

## Comparative Studies of 2-, 3-, and 4-Pyridylpalladium(II) Complexes: Synthesis and Properties

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Oxidative addition reactions of bromopyridines to tetrakis(triphenylphosphine)palladium(0) gave  $[\text{PdBr}(\text{2-pyridyl})(\text{PPh}_3)_2]$  (**1b**),  $\text{trans-}[\text{PdBr}(\text{3-pyridyl})(\text{PPh}_3)_2]$  (**2b**), and  $\text{trans-}[\text{PdBr}(\text{4-pyridyl})(\text{PPh}_3)_2]$  (**3b**), which were converted on treatment with triethylphosphine to  $\text{trans-}[\text{PdBr}(\text{2-, 3-, and 4-pyridyl})(\text{PEt}_3)_2]$  complexes (**1d**, **2d**, **3d**, respectively). Titration with perchloric acid in dioxane–water (1:1 by volume) indicated the basicity sequence of these complexes: 2-pyridyl  $\gg$  4-pyridyl  $>$  3-pyridyl. The bromide ligand in **1b–3b** can readily be replaced by  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{N}_3^-$ ,  $\text{NCO}^-$ , and  $\text{NCS}^-$ . In each corresponding series the relative thermal stability is in the sequence of 2-pyridyl  $>$  4-pyridyl  $>$  3-pyridyl. The pyridyl complexes containing triphenylphosphine react with carbon monoxide at ambient temperature and pressure to afford acyl complexes, which produce the corresponding esters by reactions with methanol. They also act as catalysts for cross coupling reactions of bromopyridines.

Oxidative addition of organic halides to palladium(0) complexes is one of the most convenient methods to prepare the  $\sigma$  bonded organopalladium(II) complexes.<sup>1)</sup> In a previous paper we have reported on the 2-pyridylpalladium(II) complexes which were prepared by the reactions of 2-halopyridines with tetrakis(triphenylphosphine)palladium(0),  $\text{Pd}(\text{PPh}_3)_4$ .<sup>2)</sup> Although the 2-pyridylnickel(II) complexes,  $[\{\text{NiX}(\text{C}_5\text{H}_4\text{N}-\text{C}^2)(\text{PPh}_3)_2\}]$  ( $\text{X}=\text{halide}$  and pseudohalide ligands), are quite stable, the corresponding 3-pyridyl complex  $[\{\text{NiCl}(\text{C}_5\text{H}_4\text{N}-\text{C}^3)(\text{PPh}_3)_2\}]$  is less stable and the 4-pyridyl complex has not been prepared.<sup>3)</sup> On the contrary, stable 3- and 4-pyridyl palladium(II) complexes have been obtained. This paper reports on the comparative studies of these complexes. A preliminary account and X-ray molecular structures of these compounds have appeared.<sup>4)</sup>

### Experimental

Unless otherwise stated, air-sensitive materials were handled under a nitrogen atmosphere. Solvents used in these experiments were redistilled in nitrogen, and vessels and reagents were also purged with nitrogen. Dioxane was distilled over Linde molecular sieves 4A before use through a fractionating column.

Commercial reagents such as halopyridines, tertiary phosphines, Grignard reagents, and carbon monoxide were used without further purification. 4-Bromopyridine was freed from its hydrogen chloride adduct by action of triethylamine. The starting complex  $\text{Pd}(\text{PPh}_3)_4$  was prepared by Coulson's method.<sup>5)</sup> The dinuclear 2-pyridyl complexes  $[\{\text{PdX}(\text{C}_5\text{H}_4\text{N}-\text{C}^2)(\text{PPh}_3)_2\}]$ ,  $\text{X}=\text{Cl}$  (**1a**) and **Br** (**1b**) were prepared by the reactions of  $\text{Pd}(\text{PPh}_3)_4$  with 2-chloro- and 2-bromopyridines as described already.<sup>2)</sup>

**Preparation of the *trans*-Bromo(3- and 4-pyridyl)bis(triphenylphosphine)palladium(II) Complexes, *trans-}[\text{PdBr}(\text{C}\_5\text{H}\_4\text{N}-\text{C}^3, \text{ and } -\text{C}^4)(\text{PPh}\_3)\_2] (**2b** and **3b**, respectively).*** 3-Bromo- or 4-bromopyridine (3.95 g, 25.0 mmol) was added to a solution of  $\text{Pd}(\text{PPh}_3)_4$  (4.21 g, 3.63 mmol) in toluene

(50  $\text{cm}^3$ ) and the mixture was allowed to react at 90 °C for 4 h. A white precipitate of **2b** separated out in a 90% yield from the reaction mixture after standing for 5 h at room temperature. In the case of **3b**, the solution was concentrated to ca. 25  $\text{cm}^3$  and kept in a refrigerator for 24 h to deposit a white precipitate in a 73% yield.

**Preparation of the *trans*-Halogeno- and *trans*-Pseudo-halogeno(3- and 4-pyridyl)bis(triphenylphosphine)palladium(II) Complexes, *trans-}[\text{PdX}(\text{C}\_5\text{H}\_4\text{N}-\text{C}^3)(\text{PPh}\_3)\_2] with **Cl** (**2a**), **I** (**2c**), **N<sub>3</sub>** (**2f**), **NCO** (**2g**) and **NCS** (**2h**) as **X** and *trans-}[\text{PdX}(\text{C}\_5\text{H}\_4\text{N}-\text{C}^4)(\text{PPh}\_3)\_2] with **Cl** (**3a**), **I** (**3c**), **N<sub>3</sub>** (**3f**), **NCO** (**3g**), and **NCS** (**3h**) as **X**.**** Methanol (10  $\text{cm}^3$ ) was added to a solution of **2b** or **3b** (0.151 g, 0.190 mmol) in dichloromethane (30  $\text{cm}^3$ ). To this solution was added a methanol solution of ten times molar amount of sodium chloride (0.112 g), iodide (0.283 g), azide (0.121 g), cyanate (0.122 g), or thiocyanate (0.151 g). In the case of sodium chloride or cyanate, a mixture (15  $\text{cm}^3$ ) of methanol and water (2:1 by volume) was used because of their poor solubilities in methanol. After the reaction at 40 °C for 1 h (for 72 h in the case of **NaCl**), dichloromethane was distilled away under reduced pressure to deposit a white precipitate, which was recrystallized from dichloromethane–methanol. The yields were 85 (**2a**), 84 (**2b**), 65 (**2f**), 60 (**2g**), 81 (**2h**), 75 (**3a**), 93 (**3c**), 71 (**3f**), 68 (**3g**), and 78% (**3h**), respectively.

**Preparation of the *trans*-Bromo(2-, 3-, and 4-pyridyl)bis(triethylphosphine)palladium(II) Complexes, *trans-}[\text{PdBr}(\text{C}\_5\text{H}\_4\text{N}-\text{C}^2, -\text{C}^3, \text{ and } -\text{C}^4)(\text{PEt}\_3)\_2] (**1d**, **2d**, and **3d**, respectively).*** Triethylphosphine (0.340 g, 2.88 mmol) was added to a suspension of **1b** (0.611 g, 0.580 mmol), **2b** (0.915 g, 1.16 mmol), or **3b** (0.915 g, 1.16 mmol) in diethyl ether (30  $\text{cm}^3$ ) and the mixture was stirred at room temperature for 24, 5, and 5 h, respectively, to result in a clear colorless solution. After concentration to 5  $\text{cm}^3$ , petroleum ether (20  $\text{cm}^3$ ) was added and the mixture was kept at –78, 0, and 0 °C, respectively, to precipitate white crystals in 30 (**1d**), 65 (**2d**), and 75% (**3d**) yields. Complexes **2d** and **3d** were recrystallized from diethyl ether–petroleum ether. Complex **1d** was dissolved in a mixture of water and methanol to be freed from triphenylphosphine and then recrystallized from petroleum ether. In order to prevent oxidation of triethylphosphine, preparation and purification of these

complexes were carried out under an argon atmosphere.

