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Organopalladium(II) Complexes Containing Carbon-Bonded Heterocycles as a Ligand

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Oxidative addition reactions of 2-chloropyridine, 2,6-dichloropyridine, 2-chloropyrazine, and 2-chlorobenzothiazole with tetrakis(triphenylphosphine)palladium(0) gave $[\{PdCl(R)(PPh_3)\}_2]$ or *trans*-$[PdCl(R)(PPh_3)_2]$ depending on the nature of the carbon-bonded heterocycles R. They are all stable and the chloride ligand is readily replaced by other halides and pseudohalides. These novel organopalladium(II) complexes were characterized by the analytical and molecular-weight data together with IR, ^1H NMR and ^{13}C NMR spectra, and the 2-pyridyl-bridged dinuclear structure of $[\{PdBr(C_5H_4N\text{-}C^2)(PPh_3)\}_2]$ was previously revealed by X-ray analysis. Both of the dinuclear and mononuclear 6-chloro-2-pyridylpalladium(II) complexes catalyze the cross coupling reaction between 2,6-dichloropyridine and methylmagnesium bromide to afford 2-methyl-6-chloropyridine selectively. The mononuclear 6-chloro-2-pyridylpalladium(II) complexes react with carbon monoxide to form the acyl complexes.

The σ-pyridyl complexes are of considerable current interest in connection with adsorption of pyridine on metal surfaces during the catalytic reactions,[1] and a fair number of these complexes have been prepared with cobalt(III),[2] gold(I),[3] titanium(III),[4] rhenium(I),[5] palladium(II),[6] and other metals.[7] We also have extensively developed σ-pyridyl nickel(II)[8] and palladium(II)[9] complexes. In the course of the studies, both the mononuclear and the dinuclear 2-pyridyl palladium(II) complexes were important starting materials for preparation of the mixed-ligand complexes containing both the pyridyl ligand and the *O,O'*-chelated or *O*-unidentate β-diketonate anion.[10] This paper describes more detailed results on the preparation, characterization and some reactivities of palladium(II) complexes containing the σ-carbon-bonded pyridyl as well as pyrazinyl and benzothiazolyl ligands. The molecular structure of a dinuclear complex $[\{PdBr(\mu\text{-}C_5H_4N\text{-}C^2, N)(PPh_3)\}_2]$ has previously been reported.[11]

Experimental

Air-sensitive materials were handled under a nitrogen atmosphere unless otherwise stated. Solvents were redistilled under nitrogen and other reagents purged with nitrogen before use. Tetrakis(triphenylphosphine)palladium(0), $Pd(PPh_3)_4$, was prepared by Coulson's method.[12] Tertiary phosphines, halopyridines, 2-chloropyrazine, 2-chlorobenzothiazole, and Grignard reagents were purchased and used without further purification.

Preparation of $[\{PdX(R)(PPh_3)\}_2]$ ($R=C_5H_4N\text{-}C^2$, X=Cl (1a) or Br (1b), and $R=C_4H_3N_2\text{-}C^2$, X=Cl (7)) and *trans*-$[PdCl(R)(PPh_3)_2]$ ($R=C_5H_3(6\text{-Cl})N\text{-}C^2$ (2a) or $C_7H_4SN\text{-}C^2$ (6)) by the Oxidative Addition. To a solution of $Pd(PPh_3)_4$ (4.21 g, 3.63 mmol) in toluene (50 cm³) was added ca. ten times molar amount of 2-chloropyridine (4.12 g), 2-bromopyridine (5.74 g), or 2-chloropyrazine (4.16 g) and the mixture was heated to 90 °C for 10, 3, and 10 h, respectively. After standing for 5h at room temperature, yellow precipitates of **1a**, **1b**, and **7** were obtained in 60, 55, and 79% yields, respectively. Complexes **2a** and **6** were obtained in a similar manner by using 2,6-dichloropyridine or 2-chlorobenzothiazole as alkyl halide. A refrigerator was utilized for depositing precipitates from the reaction mixture. The yields were 95 (**2a**) and 80% (**6**).

