

SYNTHESES AND CHARACTERIZATION OF SOME NEW 2-PICOLYLPALLADIUM(II) COMPLEXES

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Summary

The 2-picolylpalladium(II) complex $[\{\text{Pd}(\text{CH}_2\text{Py})\text{Cl}(\text{PPh}_3)\}_2]$ (CH_2Py = 2-picolyl) (I), prepared from 2-picolyl chloride and $[\text{Pd}(\text{PPh}_3)_4]$, was treated with lithium bromide, silver acetate, 4-picoline (pic) and silver perchlorate, thallium acetylacetonate $\{\text{Tl}(\text{acac})\}$, sodium dimethyldithiocarbamate-water- $(1/2) \{\text{Na}(\text{dmdc}) \cdot 2 \text{H}_2\text{O}\}$, and 1,2-bis(diphenylphosphino)ethane (dppe) to yield $[\{\text{PdBr}(\text{CH}_2\text{Py})(\text{PPh}_3)\}_2]$ (II), $[\{\text{Pd}(\text{CH}_2\text{Py})\text{OAc}(\text{PPh}_3)\}_2]$ (III), $[\{\text{Pd}(\text{CH}_2\text{Py})(\text{pic})(\text{PPh}_3)\}_2](\text{ClO}_4)_2$ (IV), $[\text{Pd}(\text{CH}_2\text{Py})(\text{acac})(\text{PPh}_3)]$ (V), $[\text{Pd}(\text{CH}_2\text{Py})(\text{dmdc})(\text{PPh}_3)]$ (VI), and $[\text{Pd}(\text{CH}_2\text{Py})\text{Cl}(\text{dppe})]$ (VII), respectively. Halogen abstraction from VII using silver perchlorate afforded an ionic complex $[\{\text{Pd}(\text{CH}_2\text{Py})(\text{dppe})\}_2](\text{ClO}_4)_2$ (VIII). It was concluded that the 2-picolyl groups in these eight complexes are σ -bonded to palladium, and that in the dinuclear complexes I, II, III, IV, and VIII, they serve as bridging ligands.

Introduction

Oxidative addition to metal complexes in a lower oxidation state has received considerable attention in terms of its application to transition-metal catalysis and synthesis of organotransition-metal compounds [1–3]. It has been reported that oxidative addition of benzyl halides to tetrakis(tertiary phosphine)palladium(0) gives η^1 -benzylpalladium(II) complexes, which are converted into the η^3 -benzylic type by a halogen-abstraction reaction using NaBPh_4 and NaBF_4 [4]. Interest in these bonding modes led us to undertake an investigation of the coordination behavior of the 2-picolyl group compared with that of the benzyl group. Two recent reports of similar investigations [5,6] prompt us to present our results. Roberts and Klabunde obtained a few 2-picolylpalladium(II) compounds from palladium vapour and 2-picolyl chloride [5], whereas Kawaguchi and his coworkers prepared some 2-picolylpalla-

dium(II) complexes from $[\text{Pd}(\text{PPh}_3)_4]$ and 2-picoly1 compounds [6].

The present work deals with a chloro(2-picoly1)palladium(II) complex, $[\{\text{Pd}(\text{CH}_2\text{Py})\text{Cl}(\text{PPh}_3)\}_2]$ (CH_2Py = 2-picoly1) (I), which was obtained from the oxidative addition between $[\text{Pd}(\text{PPh}_3)_4]$ and 2-picoly1 chloride, and with several new 2-picoly1palladium(II) complexes derived from I. The coordination of the 2-picoly1 groups in these complexes is discussed.

Experimental

General procedures

Melting points were taken in capillary tubes on a Yanagimoto MP-S3 micro-stage apparatus and are uncorrected. IR spectra were recorded on a Hitachi model 285 spectrometer and a Shimadzu IR-450 spectrometer. ^1H and ^{13}C NMR spectra were run on a Japan Electron Optics Laboratory (JEOL) model JNM-MH-100 and FX-100 spectrometers, respectively, using tetramethylsilane as the internal standard. Mass spectra were obtained with a JEOL model JMS-01SG double-focussing mass spectrometer. Molar conductivities were measured with a Toa Denpa CM-6A instrument. The molecular weight of a complex was determined in dichloromethane using a Mechrolab model 301 vapour pressure osmometer.