**Preparation of *trans*-Bromo(2-, 3-, and 4-pyridylum)bis-(triethylphosphine)palladium(II) 2,4-Dinitrophenolates, *trans*-[PdBr(C<sub>6</sub>H<sub>4</sub>NH-C<sup>2</sup>, -C<sup>3</sup>, and -C<sup>4</sup>)(PEt<sub>3</sub>)<sub>2</sub>][2,4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O] (1e, 2e, and 3e, respectively).** A dichloromethane solution (5 cm<sup>3</sup>) of 2,4-dinitrophenol (0.0730 g, 0.395 mmol) was added to a solution of 1d, 2d, or 3d (0.198 g, 0.395 mmol) in dichloromethane (5 cm<sup>3</sup>) to convert the colorless solution to yellow instantaneously. Diethyl ether (10 cm<sup>3</sup>) was added to the solution and the mixture was kept at 0 °C for 3 h to precipitate yellow crystals in 61, 64, and 63% yields, respectively, which were recrystallized from dichloromethane-diethyl ether.

**Preparation of the *trans*-Bromo(3- and 4-pyridylcarbonyl)bis(triphenylphosphine)palladium(II) Complexes, *trans*-[PdBr(C<sub>6</sub>H<sub>4</sub>N-C<sup>3</sup>-CO and -C<sup>4</sup>-CO)(PPh<sub>3</sub>)<sub>2</sub>] (2i and 3i, respectively).** Carbon monoxide was passed for 5 h through a solution of 2b or 3b (0.118 g, 0.150 mmol) in tetrahydrofuran at room temperature to convert the colorless solution to yellow. The solution was concentrated to 20 cm<sup>3</sup> by evaporation under reduced pressure. After addition of diethyl ether (60 cm<sup>3</sup>), the mixture was left standing at room temperature for 24 h to obtain yellow crystals of 2i and 3i in 80 and 81% yields, respectively, which were recrystallized from dichloromethane-diethyl ether.

**Reactions of the Acyl Complexes 2i and 3i with Methanol.** Methanol (10 cm<sup>3</sup>) was added to a solution of 2i or 3i (0.131 g, 0.160 mmol) in dichloromethane (20 cm<sup>3</sup>) with changing color of the solution from yellow to red and finally to brown. After standing for 24 h, the solvent was distilled away to dryness under reduced pressure and the residue was extracted with diethyl ether. The solvent was vaporized again and the residue was dissolved in dichloromethane-d<sub>2</sub> and identified by the <sup>1</sup>H NMR assay to be methyl nicotinate and isonicotinate, respectively.

**pH Titration of Complexes 1d, 2d, and 3d.** To a solution of 1d or 2d (0.0879 g, 0.176 mmol) in dioxane (10 cm<sup>3</sup>) was added an aqueous solution (10 cm<sup>3</sup>) of sodium perchlorate which had been adjusted to  $\mu=0.2$ , and the mixture containing the complex in  $8.78 \times 10^{-3}$  mol dm<sup>-3</sup> was kept at  $25.0 \pm 0.2$  °C under a nitrogen atmosphere. Dioxane and an aqueous solution of perchloric acid ( $9.43 \times 10^{-3}$  mol dm<sup>-3</sup>) adjusted to  $\mu=0.2$  with sodium perchlorate were added from separate burettes to the sample solution.

Each time exactly the same volumes of titrants were added and the mixture was stirred for several minutes before recording the pH value. Standardization of the perchloric acid solution had been performed in advance with a standard solution of sodium carbonate dried at 200 °C using a mixture of Bromocresol Green and Methyl Red as an indicator. For comparison pyridine dissolved in a mixture of dioxane and water (1:1 by volume) was also titrated in a similar manner as above.

Unfortunately titration of 3d in this way was not successful, since it is soluble in a mixture of dioxane and water (1:1 by volume) but not in the presence of sodium perchlorate to adjust the ionic strength. In order to compare relative basicities of 1d, 2d, and 3d, titration as above was carried out in the absence of sodium perchlorate.

**Measurements.** Infrared spectra were taken in Nujol or hexachlorobutadiene mull on JASCO IR-E (4000–650 cm<sup>-1</sup>), Hitachi EPI-L (700–200 cm<sup>-1</sup>), and FIS-3 (400–30 cm<sup>-1</sup>)

spectrophotometers. <sup>1</sup>H NMR spectra were measured at 100 MHz in CD<sub>2</sub>Cl<sub>2</sub> with Me<sub>4</sub>Si as internal reference by means of a JEOL JNM MH-100 spectrometer. A JEOL JNM FX-100 instrument was used to record <sup>13</sup>C NMR spectra in CDCl<sub>3</sub> with Me<sub>4</sub>Si as external reference at 25.0 MHz. Gas-chromatograms were obtained with a Yanagimoto G-180 instrument using nitrogen as a carrier gas through a Silicone DC-550 column, samples being injected at 200 °C. A Beckman Century SS-1 pH meter was used for titration together with glass and calomel electrodes. The Beckman buffer solution at pH 7.00 was used at 25 °C to calibrate the pH meter. The molecular weight was determined by vapor pressure osmometry in dichloromethane at 25 °C with an instrument manufactured by Knauer in Berlin, West Germany. The decomposition temperature was measured in a capillary tube under nitrogen.

## Results and Discussion

Tetrakis(triphenylphosphine)nickel(0) reacts with 2- and 3-halopyridines promptly at room temperature to afford the 2- and 3-pyridylnickel(II) complexes.<sup>9</sup> Although the former is stable, the latter complex is not so stable as to allow full characterization and the 4-pyridyl complex has not yet been obtained. On the other hand, the reactions of Pd(PPh<sub>3</sub>)<sub>4</sub> with 2-, 3-, and 4-bromopyridines did not proceed appreciably at room temperature, but occurred in toluene at 90 °C and completed after 4 h to form stable complexes. The 2-pyridylpalladium(II) complex is yellow and dinuclear as was reported previously,<sup>2</sup> while the 3- and 4-pyridyl complexes are white and mononuclear. The triphenylphosphine ligands in these complexes are readily replaced by triethylphosphine, an excess amount of which gives the mononuclear 2-pyridyl complex ultimately. Table 1 lists the complexes prepared in this study.

**Halogeno Pyridyl Complexes.** The analytical and molecular-weight data in Table 1 indicate that complexes 1d, 2a–d, and 3a–d are all mononuclear. As is seen in Table 2, decomposition temperature of these complexes is high. In the cases of 2-pyridyl nickel(II)<sup>9</sup> and palladium(II)<sup>2</sup> complexes, the relative thermal stability of halogeno complexes was in the sequence of Cl > Br > I. The same sequence holds for the 4-pyridyl complexes 3a–c, but in the case of 3-pyridyl complexes the bromo complex 2b decomposes at appreciably higher temperature than the chloro complex 2a does.