Preparation of $[\{PdX(R)(PPh_3)\}_2]$ ($R=C_5H_4N\text{-}C^2$, X=I (1c), N_3 (8a), NCO (8b), NCS (8c), or NCSe (8d), $R=C_5H_3(6\text{-Cl})N\text{-}C^2$, $X=N_3$ (10a), NCO (10b), or NCS (10c)) and *trans*-$[PdX(C_5H_3(6\text{-Cl})N\text{-}C^2)(PPh_3)_2]$ (X=Br (2b), I (2c), N_3 (9a), NCO (9b), or NCS (9c)) by the Halide Substitution Reactions. Compound **1a** (0.14 g, 0.15 mmol) was dissolved in dichloromethane (50 cm³) and methanol (20 cm³) was added to the solution. Then a methaol solution (20 cm³) of sodium iodide (4.5 g, 30 mmol) was added and the mixture was heated to 40 °C for 2 h. Dichloromethane was evaporated under reduced pressure and yellow crystals separated were filtered. The yield of **1c** was 80%. In a similar manner yellow dinuclear complexes **8** and **10** and white mononuclear complexes **2** and **9** were obtained by the halide substitution reactions of **2a** or **3a** with sodium bromide, iodide, pseudohalides and potassium selenocyanate. Solubility of sodium cyanate is low in methanol and aqueous methanol (1:3 by volume) was used as solvent. Yields of the metathesis reactions were 73 (**8a**), 65 (**8b**), 83 (**8c**), 52 (**8d**), 53 (**10a**), 48 (**10b**), 59 (**10c**), 90 (**2b**), 85 (**2c**), 81 (**9a**), 79 (**9b**), and 63% (**9c**), respectively.

Preparation of $[\{PdX(C_5H_3(6\text{-Cl})N\text{-}C^2)(PPh_3)\}_2]$ (X=Cl (3a), Br (3b), or I (3c)). To a suspension of **2a** (0.18 g, 0.23 mmol) in acetone (30 cm³) was added dropwise an 0.05 cm³ portion of 30% aqueous solution of hydrogen peroxide (ca. 0.44 mmol) by means of micropipette and the mixture was stirred. The initially white suspension turned yellow gradually. Stirring was continued for 24 h and the yellow precipitate was filtered. The yield of **3a** was 96%. Complexes **3b** and **3c** were derived from **3a** by the halide substitution reactions in 90 and 87% yields, respectively.

Complexes **3a—c** were also prepared via an alternative route. The perchlorato complex[9a] $[\{PdClO_4(C_5H_3(6\text{-Cl})N\text{-}C^2)(PPh_3)\}_2]$(0.12 g, 0.10 mmol) was dissolved in dichloro-

methane (50 cm³). To the solution was added methanol (20 cm³) followed by a methanol solution (20 cm³) of a large excess amount of sodium chloride (1.8 g), bromide (3.1 g) or iodide (4.5 g), and the mixture was heated to 40 °C for 2 h. Dichloromethane was then evaporated under reduced pressure to precipitate crystals of **3a**, **3b**, and **3c** in 32, 83, and 89% yields, respectively.

Preparation of *trans*-[PdCl(C_5H_3(6-Cl)N-C^2)(PEt_3)$_2$] (4a), *trans*-[PdCl(C_5H_3(6-Cl)N-C^2)($PPhMe_2$)$_2$] (4b), and *trans*-[PdNCO(C_5H_3(6-Cl)N-C^2)(PEt_3)$_2$] (11). In order to prevent oxidation of phosphines during long-time reactions by a trace of oxygen accompanied by cylinder nitrogen, an argon atmosphere was employed for preparation of these complexes. Triethylphosphine (0.07 g, 0.63 mmol) or phenyldimethylphosphine (0.09 g, 0.63 mmol) was added to a suspension of complex **2a** (0.16 g, 0.21 mmol) in diethyl ether (20 cm³), and the mixture was stirred at room temperature for 20 h to result in a clear colorless solution. After addition of petroleum ether (20 cm³), the solution was cooled in a Dry Ice–methanol bath for 3 h to precipitate white crystals, which were filtered promptly. The yields of **4a** and **4b** were 40 and 60%, respectively. In a similar manner **11** was obtained in a 14% yield by the reaction of **9b** with triethylphosphine.

Preparation of [{PdCl(C_5H_4N-C^2)(PEt_3)}$_2$] (5). Triethylphosphine (0.06 g, 0.52 mmol) was added to a suspension of **1a** (0.13 g, 0.13 mmol) in diethyl ether (20 cm³) and the mixture was stirred under argon at room temperature for 20 h to obtain a clear colorless solution, which was concentrated to 3 cm³ by evaporation under reduced pressure and poured onto a column (ϕ1.5 cm×30 cm) of Aluminiumoxid 60 PF_{254} (Type E by Merck). Petroleum ether (150 cm³) was used as an eluent to remove free triethyl- and triphenylphosphines. The complex was eluted by dichloromethane (70 cm³) and the yellow solution was concentrated. Complex **5** was obtained in a 50% yield by adding petroleum ether to the concentrate.