Solvents were dried and distilled by the usual methods, and all preparative operations were performed in an atmosphere of dry nitrogen. 2-(Chloromethyl)pyridine hydrochloride was prepared according to the method of Winterfeld and Flich [7].

Oxidative addition of 2-picoly1 chloride to $[\text{Pd}(\text{PPh}_3)_4]$

A sodium carbonate solution was added to an aqueous solution (5 ml) of 2-(chloromethyl)pyridine hydrochloride (7.1 mmol), until the solution reached pH 11. The resulting oil was extracted with three portions of benzene (total 25 ml). The benzene solution of 2-picoly1 chloride thus obtained was added to a benzene suspension (20 ml) of $[\text{Pd}(\text{PPh}_3)_4]$ (1.3 mmol). The mixture was heated at 45°C for 6 h, and the resulting precipitate was recrystallized from dichloromethane and diethyl ether and washed with diethyl ether to give $[\{\text{Pd}(\text{CH}_2\text{Py})\text{Cl}(\text{PPh}_3)\}_2]$ (I).

Halogen metathesis of I

A mixture of complex I (0.10 mmol) and lithium bromide (0.46 mmol) was heated in acetone at reflux for 5 h, and the solvent was evaporated in vacuo. The residue was recrystallized from dichloromethane and diethyl ether, and the resulting powder was washed successively with water, methanol, and diethyl ether, yielding the corresponding bromo complex, $[\{\text{PdBr}(\text{CH}_2\text{Py})(\text{PPh}_3)\}_2]$ (II).

Reaction of I with silver acetate

A benzene solution (40 ml) of I (0.40 mmol) and silver acetate (1.04 mmol) was heated at 40°C for 4 h, and concentrated at reduced pressure. Addition of diethyl ether to the concentrated solution afforded pale yellow needles, $[\{\text{Pd}(\text{CH}_2\text{Py})\text{OAc}(\text{PPh}_3)\}_2]$ (III).

Reaction of I with 4-picoline and silver perchlorate

A benzene solution (40 ml) containing I (0.20 mmol), 4-picoline (pic) (1.02 mmol), and silver perchlorate (0.41 mmol) was stirred at room temperature for 30 min to yield a yellow precipitate. The precipitate was recrystallized from dichloromethane and diethyl ether, followed by washing with diethyl ether, to give a pale yellow powder, $[\{\text{Pd}(\text{CH}_2\text{Py})(\text{pic})(\text{PPh}_3)\}_2](\text{ClO}_4)_2$ (IV).

Reactions of I with thallium acetylacetonate and sodium dimethyldithiocarbamate

A mixture of I (0.15 mmol) and thallium acetylacetonate $\{\text{Tl}(\text{acac})\}$ (0.40 mmol) was stirred in benzene at room temperature for 70 h. After the solvent was removed, the residue was recrystallized from dichloromethane and diethyl ether to yield a pale yellow powder, $[\text{Pd}(\text{CH}_2\text{Py})(\text{acac})(\text{PPh}_3)]$ (V).

A benzene suspension (30 ml) of I (0.20 mmol) and sodium dimethyl dithiocarbamate/water(1/2) $\{\text{Na}(\text{dmdc}) \cdot 2 \text{H}_2\text{O}\}$ (0.52 mmol) was stirred at room temperature for 20 h. The resulting solid was filtered and the filtrate was concentrated. Addition of petroleum ether to the concentrated solution yielded a reddish-yellow precipitate which was washed with diethyl ether to afford $[\text{Pd}(\text{CH}_2\text{Py})(\text{dmdc})(\text{PPh}_3)]$ (VI).

Reaction of I with 1,2-bis(diphenylphosphino)ethane

1,2-Bis(diphenylphosphino)ethane (dppe) (0.30 mmol) was added to a benzene solution of I (0.10 mmol), followed by stirring for 2 h at room temperature. Slow addition of diethyl ether afforded pale yellow microcrystals of $[\text{Pd}(\text{CH}_2\text{Py})\text{Cl}(\text{dppe})]$ (VII). Molecular weight: found 586; calcd. 632.4.