Among complexes containing the same halogeno ligand, the 4-pyridyl complexes are more stable than the corresponding 3-pyridyl complexes. The triethylphosphine complexes having distinct melting points show the decomposition temperature in the sequence of 2-pyridyl(1d) > 4-pyridyl(3d) > 3-pyridyl(2d).

Infrared spectra of these complexes show a single  $\nu(\text{Pd-P})$  band in the 410–430 cm<sup>-1</sup> region in conformity with the presumed *trans* structure and the  $\nu(\text{Pd-Cl}) : \nu(\text{Pd-Br}) : \nu(\text{Pd-I})$  ratio is 1:0.75:0.59 for

**2a—c**, resembling to that for the 2-pyridyl complexes (1:0.75:0.55),<sup>2a)</sup> although the corresponding ratio (1:0.62:0.50) for **3a—c** is a little smaller.

The methyl protons in **1d**, **2d**, and **3d** resonate at 1.0—1.1 ppm as a 1:4:6:4:1 quintet ( $J = \text{ca. } 9 \text{ Hz}$ ), indicating the trans arrangement of the triethylphosphine ligands.<sup>6)</sup> As is listed in Table 3, the ring protons of the triphenylphosphine ligands in **2a** and **3a** exhibit two multiplets at about 7.4 and 7.6 ppm, the former being assigned to the meta and para protons, and the latter to the ortho protons.<sup>7)</sup>

The NMR signals attributable to the pyridine-ring protons in **1d**, **2d**, and **3d** are shown in Fig. 1. The ring protons of 2-substituted pyridines such as methyl-, ethyl-, methoxy-, and chloropyridines show an ABB'X pattern, H<sup>3</sup> and H<sup>5</sup> resonating at the highest field with almost the same chemical shifts, and H<sup>4</sup> and H<sup>6</sup> at lower fields in this sequence.<sup>8)</sup> In the case of complex **1d**, the PdBr(PEt<sub>3</sub>)<sub>2</sub> moiety attached to C<sup>2</sup> effects the strongest influence on H<sup>3</sup>, of which the signal shifts to lower field to overlap with that of H<sup>4</sup>. Thus the signal at the highest field is assigned to H<sup>5</sup>

Table 1. Analytical Data for the  $\sigma$ -Pyridyl Palladium(II) Complexes

| Complex                                                                                                                                                             |           | Found (Calcd)    |                |                |              |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|------------------|----------------|----------------|--------------|
|                                                                                                                                                                     |           | C (%)            | H (%)          | N (%)          | Mol wt       |
| [PdBr(C <sub>5</sub> H <sub>4</sub> N-C <sup>2</sup> )(PEt <sub>3</sub> ) <sub>2</sub> ]                                                                            | <b>1d</b> | 40.50<br>(40.78) | 6.75<br>(6.84) | 2.81<br>(2.80) | 497<br>(501) |
| [PdBr(C <sub>5</sub> H <sub>4</sub> NH-C <sup>2</sup> )(PEt <sub>3</sub> ) <sub>2</sub> ]-<br>[2,4-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> O] | <b>1e</b> | 40.61<br>(40.34) | 5.53<br>(5.54) | 6.02<br>(6.14) |              |
| [PdCl(C <sub>5</sub> H <sub>4</sub> N-C <sup>3</sup> )(PPh <sub>3</sub> ) <sub>2</sub> ]                                                                            | <b>2a</b> | 65.31<br>(66.14) | 4.41<br>(4.60) | 1.86<br>(1.88) | 740<br>(745) |
| [PdBr(C <sub>5</sub> H <sub>4</sub> N-C <sup>3</sup> )(PPh <sub>3</sub> ) <sub>2</sub> ]                                                                            | <b>2b</b> | 61.51<br>(62.42) | 4.28<br>(4.34) | 1.76<br>(1.78) | 781<br>(789) |
| [PdI(C <sub>5</sub> H <sub>4</sub> N-C <sup>3</sup> )(PPh <sub>3</sub> ) <sub>2</sub> ]                                                                             | <b>2c</b> | 58.70<br>(58.91) | 4.08<br>(4.10) | 1.70<br>(1.68) | 821<br>(836) |
| [PdBr(C <sub>5</sub> H <sub>4</sub> N-C <sup>3</sup> )(PEt <sub>3</sub> ) <sub>2</sub> ]                                                                            | <b>2d</b> | 40.96<br>(40.78) | 6.84<br>(6.84) | 2.79<br>(2.80) | 499<br>(501) |
| [PdBr(C <sub>5</sub> H <sub>4</sub> NH-C <sup>3</sup> )(PEt <sub>3</sub> ) <sub>2</sub> ]-<br>[2,4-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> O] | <b>2e</b> | 40.31<br>(40.34) | 5.58<br>(5.59) | 6.09<br>(6.14) |              |
| [PdCl(C <sub>5</sub> H <sub>4</sub> N-C <sup>4</sup> )(PPh <sub>3</sub> ) <sub>2</sub> ]                                                                            | <b>3a</b> | 65.65<br>(66.14) | 4.82<br>(4.60) | 1.76<br>(1.88) | 730<br>(745) |
| [PdBr(C <sub>5</sub> H <sub>4</sub> N-C <sup>4</sup> )(PPh <sub>3</sub> ) <sub>2</sub> ]                                                                            | <b>3b</b> | 61.71<br>(62.42) | 4.30<br>(4.34) | 1.70<br>(1.78) | 770<br>(789) |
| [PdI(C <sub>5</sub> H <sub>4</sub> N-C <sup>4</sup> )(PPh <sub>3</sub> ) <sub>2</sub> ]                                                                             | <b>3c</b> | 58.33<br>(58.91) | 4.22<br>(4.10) | 1.59<br>(1.68) | 810<br>(836) |
| [PdBr(C <sub>5</sub> H <sub>4</sub> N-C <sup>4</sup> )(PEt <sub>3</sub> ) <sub>2</sub> ]                                                                            | <b>3d</b> | 41.15<br>(40.78) | 6.84<br>(6.84) | 2.77<br>(2.80) | 490<br>(501) |
| [PdBr(C <sub>5</sub> H <sub>4</sub> NH-C <sup>4</sup> )(PEt <sub>3</sub> ) <sub>2</sub> ]-<br>[2,4-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> O] | <b>3e</b> | 40.45<br>(40.34) | 5.61<br>(5.59) | 6.05<br>(6.14) |              |
| [PdN <sub>3</sub> (C <sub>5</sub> H <sub>4</sub> N-C <sup>3</sup> )(PPh <sub>3</sub> ) <sub>2</sub> ]                                                               | <b>2f</b> | 65.22<br>(65.57) | 4.53<br>(4.56) | 7.15<br>(7.46) | 740<br>(751) |
| [PdNCO(C <sub>5</sub> H <sub>4</sub> N-C <sup>3</sup> )(PPh <sub>3</sub> ) <sub>2</sub> ]                                                                           | <b>2g</b> | 66.97<br>(67.16) | 4.59<br>(4.56) | 3.71<br>(3.73) | 744<br>(751) |
| [PdNCS(C <sub>5</sub> H <sub>4</sub> N-C <sup>3</sup> )(PPh <sub>3</sub> ) <sub>2</sub> ] $\frac{1}{2}$ H <sub>2</sub> O                                            | <b>2h</b> | 64.58<br>(64.99) | 4.72<br>(4.55) | 3.54<br>(3.61) | 730<br>(776) |
| [PdN <sub>3</sub> (C <sub>5</sub> H <sub>4</sub> N-C <sup>4</sup> )(PPh <sub>3</sub> ) <sub>2</sub> ]                                                               | <b>3f</b> | 65.01<br>(65.57) | 4.41<br>(4.56) | 7.06<br>(7.46) | 748<br>(751) |
| [PdNCO(C <sub>5</sub> H <sub>4</sub> N-C <sup>4</sup> )(PPh <sub>3</sub> ) <sub>2</sub> ]                                                                           | <b>3g</b> | 66.82<br>(67.16) | 4.39<br>(4.56) | 3.41<br>(3.73) | 760<br>(751) |
| [PdNCS(C <sub>5</sub> H <sub>4</sub> N-C <sup>4</sup> )(PPh <sub>3</sub> ) <sub>2</sub> ]                                                                           | <b>3h</b> | 65.31<br>(65.76) | 4.30<br>(4.47) | 3.39<br>(3.65) | 751<br>(767) |
| [PdBr(C <sub>5</sub> H <sub>4</sub> N-C <sup>3</sup> -CO)(PPh <sub>3</sub> ) <sub>2</sub> ]                                                                         | <b>2i</b> | 61.46<br>(61.75) | 4.20<br>(4.19) | 1.46<br>(1.71) | 810<br>(817) |
| [PdBr(C <sub>5</sub> H <sub>4</sub> N-C <sup>4</sup> -CO)(PPh <sub>3</sub> ) <sub>2</sub> ]                                                                         | <b>3i</b> | 61.76<br>(61.75) | 4.22<br>(4.19) | 1.71<br>(1.71) | 805<br>(817) |