Preparation of *trans*-[PdX(C_5H_3(6-Cl)N-C^2-CO)(PPh_3)$_2$] (X=Cl (12a), Br (12b), I (12c), or NCS (12d)). Carbon monoxide was bubbled through a tetrahydrofuran solution (50 cm³) at room temperature containing ca. 0.1 mmol of **2a** (0.078 g), **2b** (0.082 g), **2c** (0.087 g), or **9c** (0.108 g). The colorless solution turned yellow on reaction. After evaporation under reduced pressure, diethyl ether was added to the concentrate (10 cm³) to separate out yellow crystals. The CO bubbling was continued for 1, 5, 48, and 170 h in the case of X=I, Br, Cl, and NCS to attain the 73 (**12a**), 85 (**12b**), 80 (**12c**), and 82% (**12d**) yields, respectively.

All of the newly-prepared complexes were purified by recrystallization from dichloromethane–methanol (for **1**, **2**, **3**, **6**, **7**, **8**, **9**, and **10**), diethyl ether–petroleum ether (for **4**, **5**, and **11**), chloroform–diethyl ether (for **12a**, **12b**, and **12d**), or dichloromethane–diethyl ether (for **12c**).

Reactions of 2a with Chlorine, Iodine, and Methyl Iodide. Gaseous chlorine was passed for 10 min through a solution of **2a** (0.11 g, 0.13 mmol) in dichloromethane (20 cm³). The initially colorless solution turned red. A 10 cm³ portion of the solution was poured onto a column of Kieselgel 60 F_{254} (Merck). Diethyl ether was used as an eluent to isolate 2,6-dichloropyridine, which was identified by IR and ultraviolet spectra and elemental analysis. Found: C, 40.36; H, 2.11; N, 9.31%. Calcd for $C_5H_3NCl_2$: C, 40.58; H, 2.04; N, 9.46%. To the other 10 cm³ portion of the red solution was added diethyl ether (40 cm³) and the mixture was left standing for 3 h to deposit red crystals, which were identified to be di-μ-chloro-dichlorobis(triphenylphosphine)dipalladium(II) on the basis of IR spectra and elemental analysis. Found: C, 49.51; H, 3.89%. Calcd for $C_{36}H_{30}P_2Cl_4Pd_2$: C, 49.18; H, 3.44%. The yield was 78%.

A dichloromethane solution (10 cm³) containing **2a** (0.11 g, 0.13 mmol) and iodine (0.03 g, 0.12 mmol) was stirred for 4 h to deposit a yellow precipitate, which was identified as **3c** by IR spectral assay. The yield was 70%. When methyl iodide (0.02 g, 0.13 mmol) was added dropwise to a solution of **2a** in dichloromethane (20 cm³), the initially colorless solution turned yellow. After 24 h standing, the solution was concentrated to 10 cm³ by evaporation under reduced pressure. Methanol (30 cm³) was added to the concentrate and the mixture was allowed to stand 2 h to separate out orange crystals, which were identified as **2c** by IR spectroscopy. The yield was 65%.

Reactions of 8a and 9a with Carbon Monoxide. Carbon monoxide was bubbled for 4 h through a solution of **8a** (0.14 g, 0.138 mmol) in a mixture (50 cm³) of dichloromethane and THF (1:1 by volume) and the mixture was stirred for five days in a sealed vessel. The solution was then concentrated to 20 cm³ by evaporation under reduced pressure to deposit a pale yellow crystalline precipitate in a 95% yield, which was identified as **8b** on the basis of IR spectra and elemental analysis. Found: C, 58.30; H, 3.87; N, 5.30%.