Reaction of VII with silver perchlorate

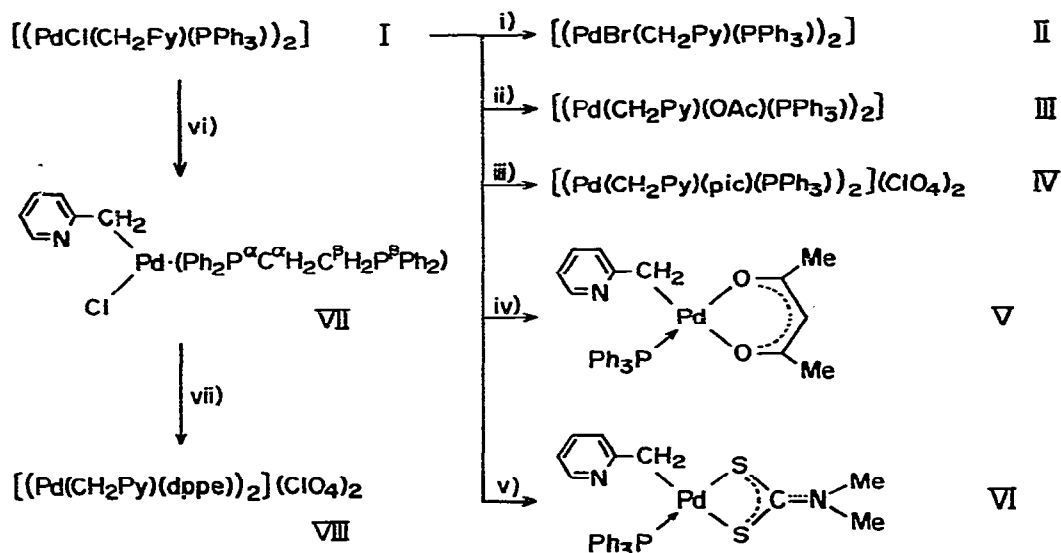
A benzene solution of silver perchlorate (0.22 mmol) was added to a benzene solution of VII (0.22 mmol) at room temperature. A mixture was stirred for 30 min and the solvent was evaporated. The residue was washed with benzene and recrystallized from acetone and diethyl ether to give $[\{\text{Pd}(\text{CH}_2\text{Py})(\text{dppe})\}_2](\text{ClO}_4)_2$ (VIII).

Results and discussion

Oxidative addition of 2-picolyl chloride to $[\text{Pd}(\text{PPh}_3)_4]$ afforded I, as recently reported by Kawaguchi and his coworkers [6]. Complex I was treated with LiBr, AgOAc, 4-picoline and AgClO_4 , $\text{Tl}(\text{acac})$, $\text{Na}(\text{dmdc}) \cdot 2 \text{H}_2\text{O}$, and dppe to give the corresponding 2-picolylpalladium(II) complexes II–VII, respectively. Halogen abstraction from VII using AgClO_4 afforded the ionic complex VIII. Complexes I–VIII are stable and soluble in dichloromethane and chloroform. Yields, analyses, and some properties of these new palladium complexes are given in Tables 1 and 2. All these complexes showed two bands near 1430 and 1470 cm^{-1} , attributable to $\nu(\text{P}-\text{C})$ frequencies of the tertiary phosphine group, and two bands near 1550 and 1575–1600 cm^{-1} , assignable to the $\nu(\text{C}=\text{C}, \text{C}=\text{N})$ bands of the pyridine ring (Table 2).

Dinuclear complexes I–IV

The ^1H NMR spectrum of I in CD_2Cl_2 showed non-equivalent methylene pro-



SCHEME 1

i) LiBr. ii) AgOAc. iii) pic + AgClO₄. iv) Tl(acac). v) Na(dmde) · 2 H₂O. vi) dppe. vii) AgClO₄.

tons [a doublet (²J 9.6 Hz) at δ 3.78 and a virtual triplet at δ 2.41]. On irradiation of the former signal, the latter changed to a doublet due to a coupling with the ³¹P nucleus in triphenylphosphine ligand. The same geminal coupling of the two methylene protons and the coupling of the ³¹P nucleus to one of the two protons were observed for I by Kawaguchi et al [6]. They proposed a chloro-bridged dinuclear structure of I, as shown in Fig. 1-A, on the basis of the ¹H NMR spectrum, its molecular weight (found 924, calcd. 993) and far-infrared spectrum [6].