and that at the lowest field to H<sup>6</sup>. The ABMX pattern of the ring proton signals from **2d** is similar to that from methyl nicotinate,<sup>8,9</sup> and four signals are assigned as is seen in Fig. 1. The 4-pyridyl complex **3d** has the highest symmetry and exhibits only two doublets, of which the higher-field one is attributed to H<sup>3</sup> and H<sup>5</sup>, and the lower-field one to H<sup>2</sup> and H<sup>6</sup>. Assignment of signals from pyridine ring protons in **2a** and **3a** was made by reference to **2d** and **3d**, respectively.

Table 4 lists the <sup>13</sup>C NMR data from complexes **1d**, **2d**, and **3d**. The methyl and methylene carbons of triethylphosphine resonate at about 8 and 15 ppm, respectively, and the latter signal appears as a triplet with  $J(\text{C-P}) = \text{ca. } 13 \text{ Hz}$ , indicating the trans arrangement of the two phosphine ligands.<sup>10</sup> Assignment of the pyridine-ring carbons was made based on both the completely and selectively <sup>1</sup>H-decoupled studies as well as measurements without <sup>1</sup>H-decoupling.

Figure 2 shows the <sup>13</sup>C NMR spectra of **1d**, **2d**, and **3d** under <sup>1</sup>H-decoupled (A<sub>1</sub>, B<sub>1</sub>, and C<sub>1</sub>) and nondecoupled (A<sub>2</sub>, B<sub>2</sub>, and C<sub>2</sub>) conditions. The  $^1J(\text{C-H})$  values given therein were determined by spectral measurements without proton irradiation. The triplet signal at 179.7 ppm lacks in <sup>1</sup>H-coupling and assigned to C<sup>2</sup> in **1d**. All of the other signals for pyridine-ring carbons exhibit <sup>1</sup>H-coupling (A<sub>2</sub>). Irradiation at the resonance frequency of H<sup>6</sup> (8.3 ppm) reduced only the doublet at 149.1 ppm to a singlet, which is then assigned to C<sup>6</sup>. In a similar way the 117.5 ppm signal was attributed to C<sup>5</sup>. The remaining two signals at 133.3 and 132.5 ppm are so close to each other that the spin-decoupling method is not applicable. However the triplet at 133.3 ppm is assigned to C<sup>3</sup> because of its coupling to <sup>31</sup>P, since the carbon atoms adjacent (ortho) to the quaternary carbon bonded to the metal in **2d** and **3d** showed coupling to <sup>31</sup>P (Fig. 2 and Table 4).

In a similar manner the <sup>13</sup>C{<sup>1</sup>H} spectra of **2d** (B<sub>1</sub>) and **3d** (C<sub>1</sub>) in Fig. 2 were assigned to each pyridine-ring carbon. It is worth noting that the value of

$^1J(\text{C-H})$  decreases with the distance of the carbon from the nitrogen atom in the sequence of  $^1J(\text{C}^2\text{-H}) > ^1J(\text{C}^3\text{-H}) > ^1J(\text{C}^4\text{-H})$  and  $^1J(\text{C}^6\text{-H}) > ^1J(\text{C}^5\text{-H}) > ^1J(\text{C}^4\text{-H})$ . This is analogous to the situation observed for free pyridine.<sup>11</sup> All of the spectral data obtained for **1d**, **2d**, and **3d** are consistent with their trans structures which were confirmed by X-ray analysis.<sup>4)</sup>

Compared with the <sup>13</sup>C shieldings for uncoordinated pyridine carbons (C<sup>2</sup>, 149.7; C<sup>3</sup>, 123.6; C<sup>4</sup>, 135.5 ppm),<sup>12</sup> ring carbons in **1d**, **2d**, and **3d** show the following tendency. (i) The carbon atom bonded to palladium shows a very large down-field shift of ca. 30 ppm. (ii) The carbon atoms adjacent to the quaternary carbon also shift to lower field by 6–10 ppm, appearing as triplets due to coupling to <sup>31</sup>P as does the metal-bonded carbon. (iii) Carbons at the meta position of the quaternary carbon suffer the least effect on coordination, showing up-field shift less than 3 ppm. (iv) Carbons at the para position of the quaternary carbon also experience up-field shift by about 6 ppm.

Substituent effect similar to (i) has been reported for monosubstituted benzenes<sup>13,14</sup> and pyridines,<sup>12,15</sup> showing that the quaternary carbon is susceptible

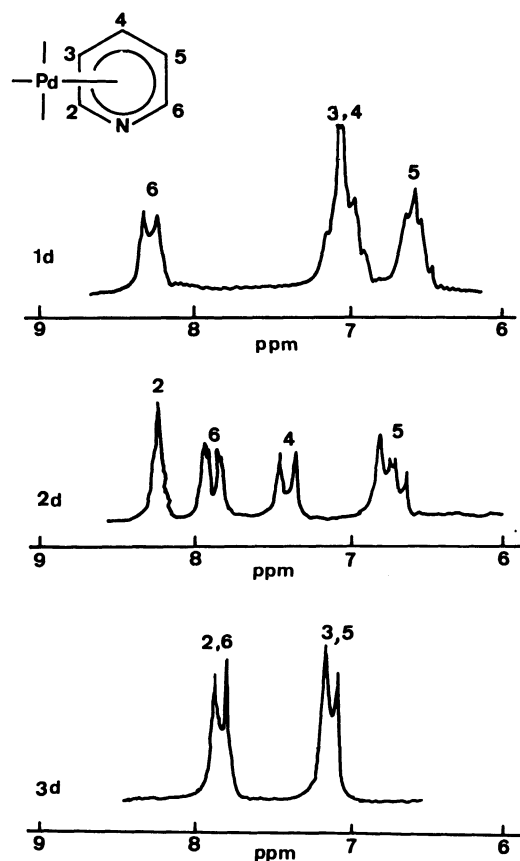


Fig. 1. <sup>1</sup>H NMR spectra at 100 M Mz in CD<sub>2</sub>Cl<sub>2</sub> with Me<sub>4</sub>Si as internal reference for pyridine ring protons in *trans*-[PdBr(C<sub>5</sub>H<sub>4</sub>N-C<sup>2</sup>, C<sup>3</sup>, and C<sup>4</sup>)(PEt<sub>3</sub>)<sub>2</sub>] (**1d**, **2d**, and **3d**, respectively).