In a similar manner carbon monoxide was passed for 4 h through a solution of **9a** (0.20 g, 0.256 mmol) in THF (50 cm³). The solvent was evaporated to 10 cm³ and diethyl ether (20 cm³) was added to the concentrate to deposit a brown precipitate, which was washed thoroughly with methanol and dried. Recrystallization from dichloromethane–methanol afforded white crystals which were identified as **9b**. Found: C, 64.05; H, 4.11; N, 3.12%. When carbon monoxide was passed through the solution of **9a** for more than 4 h, the solution turned red gradually. After 10 h passage, the mixture was stirred for 2 days in a stoppered vessel. Then the solution was concentrated to 10 cm³ by evaporation under reduced pressure and diethyl ether (30 cm³) was added to the concentrate to deposit red crystals of $Pd_3(PPh_3)_3(CO)_3$. Found: C, 57.43; H, 4.04%. Calcd for $C_{57}H_{45}O_3P_3Pd_3$: C, 57.53; H, 3.81%.

Reaction of 12b with Methanol to Afford an Ester. When methanol (10 cm³) was added to a solution of **12b** (0.11 g, 0.123 mmol) in chloroform (20 cm³), color of the solution turned from red to brown. After standing for 24 h, the solvent was evaporated to dryness under reduced pressure and the residue was extracted with diethyl ether. Methyl 6-chloropicolinate in ether solution was identified by ^{1}H NMR spectroscopy: δ(CH_3), 4.01 s; δ(H^4 and H^5), 7.40 m; δ(H^3), 8.00 m ppm. The yield was 60%. IR assay showed that the residue contained *trans*-dibromobis(triphenylphosphine)palladium(II) and free triphenylphosphine.

Cross Coupling Reactions of Methylmagnesium Bromide with 2-Chloropyridine and 2,6-Dichloropyridine Catalyzed by 1a, 2a, and 3a. A solution of methylmagnesium bromide (13 mmol) in THF (13 cm³) was added dropwise to