In the proton-decoupled ¹³C NMR spectrum of I in CDCl₃, the picolyl group gave two singlets, one doublet, and three slightly broadened singlets without any virtual splitting. The former two singlets at δ 135.3 and 169.2 ppm were assignable to 4-C and 2-C, respectively. The doublet at δ 123.0 (⁴J(HP) 3.9 Hz)

TABLE 1
SYNTHESES OF THE 2-PICOLYLPALLADIUM COMPLEXES

Complex	Yield ^a (%)	Color	M.p. (°C) ^b	Analysis, found (calcd.) (%)		
				C	H	N
I	47 ^c	Pale yellow	208–114	58.24(58.09)	4.17(4.27)	2.70(2.82)
II	37	Yellow	191–193	52.80(53.31)	3.95(3.91)	2.48(2.59)
III	51	Pale yellow	171–174	58.95(60.07)	4.52(4.65)	2.72(2.69)
IV	52	Pale yellow	181–183	55.00(55.15)	4.34(4.32)	4.14(4.29)
V	30	Pale yellow	125–140	44.59(44.39)	4.26(4.40)	4.46(4.71)
VI	67	Reddish yellow	174–176	55.94(55.82)	4.63(4.68)	4.76(4.82)
VII	58	Greenish yellow	181–183	60.87(60.78)	4.89(4.78)	2.17(2.21)
VIII	41 ^d	Yellow	215–220	55.01(55.19)	4.29(4.34)	1.94(2.10)

^a Based on I, unless noted elsewhere. ^b With decomposition. ^c Based on [Pd(PPh₃)₄]. ^d Based on VII.

and one of the latter three signals at δ 117.3 were assigned to 3-C and 5-C, the remaining two signals at δ 28.6 and 151.3 to methylene carbon and 6-C, respectively. It is noted that the methylene carbon exhibited no coupling with the ^{31}P nucleus. This fact indicates that the methylene carbon is situated *cis* to the triphenylphosphine ligand. Our conductivity measurements of I and its bromo derivative II in acetone showed them to be non-ionic, and treatment with an excess of methyl iodide at ca. 50°C did not increase their conductivities, indicating that no quarterization of the 2-picolyyl nitrogen had taken place. Although I hardly sublimed, its mass spectrum, observed at ca. 150°C , showed a weak fragment ion centered at m/e 496, which corresponds to $[\text{Pd}(\text{CH}_2\text{Py})\text{Cl}(\text{PPh}_3)]$ and no fragment above m/e 500. It is tempting to suggest that dimeric I might be fragmented into the monomer at high temperature.

Chlorine abstraction from I with silver perchlorate in the presence of 4-picoline gave an ionic complex, IV, which was confirmed both by its high conductivity in acetone and by detection of a $T_2(\text{OCIO})$ bending mode at 626 cm^{-1} and a $T_2(\text{ClO})$ stretching mode at 1090 cm^{-1} without any significant splitting. Lack of perchlorate coordination was also supported by the absence of an $A_1(\text{ClO})$ stretching mode (ca. 935 cm^{-1}), expected for a coordinated perchlorate. Moreover, the ^1H NMR spectra of II, III, and IV showed geminal coupling of the two methylene protons and coupling of the ^{31}P nucleus to one of the two protons, similar to I (Table 2). This evidence indicates unambiguously that IV, which involves no chlorine ligand, has a structure similar to I, II, and III, and, accordingly, that the dinuclear complexes I, II, and IV do not have a halogeno-bridged structure (Fig. 1-A), but a 2-picolyyl-bridged one, as depicted in Fig. 1-B and Fig. 2. In the latter structure, the 2-picolyyl group is bonded to one palladium atom with the methylene carbon and to another palladium atom with the 2-picolyyl nitrogen, causing the non-equivalence and the geminal coupling of the methylene protons. This structure is consistent with the conductivity measurements, and is reasonable since the pyridine group generally acts as a typical bridge-splitting reagent.