Table 2. Decomposition Temperatures and Some FIR Data

| Complex   | Dec. temp <sup>a)</sup><br>°C | $\nu(\text{Pd-X})$<br>cm <sup>-1</sup> | $\nu(\text{Pd-P})$<br>cm <sup>-1</sup> |
|-----------|-------------------------------|----------------------------------------|----------------------------------------|
| <b>1d</b> | 181 (79)                      |                                        | 412 m                                  |
| <b>2a</b> | 165                           | 297 s                                  | 420 w                                  |
| <b>2b</b> | 182                           | 223 m                                  | 420 w                                  |
| <b>2c</b> | 147                           | 175 m                                  | 418 w                                  |
| <b>2d</b> | 149 (121)                     |                                        | 416 m                                  |
| <b>3a</b> | 215                           | 305 s                                  | 430 m                                  |
| <b>3b</b> | 210                           | 189 m                                  | 430 m                                  |
| <b>3c</b> | 170                           | 154 w                                  | 425 m                                  |
| <b>3d</b> | 175 (128)                     |                                        | 415 m                                  |

a) Figure in parenthesis is melting point.

Table 3.  $^1\text{H}$  Chemical Shifts in  $\text{CD}_3\text{Cl}_2$  (ppm from internal  $\text{Me}_4\text{Si}$ )

| Complex          | Pyridine ring protons |              |              |              |              | Benzene ring protons |              |              |              |              | Other protons                                                                      |
|------------------|-----------------------|--------------|--------------|--------------|--------------|----------------------|--------------|--------------|--------------|--------------|------------------------------------------------------------------------------------|
|                  | $\text{H}^2$          | $\text{H}^3$ | $\text{H}^4$ | $\text{H}^5$ | $\text{H}^6$ | $\text{H}^3$         | $\text{H}^4$ | $\text{H}^5$ | $\text{H}^2$ | $\text{H}^6$ |                                                                                    |
| <b>1d</b>        |                       | 7.06 m       | 7.06 m       | 6.62 m       | 8.28 d       |                      |              |              |              |              | 1.08 q ( $\text{CH}_3$ ) <sup>a</sup><br>1.57 m ( $\text{CH}_2$ )                  |
| <b>1e</b>        |                       | 7.75 d       | 7.68 m       | 7.26 m       | 8.52 d       | 8.80 d               |              | 7.94 dd      |              | 6.66 d       | 1.06 q ( $\text{CH}_3$ ) <sup>a</sup><br>1.70 m ( $\text{CH}_2$ )<br>14.76 br (NH) |
| <b>2a</b>        | 7.95 s                |              | 6.83 m       | 6.10 m       | 6.83 m       |                      | 7.41 m       |              | 7.58 m       |              | 1.04 q ( $\text{CH}_3$ ) <sup>a</sup><br>1.56 m ( $\text{CH}_2$ )                  |
| <b>2d</b>        | 8.32 s                |              | 7.47 d       | 6.86 dd      | 7.95 dd      |                      |              |              |              |              | 1.04 q ( $\text{CH}_3$ ) <sup>a</sup><br>1.60 m ( $\text{CH}_2$ )<br>13.14 s (NH)  |
| <b>2e</b>        | 8.40 br               |              | 7.96 br      | 7.28 br      | 8.16 br      | 8.83 d               |              | 8.04 br      |              | 6.88 d       |                                                                                    |
| <b>3a</b>        | b)                    | 6.75 m       |              | 6.75 m       | b)           |                      | 7.44 m       |              | 6.63 m       |              | 1.07 q ( $\text{CH}_3$ ) <sup>a</sup><br>1.61 m ( $\text{CH}_2$ )                  |
| <b>3d</b>        | 7.96 d                | 7.22 d       |              | 7.22 d       | 7.96 d       |                      |              |              |              |              | 1.08 q ( $\text{CH}_3$ ) <sup>a</sup><br>1.64 m ( $\text{CH}_2$ )                  |
| <b>3e</b>        | 8.02 br               | 7.81 br      |              | 7.81 br      | 8.02 br      | 8.83 d               |              | 8.06 br      |              | 6.80 d       |                                                                                    |
| <b>2f</b>        | 7.93 s                |              | 6.85 m       | 6.16 m       | 6.85 m       |                      |              | 7.45 m       |              |              |                                                                                    |
| <b>2g</b>        | 7.92 s                |              | 6.83 m       | 6.15 m       | 6.83 m       |                      |              | 7.44 m       |              |              |                                                                                    |
| <b>2h</b>        | 7.91 s                |              | 6.81 m       | 6.17 m       | 6.81 m       |                      |              | 7.49 m       |              |              |                                                                                    |
| <b>3f</b>        | b)                    | 6.74 m       |              | 6.74 m       | b)           |                      |              | 7.45 m       |              |              |                                                                                    |
| <b>3g</b>        | b)                    | 6.75 m       |              | 6.75 m       | b)           |                      |              | 7.47 m       |              |              |                                                                                    |
| <b>3h</b>        | b)                    | 6.75 m       |              | 6.75 m       | b)           |                      |              | 7.49 m       |              |              |                                                                                    |
| <b>2i</b>        | 8.96 s                |              | 6.89 m       | 6.89 m       | 8.38 m       |                      | 7.77 m       |              | 7.41 m       |              |                                                                                    |
| <b>3i</b>        | 8.23 d                | b)           |              | b)           | 8.23 d       |                      | 7.77 m       |              | 7.44 m       |              |                                                                                    |
| py <sup>c)</sup> | 8.60 m                | 7.25 m       | 7.64 m       | 7.25 m       | 8.60 m       |                      |              |              |              |              |                                                                                    |

a) 1 : 4 : 6 : 4 : 1 quintet with  $J = \text{ca. } 9 \text{ Hz}$ . b) Indiscernible due to overlapping with the phenyl protons. c) Uncoordinated pyridine in  $\text{CDCl}_3$  (from Ref. 7).  
s: singlet, d: doublet, dd: a doublet of doublets, m: multiplet.