Table 1. Analytical Data for the σ-Pyridyl and Related Palladium(II) Complexes

Complex		Found(Calcd)			
		C (%)	H (%)	N (%)	Mol wt
[{PdCl(C_5H_4N-C^2)(PPh_3)}$_2$]	**1a**	57.72 (57.29)	4.10 (3.97)	2.81 (2.91)	945 (964)
[{PdBr(C_5H_4N-C^2)(PPh_3)}$_2$]	**1b**	52.38 (52.45)	3.64 (3.64)	2.67 (2.66)	1028 (1053)
[{PdI(C_5H_4N-C^2)(PPh_3)}$_2$]	**1c**	47.37 (48.15)	3.47 (3.34)	2.38 (2.44)	890[a] (1147)
[PdCl(C_5H_3(6-Cl)N-C^2)(PPh_3)$_2$]	**2a**	63.18 (63.22)	4.24 (4.27)	1.80 (1.80)	782 (779)
[PdBr(C_5H_3(6-Cl)N-C^2)(PPh_3)$_2$]	**2b**	60.07 (59.81)	4.03 (4.04)	1.70 (1.70)	810 (823)
[PdI(C_5H_3(6-Cl)N-C^2)(PPh_3)$_2$]	**2c**	55.81 (56.58)	3.79 (3.82)	1.57 (1.61)	853 (870)
[{PdCl(C_5H_3(6-Cl)N-C^2)(PPh_3)}$_2$]	**3a**	53.19 (53.47)	3.40 (3.51)	2.60 (2.71)	1023 (1033)
[{PdBr(C_5H_3(6-Cl)N-C^2)(PPh_3)}$_2$]	**3b**	48.52 (49.23)	3.18 (3.23)	2.43 (2.50)	1097 (1122)
[{PdI(C_5H_3(6-Cl)N-C^2)(PPh_3)}$_2$]	**3c**	44.70 (45.43)	2.88 (2.98)	2.12 (2.30)	b)
[PdCl(C_5H_3(6-Cl)N-C^2)(PEt_3)$_2$]	**4a**	41.43 (41.61)	6.95 (6.78)	2.86 (2.85)	487 (491)
[PdCl(C_5H_3(6-Cl)N-C^2)($PPhMe_2$)$_2$]	**4b**	47.25 (47.53)	4.76 (4.71)	2.44 (2.64)	523 (531)
[PdCl(C_5H_4N-C^2)(PEt_3)}$_2$]	**5**	38.84 (39.08)	5.58 (5.66)	4.22 (4.14)	673 (676)
[PdCl(C_7H_4SN-C^2)(PPh_3)$_2$]	**6**	64.09 (64.51)	4.36 (4.28)	1.60 (1.75)	783 (801)
[{PdCl($C_4H_3N_2$-C^2)(PPh_3)}$_2$]	**7**	54.09 (54.68)	3.71 (3.76)	5.78 (5.80)	961 (967)
[{PdN$_3$(C_5H_4N-C^2)(PPh_3)}$_2$]	**8a**	55.81 (56.52)	3.86 (3.92)	10.90 (11.46)	905 (978)
[{PdNCO(C_5H_4N-C^2)(PPh_3)}$_2$]	**8b**	57.88 (58.97)	3.99 (3.92)	5.45 (5.73)	966 (978)
[{PdNCS(C_5H_4N-C^2)(PPh_3)}$_2$]	**8c**	56.80 (57.10)	3.61 (3.79)	5.11 (5.55)	967 (1010)
[{PdNCSe(C_5H_4N-C^2)(PPh_3)}$_2$]	**8d**	50.08 (52.24)	3.42 (3.47)	4.70 (5.08)	
[PdN$_3$(C_5H_3(6-Cl)N-C^2)(PPh_3)$_2$]	**9a**	62.73 (62.67)	4.31 (4.23)	6.89 (7.13)	687 (786)
[PdNCO(C_5H_3(6-Cl)N-C^2)(PPh_3)$_2$]	**9b**	64.08 (64.22)	4.30 (4.23)	3.33 (3.57)	695 (786)
[PdNCS(C_5H_3(6-Cl)N-C^2)(PPh_3)$_2$]	**9c**	62.76 (62.93)	4.12 (4.15)	3.61 (3.50)	703 (802)
[{PdN$_3$(C_5H_3(6-Cl)N-C^2)(PPh_3)}$_2$]	**10a**	52.45 (52.80)	3.50 (3.47)	10.83 (10.71)	1022 (1047)
[{PdNCO(C_5H_3(6-Cl)N-C^2)(PPh_3)}$_2$]	**10b**	54.70 (55.09)	3.50 (3.47)	5.01 (5.38)	1007 (1047)
[{PdNCS(C_5H_3(6-Cl)N-C^2)(PPh_3)}$_2$]	**10c**	53.30 (53.45)	3.37 (3.36)	5.21 (5.19)	1024 (1079)
[PdNCO(C_5H_3(6-Cl)N-C^2)(PEt_3)$_2$]	**11**	43.56 (43.48)	6.60 (6.69)	5.52 (5.63)	488 (497)
[PdCl(C_5H_3(6-Cl)N-C^2-CO)(PPh_3)$_2$]	**12a**	62.48 (62.51)	4.25 (4.12)	1.68 (1.74)	801[c] (807)
[PdBr(C_5H_3(6-Cl)N-C^2-CO)(PPh_3)$_2$]	**12b**	59.27 (59.25)	4.09 (3.91)	1.66 (1.65)	831[c] (851)
[PdI(C_5H_3(6-Cl)N-C^2-CO)(PPh_3)$_2$]	**12c**	55.81 (56.15)	3.70 (3.70)	1.56 (1.56)	827 (898)
[PdNCS(C_5H_3(6-Cl)N-C^2-CO)(PPh_3)$_2$]	**12d**	62.26 (62.25)	4.20 (4.01)	3.25 (3.38)	827[c] (830)

a) The value is unreliable due to low solubility. b) Undetermined because of poor solubility. c) Determined in chloroform.

a THF solution (50 cm^3) containing **1a** (0.10 g, 0.10 mmol) and 2-chloropyridine (1.14 g, 10 mmol), but the reaction did not occur at room temperature, the solution maintaining yellow color. When the solution was heated under reflux (about 66 °C), the reaction took place, color of the solution changing via reddish brown to deep green. After the reaction for 5 h, a 10 cm^3 aliquot was evaporated under reduced pressure and the residue was extracted with diethyl ether (20 cm^3). The ether solution was concentrated to 1 cm^3 and applied to the GLC analysis. 2-Methylpyridine was identified in a 13% yield accompanied by unreacted 2-chloropyridine. Prolonged refluxing did not improve the yield of 2-methylpyridine.

A mixed THF solution (55 cm^3) containing **2a** (0.14 g, 0.183 mmol), triphenylphosphine (4.81 g, 18.3 mmol), 2,6-dichloropyridine(2.96 g 20 mmol), and methylmagnesium bromide (25 mmol) was heated under reflux for 3 h. The resulting brown solution was concentrated and made up to 50 cm^3. 2-Methyl-6-chloropyridine was identified by GLC in a 53% yield accompanied by unreacted 2,6-dichloropyridine.