The IR spectrum of III in a KBr disk showed two bands at 1382 and 1575 cm^{-1} , assignable to $\nu_s(\text{OCO})$ and $\nu_{as}(\text{OCO})$, respectively. Both the former band

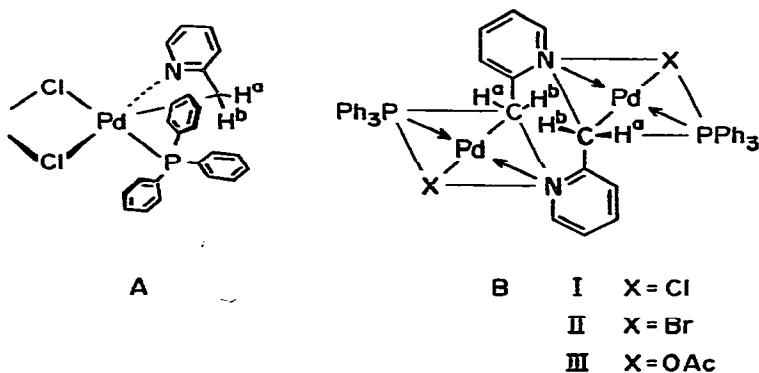
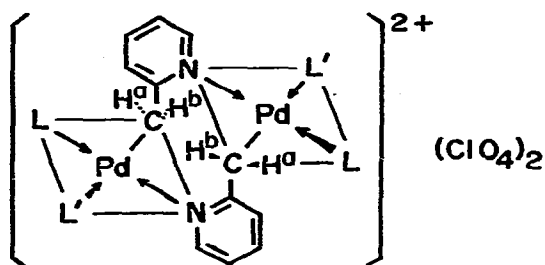


Fig. 1. Possible structures for I-III. A) The halogeno-bridged structure. B) The 2-picolyyl-bridged structure.

TABLE 2
SOME PROPERTIES OF THE 2-PICOLYL-PALLADIUM COMPLEXES

Complex	IR data ^a $\nu(\text{C}=\text{C}, \text{C}=\text{N})$ (cm^{-1})	H NMR data ^c		δ	J(PH) (Hz)	Other protons ^e						ΔM^f ($\Omega^{-1} \text{cm}^2 \text{M}^{-1}$)
		CH ₂ Py	δ			3-H ^d δ	4-H ^d δ	5-H ^d δ	6-H ^d δ	Other protons ^e δ		
I	1590, 1550	2.41t ^g , 3.78d ^g	9.6	6.91d	6.53t	7.22t	— ^h	—	—	—	0.9	
II	1599, 1556	2.47t ^g , 3.90d ^g	9.2	6.82d	6.43t	7.11t	— ^h	—	—	—	2.0	
III	1598, — ⁱ	2.65dd ^j , 4.06d ^j	12	6.47d	6.40t	7.07t	— ^h	1.16s(Me) ^k	—	—	—	
IV	1597, 1560	2.81t ^g , 3.79d ^g	10	7.09d	6.56t	7.25t	8.18t	2.08s(Me) ^k	—	—	176	
V	1580 ⁱ , 1560sh	2.89d	3.9	— ^h	6.85t	— ^h	8.14d	6.72d (H _g) ^k , 7.80d (H _g) ^k	—	—	—	
VI	1574, 1540sh	2.61d	6.3	6.57d	6.64t	— ^h	8.27d	1.70s (2 Me), 5.15s (CF)	—	—	0.43	
VII	1578, 1547	— ^h	—	6.61d	6.19b	— ^h	— ^h	3.16s (Me), 3.22s (Me)	—	—	—	
VIII	1593, 1545	— ^h	—	6.95d	6.27t	6.87t	8.02d	2.6–3.7c (CH ₂ CH ₂) 2.4–3.0c (CH ₂ CH ₂)	—	—	5.5 120 ^l	

^a In KBr disk. ^b Due to the pyridine ring. ^c δ value (ppm) from TMS, in CDCl₃ as for II–VII, and in CD₂Cl₂ as for I and VIII. Abbreviations used; b = broad, c = complicated, d = doublet, s = singlet, and t = triplet, dd = double doublet. Phenyl protons are omitted. ^d Coupling constants, ³J(3,4), ³J(4,5), and ³J(5,6) are 6–8 Hz. ^e Assignment is given in the parentheses. ^f Molar conductivity at 25°C. In 10⁻³ M in acetone, unless noted elsewhere. ^g Geminal coupling constant is virtually the same as the J(PH). ^h Overlapping with the other protons. ⁱ Overlapping with other band. ^j Geminal coupling constant is 8.6 Hz. ^k J(H_gH_g) is 6 Hz. ^l In dichloromethane.