Table 4.  $^{13}\text{C}$  Chemical Shifts (ppm from external  $\text{Me}_4\text{Si}$ ) and Coupling Constants (Hz) in  $\text{CDCl}_3$ 

| Complex       | Pyridine ring carbons                                     |                                                           |                                                           |                                  |                                  | Phosphine ligand ( $\text{PEt}_3$ or $\text{PPh}_3$ )   |                                |                              |
|---------------|-----------------------------------------------------------|-----------------------------------------------------------|-----------------------------------------------------------|----------------------------------|----------------------------------|---------------------------------------------------------|--------------------------------|------------------------------|
|               | $\text{C}^2$                                              | $\text{C}^3$                                              | $\text{C}^4$                                              | $\text{C}^5$                     | $\text{C}^6$                     | $\text{CH}_2$<br>$\text{C}^1$                           | $\text{CH}_3$<br>$\text{C}^3$  | $\text{C}^4$                 |
| <b>1d</b>     | 179.7                                                     | 133.3<br>$^1J(\text{C-H})=163.2$<br>$^3J(\text{C-P})=7.3$ | 132.5<br>$^1J(\text{C-H})=161.8$                          | 117.5<br>$^1J(\text{C-H})=163.2$ | 149.1<br>$^1J(\text{C-H})=176.5$ | 14.9<br>$^1J(\text{C-H})=129.4$<br>$J(\text{C-P})=13.0$ | 8.1<br>$^1J(\text{C-H})=129.4$ |                              |
| <b>2b</b>     | 164.6<br>$^3J(\text{C-P})=3.4$                            | 152.8<br>$^2J(\text{C-P})=3.6$                            | 135.7<br>$^3J(\text{C-P})\approx 3$                       | 130.1                            | 151.4                            | 138.2<br>$J(\text{C-P})=23.0$                           | 142.4<br>$J(\text{C-P})=5.0$   | 137.2<br>$J(\text{C-P})=4.4$ |
| <b>2d</b>     | 155.3<br>$^1J(\text{C-H})=177.2$<br>$^3J(\text{C-P})=3.7$ | 150.8<br>$^2J(\text{C-P})=6.1$                            | 144.0<br>$^1J(\text{C-H})=160.3$<br>$^3J(\text{C-P})=2.4$ | 123.9<br>$^1J(\text{C-H})=161.0$ | 143.7<br>$^1J(\text{C-H})=179.4$ | 15.0<br>$^1J(\text{C-H})=133.8$<br>$J(\text{C-P})=13.4$ | 8.1<br>$^1J(\text{C-H})=128.0$ |                              |
| <b>3b</b>     | 155.2                                                     | 140.8<br>$^2J(\text{C-P})=3.9$                            | 186.5<br>$^2J(\text{C-P})\approx 5$                       | 140.8<br>$^3J(\text{C-P})=3.9$   | 155.2                            | 137.9<br>$J(\text{C-P})=23.5$                           | 142.2<br>$J(\text{C-P})=6.5$   | 137.2<br>$J(\text{C-P})=5.0$ |
| <b>3d</b>     | 146.8<br>$^1J(\text{C-H})=175.0$                          | 133.8<br>$^2J(\text{C-P})=3.7$                            | 170.8<br>$^2J(\text{C-P})=5.9$                            | 133.8<br>$^3J(\text{C-P})=3.7$   | 146.8<br>$^1J(\text{C-H})=175.0$ | 14.8<br>$^1J(\text{C-H})=133.8$<br>$J(\text{C-P})=13.5$ | 8.0<br>$^1J(\text{C-H})=128.0$ |                              |
| $\text{py}^a$ | 149.7<br>$^1J(\text{C-H})=170.0$                          | 123.6<br>$^1J(\text{C-H})=163.0$                          | 135.5<br>$^1J(\text{C-H})=152.0$                          | 123.6<br>$^1J(\text{C-H})=163.0$ | 149.7<br>$^1J(\text{C-H})=170.0$ |                                                         |                                |                              |

a) Data for uncoordinated pyridine from Ref. 10 and 11.

to the inductive, resonance, and anisotropic effects of the substituent.<sup>16)</sup> However, variation in shielding for the present complexes is the highest among values reported so far. Thus the  $^{13}\text{C}$  shieldings of the benzene-ring carbons in *trans*- $[\text{Pt}(\text{C}_6\text{H}_5)\text{L}(\text{AsMe}_3)_2]\text{PF}_6$  with various neutral ligands as L show a quite similar pattern to (i)–(iv) above,<sup>17)</sup> but the extent of downfield shift for the carbon bonded to platinum is not so large as the present case.

The deshielding effect on the adjacent carbons (ii) may be attributed to the anisotropic effect by the palladium moiety rather than  $\sigma$ ,  $\pi$ -inductive and resonance effects.<sup>16,17)</sup> The  $\text{PtX}(\text{PEt}_3)_2$  group with a variety of negative ligands as X, when bound to fluorobenzene, was said to be an electron donor in both the inductive and resonance senses.<sup>6)</sup> On the other hand a bonding model was proposed for *trans*- $[\text{Pt}(\text{C}_6\text{H}_5)\text{L}(\text{AsMe}_3)_2]\text{PF}_6$  in which  $\sigma$  rather than  $\pi$  interactions are dominant in the phenyl-platinum bond,<sup>17)</sup> whereas evidence was presented supporting the presence of significant  $\pi$  interactions between platinum and an aryl ligand in a series of complexes of the type *trans*- $[\text{PtX}(\text{C}_6\text{H}_5)(\text{PEt}_3)_2]$ .<sup>16)</sup> The effects (iii) and (iv) in the present case may be due to inductive and/or resonance effects of palladium.

The pyridine ring carbons in **2b** and **3b** except  $\text{C}^4$  in **2b** resonate at lower fields than corresponding carbons in **2d** and **3d** (Table 4). These results may be related to the lower electron-donating ability of palladium in **2b** and **3b** than that in **2d** and **3d**, respectively, caused by lower basicity and higher  $\pi$ -acceptability of triphenylphosphine compared with triethylphosphine. Ring carbons of the triphenylphosphine ligands in **2b** resonate in a usual region, appearing as triplets except the para carbon in conformity with the proposed *trans* configuration. The chemical shifts and the coupling constants for carbons in the triphenylphosphine ligands in **3b** are very close to those for **2b** (Table 4).

**pH Titration of the *trans*-Bromo(2-, 3-, and 4-pyridyl)bis(triethylphosphine)palladium(II) Complexes.** Complexes **1d** and **2d** as well as pyridine are readily soluble in dioxane–water (1:1 by volume) adjusted to  $\mu=0.1$  with sodium perchlorate, and were titrated with perchloric acid. Complex **3d**, on the other hand, is enough soluble in dioxane–water only in the absence of sodium perchlorate and titration was carried out under these conditions to compare the basicity of **3d** with that of **1d** and **2d**. Titration curves at  $\mu=0.1$  are shown in Fig. 3. In a mixture of dioxane and water the reading of a pH meter is usually 0.10 higher than the true value of  $-\log [\text{H}^+]$  in the whole range.<sup>18)</sup> The  $\text{pK}_a$  values of the conjugate acids of **1d**, **2d**, and py were calculated to be 8.04, 5.47 and 4.47, respectively, by using corrected values of  $[\text{H}^+]$ . Thus the basicity of **1d** is ca. 3700 times higher than that of uncoordinated pyridine, indicating substantial charge donation from the  $\text{PdB}(\text{PEt}_3)_2$  moiety to nitrogen.