A mixed THF solution (55 cm^3) containing **3a** (0.09 g, 9.14×10^{-5} mol), 2,6-dichloropyridine (2.96 g, 20 mmol), and methylmagnesium bromide (25 mmol) was refluxed for 3 h. The resulting brown solution was concentrated and made up to 50 cm^3. 2,6-Dimethylpyridine was identified in a 4% yield in this case together with 2-methyl-6-chloropyridine (58% yield) and unreacted 2,6-dichloropyridine.

Measurements. IR spectra were recorded in Nujol on JASCO IR-E (4000-650 cm^{-1}), Hitachi EPI-L (700-200 cm^{-1}) and FIS-3 (400-30 cm^{-1}) spectrophotometers. ^1H NMR spectra were taken at 100 MHz with JEOL JNM MH-100 and PS-100 spectrometers using tetramethylsilane as internal reference. ^{13}C NMR spectra were obtained at 25.0 MHz by 6000 times scan on a JEOL JNM FX-100 instrument with tetramethylsilane as external reference. ^{15}N NMR spectra were recorded at 9.04 MHz by 3000 times scan on a JEOL JNM FX-90Q spectrometer with ammonium nitrate-^{15}N aqueous solution as external reference. Mass spectra were taken with a JEOL GC-mass spectrometer JMS D-300 and gas chromatography was performed on a Yanagimoto G-180 instrument with Silicone DC-550 and nitrogen gas, injection temperature being 200 °C. The decomposition temperatures of the newly-prepared compounds were determined in a capillary tube under nitrogen. The molecular weight was measured in dichloromethane at 25 °C by vapor pressure osmometry with an instrument manufactured by Knauer in Berline, West Germany.

Results and Discussion

Although tetrakis(triphenylphosphine)nickel(0) reacted readily with halopyridines in toluene at room temperature,[8] the reactions of $Pd(PPh_3)_4$ with halopyridines did not occur at room temperature, but heating for a long time, e.g. 3 h for 2-bromopyridine and 10 h for 2-chloropyridine at 90 °C, was necessary to afford the pyridylpalladium(II) complexes in high yields. 2-Chloropyrazine and 2-chlorobenzothiazole also reacted with $Pd(PPh_3)_4$ in toluene at 90 °C to produce the σ-carbon-bonded complexes in ca. 80% yields, although the 2-benzothiazolylnickel(II) complex could not be prepared.[8] Results of elemental analysis and molecular weight determination of newly-prepared complexes are collected in Table 1.

Properties of Halogeno 2-Pyridyl and Related Complexes. The analytical and molecular-weight data for compounds **1a—c**, **3a—c**, **5**, and **7** indicate that they are essentially dinuclear, although the observed molecular weight of **1c** in dichloromethane is appreciably lower than the calculated value. The dinuclear structure with bridging halide anions is quite common among palladium(II) complexes,[13] and is usually subject to cleavage by bonor ligands to give mononuclear species.

As is seen in Table 2, the ν(Pd-X) frequencies observed for **1a—c** are not unreasonable for the bridging halides. However the dinuclear structure in these complexes is very stable and is not cleaved by excess bases such as triphenylphosphine, pyridine, and thiourea. X-Ray analysis denied the halide-bridged structure and disclosed the bridging role of the 2-pyridyl ligand in **1b** (Fig. 1).[11] A similar μ-pyridyl(C^2,N) structure was also confirmed for (μ-H)$Re_2(CO)_8$(μ-C_5H_4N-C^2,N) and (μ-H)$Re_2(CO)_7$(μ-C_5H_4N-C^2,N)(Me_3NO).[5b] Basicity of the 2-pyridyl ligand coordinated to palladium(II) was reported to be 3700 times greater than that of free pyridine.[9b] This enhanced basicity enables the stable bridging of the 2-pyridyl ligand.*1 A similar bridged structure

Table 2. Decomposition Temperatures and Some FIR Data

Complex	Decomp temp[a] °C	ν(Pd-X) cm^{-1}	ν(Pd-P) cm^{-1}
1a	196	263 m	420 s
1b	185	196 m	420 m
1c	140	144 w	420 m
2a	250 (232)	295 s	351 m
2b	240 (230)	187 s	350 m
2c	205	172 s	346 s
3a	205	278 m	380 m
3b	197	221 m	379 m
3c	195	174 w	376 m
4a	249 (65)	300 s	350 m
4b	233 (117)	292 m	348 m
5		260 s	420 m
6	197	302 s	364 w
7	197	270 m	430 m

a) Numerals in parentheses give melting points in °C. s: strong, m: medium, w: weak.