IV $L = PPh_3$, $L' = pic$

VIII $L, L' = dppe$

Fig. 2. Proposed structures for IV and VIII.

and the difference [$\nu_{as}(OCO) - \nu_s(OCO)$] are consistent with the unidentate coordination of the carboxylato ligand [8]. On the basis of these facts and the 1H NMR data, discussed just above, III was ascribed to a 2-picoly-bridged dinuclear complex, similar to I, II, and IV, too (Fig. 1-B).

Acetylacetonato and dimethyldithiocarbamato complexes

A non-ionic complex, V, exhibited three bands at 1580, 1510, and 1390 cm^{-1} , characteristic of O, O' -chelation of an acetylacetonato ligand. In the 1H NMR spectrum of V, the protons of two methyl groups appeared as a slightly broadened singlet at δ 1.70 ppm in satisfactory intensity. The singlet broadened near $2^\circ C$ and changed into two sharp singlets at δ 1.61 and 1.81 ppm at $-20.5^\circ C$. This implies that the methyl groups in V exchange with each other fairly rapidly above $2^\circ C$, analogously to those in (acetylacetonato)(acyl)-triphenylphosphinenickel(II) [9]. It appears that the exchange of the two methyl groups is caused by the relatively strong *trans* influence of the 2-picoly group and triphenylphosphine, located at *trans* positions to the O, O' -bonded acetylacetonato ligand.

As for the 2-picoly group, two equivalent methylene-protons gave a doublet at δ 2.83 ppm [$J(PH)$ 3.9 Hz], which was due to coupling to the ^{31}P nucleus in a triphenylphosphine ligand situated *cis* to the group. Accordingly, the 2-picoly group is believed to be σ -bonded to palladium without coordination of the picoly nitrogen. Similarly, the 2-picoly group in dimethyldithiocarbamato complex VI was ascribed to monodentate coordination with the methylene carbon in a σ -bonding mode on the basis of its 1H NMR spectrum (Table 2).

2-Picolylpalladium(II) complexes with dppe

Complex I reacted with dppe in benzene to yield a pale yellow powder, VII, which exhibited a low conductivity indicative of non-ionic character. The molecular weight of VII, observed in dichloromethane, indicated a mononuclear structure formulated as $[Pd(CH_2Py)Cl(dppe)]$, and a band at $281\ cm^{-1}$ (KBr disk) was assigned to terminal $\nu(Pd - Cl)$. The 1H NMR spectrum in $CDCl_3$ showed a broad complicated pattern of signals overlapping each other in

the region of δ 1.8 to 3.8 ppm, attributable to methylene protons both of the 2-picoyl group and of dppe. The characteristic ^1H NMR pattern of the two non-equivalent methylene protons in the picoyl group disappeared on going from I to VII.

In ^{13}C NMR spectrum of VII, the picoyl group gave two doublets coupled to the ^{31}P nucleus at δ 33.5 ppm (J 75.5 Hz) for the methylene carbon and at δ 168.2 ppm (J 6.1 Hz) for 2-C. The comparatively large coupling constant of the former carbon is appropriate for the coupling to the ^{31}P nucleus in a diphenylphosphino group *trans* to the carbon. Two singlets at δ 122.6 and 117.5 ppm were associated with 3-C and 5-C. The spectrum showed also a singlet at δ 150.0 ppm assignable to 6-C in the picoyl group, and two double doublets at δ 25.0 [$J(\text{C}^\alpha\text{P}^\alpha)$ 27, $J(\text{C}^\alpha\text{P}^\beta)$ 9 Hz] and 30.4 ppm [$J(\text{C}^\beta\text{P}^\beta)$ 36 Hz, $J(\text{C}^\beta\text{P}^\alpha)$ 18 Hz] for two methylene carbons in dppe.