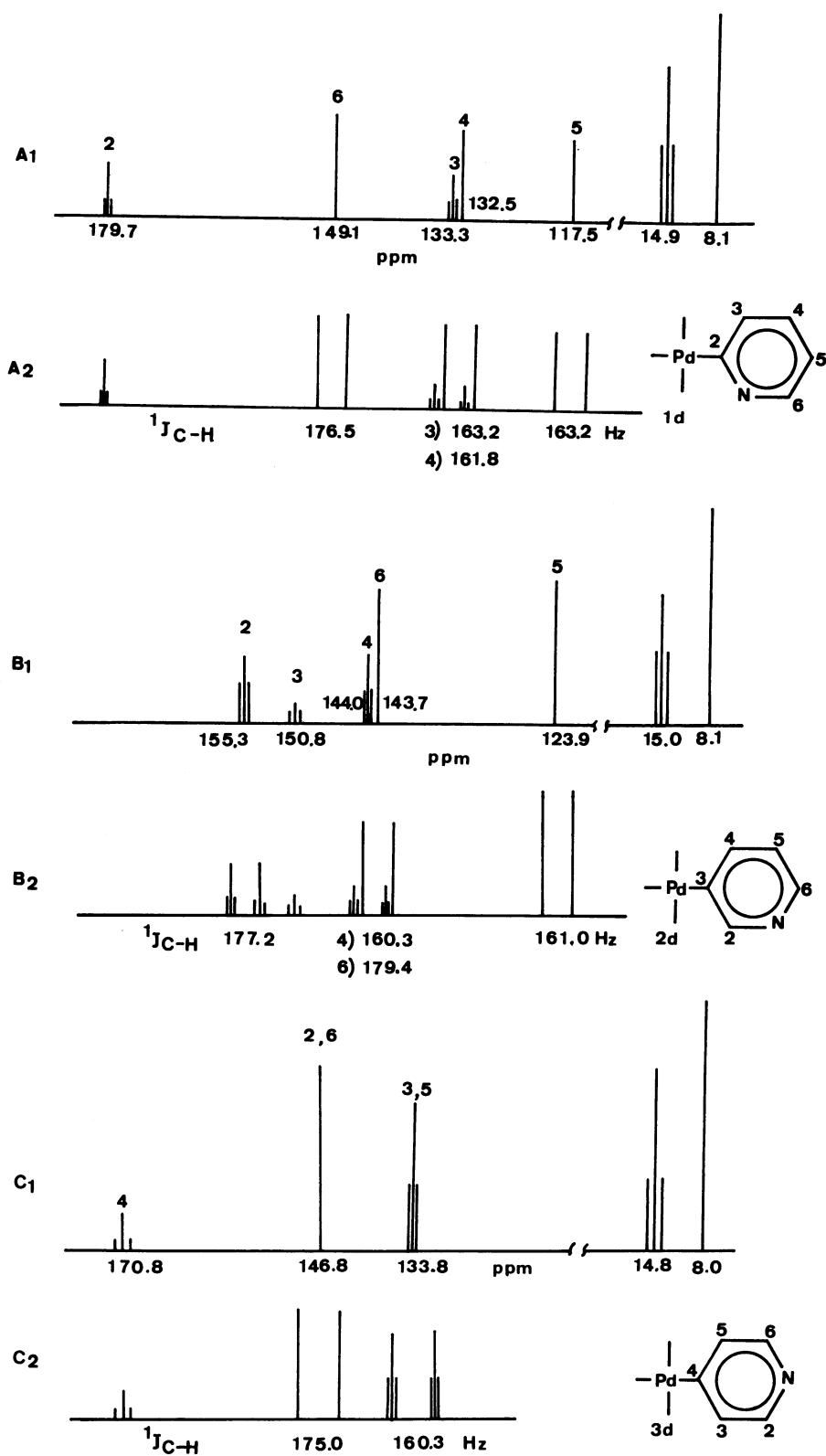


Fig. 2.  $^{13}\text{C}$  NMR spectra at 25.0 MHz in  $\text{CDCl}_3$  of *trans*-[PdBr(C<sub>5</sub>H<sub>4</sub>N-C<sup>2</sup>, C<sup>3</sup>, and C<sup>4</sup>)(PEt<sub>3</sub>)<sub>2</sub>] (**1d**, **2d**, and **3d**, respectively) under  $^1\text{H}$ -decoupled (A<sub>1</sub>, B<sub>1</sub>, and C<sub>1</sub>) and nondecoupled (A<sub>2</sub>, B<sub>2</sub>, and C<sub>2</sub>) conditions, the chemical shift being given in ppm from external Me<sub>4</sub>Si and the  $^1J_{\text{C-H}}$  in Hz.

Titration in the absence of supporting electrolytes gave the  $pK_a$  values of 7.44, 5.01, and 5.38 to **1d**, **2d**, and **3d**. Thus the relative basicity is in the sequence of 2-pyridyl (**1d**) > 4-pyridyl (**3d**) > 3-pyridyl (**2d**).

The enhancement of basicity of pyridine by substitution with electron-donating groups such as  $\text{CH}_3$  and  $\text{NH}_2$  also depends upon the position attached on the ring and is in the sequence of 4 > 2 > 3.<sup>19</sup> The relative basicities of the present complexes do not follow this sequence and may not be rationalized only by simple inductive effect as applied to the methyl and amino substituents. The charge density donated by the  $\text{PdBr}(\text{PEt}_3)_2$  substituent attached to  $\text{C}^2$  seems not to be dissipated throughout the ring but to be accumulated at the adjacent nitrogen. The extraordinarily large  $^3J(\text{C-P})$  value of 7.3 at  $\text{C}^3$  in **1d** as compared with  $^3J(\text{C-P})$  values for carbons adjacent to the quaternary carbons in **2d** and **3d** might be brought by a similar mechanism.

Johnson and Winterton<sup>20</sup> also found that the  $pK_a$  values of pyridinium salts with the  $\text{CH}_2\text{Co}(\text{CN})_5^{3-}$  substituent depend on the position of substitution, decreasing in the sequence of 2(10.6) > 4(9.2) > 3(8.3). In order to compare the bonding parameters and distribution of charge densities in **1d**, **2d**, and **3d**, X-ray analysis and MO calculations of these complexes have been carried out and the results were reported previously.<sup>4)</sup>

**Pyridylum Complexes.** An equimolar amount of 2,4-dinitrophenol reacts with **1d**, **2d**, and **3d** to afford adducts **1e**, **2e**, and **3e**, respectively. Fig. 4 compares the IR bands related to the  $\text{>C=N}^+\text{<H}$  group of these

complexes and pyridinium 2,4-dinitrophenolate(**A**). The frequencies of vibration due to the iminium group in **1e** and **3e** are appreciably higher than those for **A** and **2e** which are comparable.

The  $\text{NH}^+$  proton in these complexes resonates at substantially lower field than that of **A** does. When compared at a constant concentration of  $0.409 \text{ mol dm}^{-3}$ , the chemical shifts were 14.76, 13.14, 14.07, and 11.03 ppm for **1e**, **2e**, **3e**, and **A**, respectively, though they varied somewhat with concentration. (The OH proton of free 2,4-dinitrophenol resonates at 10.94 ppm.)

On adduct formation the pyridine-ring protons in the complexes show large down-field shifts (Table 3) and the phenol-ring protons do large up-field shifts compared with those in a free molecule ( $\text{H}^3$ , 9.06;  $\text{H}^5$ , 8.43;  $\text{H}^6$ , 7.34 ppm). The extent of variation is much larger than that for **A** in which the pyridine-ring protons resonate at 8.97 ( $\text{H}^2$  and  $\text{H}^6$ ), 7.36 ( $\text{H}^3$  and  $\text{H}^5$ ), and 7.78 ( $\text{H}^4$ ) ppm, the phenol-ring protons appearing at 8.97 ( $\text{H}^3$ ), 8.42 ( $\text{H}^5$ ), and 7.31 ( $\text{H}^6$ ) ppm. These IR and  $^1\text{H}$  NMR evidences indicate that proton is more strongly interacting with nitrogen in these adducts than in **A** probably in the sequence of 2-pyridyl(**1e**) > 4-pyridyl(**3e**) > 3-pyridyl(**2e**) > **A**.

