldimethylphosphine. Figure 4 compares the methylene-proton signals exhibited by solutions of **1a** in CD_2Cl_2 at room temperature containing various amounts of $PPhMe_2$. An equimolar mixture of **1a** and $PPhMe_2$ shows signals assignable mainly to **1a** and **1c** accompanied by a small amount of **2b** giving the signal at δ 2.78. When a three times molar amount of $PPhMe_2$ is added to **1a**, the predominant species is **1c** and the amount of **2b** is also increased. The last spectrum in Fig. 4, which is given by a 1:6 mixture of **1a** and $PPhMe_2$, is composed of broad signals assignable solely to **2b**. Such a sequence of spectra indicates that the phosphine substitution reaction of **1a** with $PPhMe_2$ to produce **1c** takes place prior to the bridge cleavage to result in a mononuclear complex **2b**.

As was described in the Experimental section, the mononuclear complexes **2a** and **2b** were obtained upon direct crystallization from the reaction mixture, but the dinuclear complexes **1b** and **1c** were isolated by virtue of the chromatographic separation of the mixture.

Characterization of the 2-Pyridylacetyl Complex 3. Complex **1a** reacted readily with carbon monoxide in THF to afford white crystals of **3**, which is shown to be mononuclear by the analytical and molecular-weight data in Table 1. A very strong IR band at 1690 cm^{-1} is assigned to the ν(C=O) vibration and a weak band at 330 cm^{-1} may be tentatively assigned to the ν(Pd-N) vibration. The ^{1}H NMR spectrum shows the methylene signal as a sharp singlet at δ 4.11. These spectral data for **3** conform with the following (*C,N*) chelate structure.



3

In this structure the pyridyl ring lies on the coordination plane and the methylene protons experience equal magnetic environment. Although the signals from the pyridyl-ring protons except H^6 are indiscernible because of overlapping with those from the phenyl-ring protons, H^6 resonates at δ 9.57. Such a remarkable downfield shift of H^6 may be caused by the deshielding anisotropic effect of the carbonyl group. Similar 2-pyridylacetyl complexes (C_5H_4N-2-CH_2CO)$Mn(CO)_4$ and (C_5H_4N-2-CH_2CO)$Mo(CO)_2$-(η^5-C_5H_5), to both of which the (C,N) chelate structure is proposed, show the methylene singlet at δ 4.00 and the pyridyl-ring H^6 doublet at δ 8.99 and 8.96, respectively.[12a]

Reactions of the Picolyl Ligand with Some Reagents. As was described in the Experimental section, reactions of the picolyl ligand with some reagents were examined. Hydrogen chloride decomposed **1a** in dichloromethane to produce 2-picoline hydrochloride and *trans*-$PdCl_2(PPh_3)_2$. The reaction of **1a** with silver acetate in benzene gave a small amount of 2-picolyl acetate and a complex which was presumed to be [{$PdOCOCH_3$(C_5H_4N-2-CH_2)-PPh_3}$_2$]. The acetato complex may be formed by the ligand substitution of **1a** and function as an intermediate for production of 2-picolyl acetate. Production of benzyl acetate by the reaction of *trans*-benzylchlorobis(triphenylphosphine)palladium(II) with silver acetate was similarly presumed to be preceded by replacement of chloride with acetate.[3] The reaction between **1a** and phenylacetyl chloride was tried with the aim of getting 2-picolyl benzyl ketone, but identification of organic products was unsuccessful, although [{$PdCl_2(PPh_3)$}$_2$] was obtained in a high yield. Carbonylation of **1a** followed by the reaction with methoxide gave methyl 2-pyridylacetate. This is analogous to the reactions reported for the benzylpalladium(II) complex.[4,7] Thus complex **1a** is a useful intermediate for preparation of various pyridine derivatives.

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