Detachment of the 2-picoyl nitrogen from palladium was confirmed by an increased conductivity ($110 \Omega^{-1} \text{cm}^2 \text{M}^{-1}$) observed after treatment with an excess of methyl iodide at ca. 50°C of an acetone solution of VII (10^{-3}M). The addition of methyl iodide gave a new singlet at δ 3.00 ppm in the ^1H NMR spectrum, attributable to a methyl group attached to the 2-picoyl nitrogen, in addition to a singlet due to unreacted methyl iodide, indicating quarterization of the nitrogen.

Chlorine-abstraction from VII with silver perchlorate gave an ionic complex, VIII, which was confirmed both by its high conductivity in dichloromethane and by detection of the $T_2(\text{OCIO})$ bending mode and the $T_2(\text{ClO})$ stretching mode, similar to IV. It has been reported that both substituted and unsubstituted pyridines generally exhibit a band near 400cm^{-1} for the out-of plane deformation mode and that the band is shifted towards higher frequency upon coordination to a metal via a nitrogen atom [10]. When going from VII to VIII, the band in KBr disk was shifted from 399 to 418cm^{-1} , indicating coordination of the 2-picoyl nitrogen to palladium.

The ^{13}C NMR spectrum of VIII was observed in CD_2Cl_2 . The methylene carbon in the 2-picoyl group gave a doublet at δ 33.6 ppm with a relatively large coupling constant (J 76.5 Hz), in conformity with the carbon situated *trans* to one of two diphenylphosphino groups. Carbons in the 2-pyridyl ring showed a pattern of signals similar to that of VII, whereas their coupling to the ^{31}P nucleus was not measured owing to the slight solubility of VIII. In its ^1H NMR spectrum, the methylene resonances of the 2-picoyl group overlapped with those of dppe, and gave no information about the bonding mode of the 2-picoyl group. However, VIII is believed to have the 2-picoyl-bridged dinuclear structure similar to IV (Fig. 2), on the basis of the IR data and of the similarity of the compositions between VIII and IV.

Coordination behavior of the 2-picoyl group

The ^{13}C NMR spectra of the 2-picoyl groups in I and VII did not show any coupling of 3-C to the ^{31}P nucleus. This is indicative of the absence of a π -allylic moiety consisting of the methylene carbon, 2-C, and 3-C, supposed for "Pd(CH₂Py)Cl(ClCH₂Py)" [5]. A π -azaallylic coordination of the 2-picoyl group in I, consisting of the methylene carbon, 2-C, and N, also was inconsistent with its dinuclear structure. However, the comparatively higher field reso-

nances of the methylene carbons in I, VII, and VIII were probably correlated to a shielding effect by palladium through the σ -bond. Moreover, the non-equivalence of the methylene protons in IV ruled out the halogeno-bridged structure of I or II, in which the 2-picoyl group was supposed to be σ -bonded to palladium with an additional interaction to the same metal via the 2-picoyl nitrogen [6]. Thus the results obtained in the present study indicate that the 2-picoyl group prefers the σ -type bonding to palladium with or without the formation of the 2-picoyl bridge to the η^3 -2-picoyl-CH₂, 2-C, 3-C coordination seen with the benzyl group [4].

In complexes V, VI, and VII, which have no 2-picoyl-bridged structure, there are other coexisting ligands which have relatively weak π -accepting and/or moderately strong σ -donating character. In these complexes, the comparatively high electron density at palladium probably prevents the palladium from interaction with a neighboring 2-picoyl nitrogen to form the 2-picoyl-bridged structure. On the other hand, I, II, and III have two electronegative ligands, such as halogeno or acetato, and each of IV and VIII has one positive charge per palladium atom. These factors decrease the electron density upon the palladium atom and permit the coordination of the palladium atom with a neighboring 2-picoyl nitrogen to form the 2-picoyl bridge. A similar trend has been observed for the 2-picoylpalladium(II) complexes with various tertiary phosphine by Kawaguchi et al [6].

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