**Pseudohalogeno Pyridyl Complexes.** The pseudohalogeno 3- and 4-pyridyl complexes **2f-h** and **3f-h** were derived in high yields from **2b** and **3b**, respectively, by ligand substitution with pseudohalides. Analytical and molecular-weight data in Table 1 as well as single  $\nu(\text{Pd-P})$  bands in the  $420\text{--}435 \text{ cm}^{-1}$  region (Table 5) indicate that these complexes have the trans mononuclear structure. Frequencies of the  $\nu(\text{CN})$  and  $\nu(\text{CS})$  vibrations observed for **2h** and **3h** indicate that each NCS ligand in these complexes is

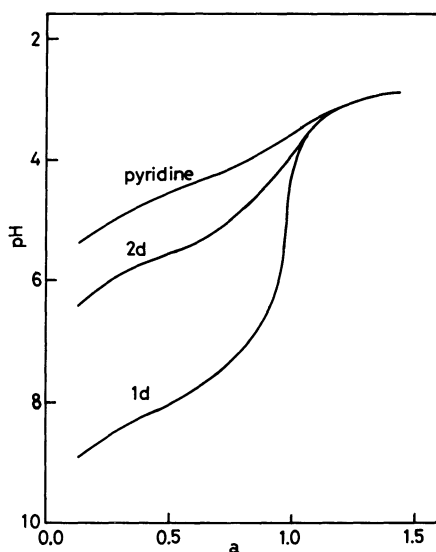


Fig. 3. pH Titration of  $\text{trans-[PdBr(C}_5\text{H}_4\text{N-C}^2\text{ and C}^3\text{)(PEt}_3)_2]$  (**1d** and **2d**, respectively) and pyridine with perchloric acid in dioxane-water (1 : 1 by volume) at  $25.0^\circ\text{C}$  and  $\mu=0.1$  ( $\text{NaClO}_4$ ) under nitrogen. The abscissa gives the mole ratio of (acid added/complex) : a.

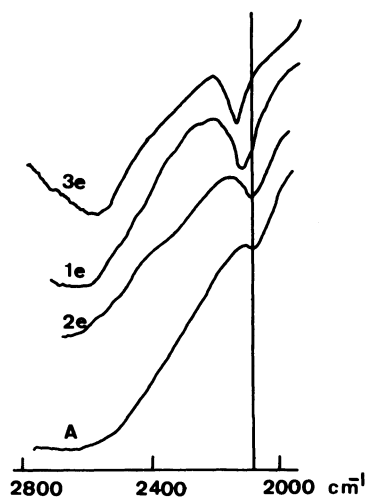


Fig. 4. IR spectra in the  $2000\text{--}2800 \text{ cm}^{-1}$  region of pyridinium 2,4-dinitrophenolate (**A**) and  $\text{trans-[PdBr(C}_5\text{H}_4\text{NH-C}^2\text{, C}^3\text{, and C}^4\text{)(PEt}_3)_2][2,4\text{-(NO}_2)_2\text{-C}_6\text{H}_3\text{O}]$  (**1e**, **2e**, and **3e**, respectively) in Nujol.



Table 5. Characteristic IR in Nujol( $\text{cm}^{-1}$ ) for the Pseudohalogeno Complexes<sup>a)</sup>

| Complex   | $\nu(\text{CN})$ or $\nu_{\text{a}}(\text{NNN})$ | $\nu(\text{CY})$ or $\nu_{\text{b}}(\text{NNN})$ | $\delta(\text{NCY})$ or $\delta(\text{NNN})$ | $\nu(\text{Pd-P})$ |
|-----------|--------------------------------------------------|--------------------------------------------------|----------------------------------------------|--------------------|
| <b>2f</b> | 2048 vs                                          | 1330 m                                           | 595 w                                        | 433 m              |
| <b>2g</b> | 2215 vs                                          | 1328 m                                           | 605 m                                        | 430 m              |
| <b>2h</b> | 2082 vs                                          | 820 w                                            | b)                                           | 430 m              |
| <b>3f</b> | 2040 vs                                          | 1330 m                                           | 594 w                                        | 430 m              |
| <b>3g</b> | 2210 vs,<br>2195 vs                              | 1328 w                                           | 605 w                                        | 430 m              |
| <b>3h</b> | 2080 vs                                          | 818 m                                            | b)                                           | 423 m              |

a) Y=O or S. b) Indiscernible.

N-bonded.<sup>21)</sup> Preliminary X-ray analysis has confirmed the proposed molecular structure of **2h** unequivocally.<sup>22)</sup>

Similarly the  $\nu(\text{CN})$ ,  $\nu(\text{CO})$ , and  $\delta(\text{NCO})$  frequencies for the cyanate ligand in **2g** and **3g** (Table 5) are in the range assigned to N-bonding.<sup>21)</sup> In accordance with the fact that each of the pseudohalides in **2f—h** and **3f—h** is bound to palladium through the same donor atom, the chemical shifts of pyridine-ring protons in **2f—h** and **3f—h** completely coincide with each other, respectively, in the range of experimental error (Table 3).

**The trans-Bromo(3- and 4-pyridylcarbonyl)bis(triphenylphosphine)palladium(II) Complexes.** Complexes **2b** and **3b** reacted with carbon monoxide in THF at room temperature to give the insertion products **2i** and **3i**. The analytical and molecular-weight data in Table 1 as well as the single  $\nu(\text{Pd-P})$  band at 427 and 430  $\text{cm}^{-1}$  for **2i** and **3i**, respectively, suggest that they are mononuclear complexes of trans structure. The  $\nu(\text{CO})$  bands are observed at 1642(**2i**) and 1644(**3i**)  $\text{cm}^{-1}$ , respectively. Both of these complexes readily reacted with methanol in the absence of base to produce methyl nicotinate ( $\text{CH}_3$ , 3.98 s;  $\text{H}^2$ , 9.20d;  $\text{H}^4$ , 8.20 m;  $\text{H}^5$ , 7.35 m;  $\text{H}^6$ , 8.85 m ppm) and isonicotinate ( $\text{CH}_3$ , 4.00 s;  $\text{H}^2$ ,  $\text{H}^6$ , 8.80 d;  $\text{H}^3$ ,  $\text{H}^5$ , 7.90 d ppm) in 48 and 54% yields, respectively. As was reported in a previous paper,<sup>2a)</sup>  $[\text{PdBr}(\text{C}_5\text{H}_3(6\text{-Cl})\text{N-C}^2)(\text{PPh}_3)_2]$  is also carbonylated. It may be interesting from the standpoint of organic synthesis that one carbon unit can easily be added to any carbon of pyridine. It should also be noted that the corresponding triethylphosphine complexes **1d**, **2d**, and **3d** are not carbonylated. The Pd-C bonds in these complexes seem again to be more stable and/or more inert than those in the corresponding triphenylphosphine complexes.

**Cross Coupling Reactions.** Catalysis of the 2-pyridyl palladium(II) complexes on the cross coupling reactions of 2-chloro- and 2,6-dichloropyridines with methylmagnesium bromide was reported in a previous paper.<sup>2a)</sup> Now one-hundredth molar amount of **2b** and **3b** were found to promote the reactions of 3- and 4-bromopyridines with methylmagnesium bro-

mide in refluxing THF to give 3- and 4-methylpyridines in 12 and 6% yields, respectively, although the reactions did not occur at room temperature. Further improvement in yields may be desirable to make these catalytic reactions useful in organic synthesis.

We wish to thank Mr. Junichi Gohda for elemental analyses.

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