*1 The reaction of $LPd_2(CH_3CO_2)$ (L=bridging benzenethiolate derivatives) with pyridines containing electron-donating substituents (X) at the 3-position also gave $LPd_2(C_5H_3XN$-C^2,$N)$ in low yields.[6]

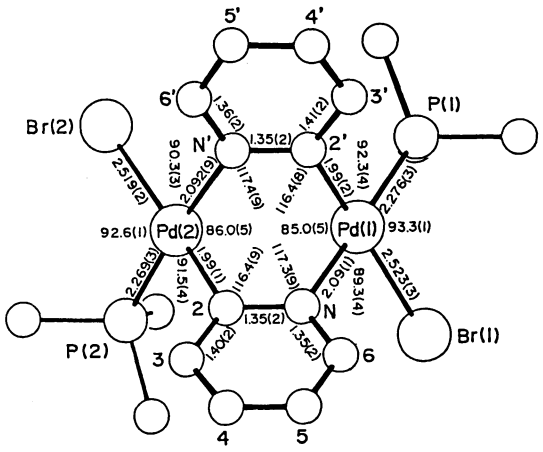

Fig. 1. Stereochemistry of *trans*-(*P*, *N*)-[{PdBr(μ-C_5H_4N-C^2,*N*)(PPh_3)}$_2$] (**1b**) viewed perpendicular to the plane containing C(2), N, C(2′), and N′. Phenyl groups are not shown for clarity, except the three carbon atoms bonded to each phosphorus atom. Important bond lengths (in Å) and angles (in degree) are also given with e.s.d.'s in parenthsses.[11]

has also been presumed for the 2-pyridyl group involved in triosmium clusters[7b] and a gold(I) complex[3] in which the 2-pyridyl ligand serves as a three-electron donor.

Complex **1a** was prepared under the same conditions as **1b**, and **1c** was derived from **1a** by the halide substitution. The patterns of ^{1}H NMR and IR spectra for **1a—c** are quite similar to each other. Furthermore, all of the IR absorption bands of these complexes in the region 1600—300 cm^{-1} are superimposable on each other within experimental errors. These facts suggest that **1a**, **1b**, and **1c** will have the identical structure. The ν(Pd–P) frequencies (in Table 2) are close to each other and the ν(Pd–Cl):ν(Pd–Br):ν(Pd–I) ratio (1:0.75:0.55) is similar to the value 1:0.75:0.61 observed for *trans*-$PdX_2(PEt_3)_2$ (X=Cl, Br, and I, respectively) and 1:0.73 for *cis*-$PdX_2(PMe_3)_2$ (X=Cl and Br).[14] Thus complexes **1a** and **1c** are considered to have the pyridyl-bridged structure analogous to **1b**. In each complex the halide anion occupies the coordination site trans to the pyridyl carbon, and the rather lower frequencies of the ν(Pd–X) vibrations are caused by the strong trans influence of the σ-carbon-bonded pyridyl ligand. Thermal stabilites of these complexes are in the sequence of **1a**>**1b**>**1c**. Stronger trans influence of the iodide anion compared with that of chloride may destabilize the Pd–C linkage.

When 2,6-dichloropyridine was used as a reagent, the mononuclear 6-chloro-2-pyridyl complexes **2a—c** were obtained. Complexes **4a** and **4b**, which were derived from **2a** by the phosphine exchange reactions, and the benzothiazolyl complex **6** are also mononuclear. When a dichloromethane solution of **2a** was allowed to stand at room temperature for a long time as weeks, one of the phosphine ligands was lost to form **3a**. A precipitate of **3a** thus produced was readily reconverted to **2a** on addition of excess triphenylphosphine, indicating that reaction (1) is reversible.

$$2[PdCl(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)_2] \rightleftarrows [\{PdCl(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)\}_2] + 2PPh_3 \quad (1)$$

By oxidizing the freed phosphine equilibrium (1) was shifted to right to obtain **3a** conveniently.[15] As was described in Experimental section, the reaction of $Pd(PPh_3)_4$ with 2,6-dichloropyridine gave **2a** exclusively without appreciable contamination with **3a** in spite of much lower solubility of the latter, indicating that the thermodynamic stability of **2a** is much higher than that of **3a**. A molecular model suggests that the dinuclear structure of **3a** analogous to **1b** is unfavorable because of the steric interaction between the chloro substituent on the pyridine ring and the benzene rings.

Mononuclear complexes **2a—c** are thermally more stable than the corresponding dinuclear complexes **3a—c**, the Cl>Br>I sequence holding again in either case, and **2a**, **2b**, **4a**, and **4b** showing clear melting points. The mononuclear complexes exhibit a single ν(Pd–X) band in the region reasonable for the terminal halide trans to the carbon-bonded organic ligand,[16] and a single ν(Pd–P) band at about 350 cm^{-1} in accordance with the trans structure. Data of ^{1}H NMR spectra included in Table 3 also support the trans structure. Thus the methyl protons of triethylphosphine in **4a** resonate at 1.11 ppm as a 1:4:6:4:1 quintet[17] with J=ca. 8.0 Hz and the methyl protons of phenyldimethylphosphine in **4b** at 1.53 ppm as a 1:2:1 triplet.[18]

As is shown in Table 3, the ring protons of triphenylphosphine in complex **1** through **7** resonate generally as two multiplets with the area ratio of 3:2 in the 7.33—7.42 and 7.45—7.86 ppm regions, respectively. The higher-field signal is assigned to the meta and para protons and the lower-field one to the ortho protons.[19] The pyridine-ring protons were assigned in a similar manner as those of the pyridylnickel(II) complexes.[8] In the case of the 2-benzothiazolyl complex **6**, signals of the hetero-ring protons overlapped with those of the benzene-ring protons.

The most remarkable feature of the ^{1}H NMR data for the 2-pyridyl complexes containing triphenylphosphine as the ancillary ligands is the up-field shift of the resonances of pyridine-ring protons at the 3, 4, and 5 positions as compared with those of uncoordinated pyridine (H^2 8.5, H^3 7.2, H^4 7.6 ppm), although the chemical shifts of pyridine-ring protons in **1a** and some other complexes such as **3a** and **4b** are so close to each other, exhibiting composite signals.

Table 3. Proton Chemical Shifts from Internal Me_4Si in CD_2Cl_2 (ppm)

Complex	Hetero-ring proton at the position 3	4	5	6	Benzene-ring proton at the position meta and para	ortho	Other protons
1a	———	(6.56 m)	———	8.47 m	7.36 m	7.86 m	
2a	6.13 d	6.29 t	6.64 d		7.42 m	7.65 m	
3a		(6.53 m)			7.33 m	7.45 m	
4a	6.72 d	7.05 t	7.13 d				1.11 quin (CH_3),[b] 1.57 m (CH_2)
4b	———	(6.70 m)	———		7.38 m	7.53 m	1.53 t (CH_3)
5	7.17 s	7.10 t	6.76 t	8.36 s			1.14 quin (CH_3),[c] 1.83 m (CH_2)
6					7.33 m	7.70 m	7.01 m (thiazolyl H)
7	8.40 m		———	(7.83 m) —	7.38 m	7.83 m	
8a	———	(6.64 m)	———	8.39 m	7.41 m	7.75 m	
8b	———	(6.63 m)	———	8.37 m	7.43 m	7.80 m	
8c	———	(6.60 m)	———	8.36 m	7.47 m	7.78 m	
9a	6.14 d	6.27 t	6.62 d		———	(7.39 m) ———	
9b	6.12 d	6.26 t	6.62 d		———	(7.42 m) ———	
9c	6.15 d	6.27 t	6.59 d		———	(7.44 m) ———	
10a	———	(6.70 m)	———		7.48 m	7.84 m	
10b	———	(6.66 m)	———		7.47 m	7.87 m	
10c	———	(6.67 m)	———		7.43 m	7.82 m	
11	7.13 m	6.79 m	7.13 m				1.09 quin (CH_3),[d] 1.50 m (CH_2)
12a[a]	— (6.90 m)	———		6.00 d	7.22 m	7.72 m	

a) In $CDCl_3$. b) 1 : 4 : 6 : 4 : 1 quintet with J = ca. 8.0 Hz. c) 1 : 2 : 2 : 2 : 1 quintet with ^3J(P-H) = ca. 17.0 Hz and ^3J(H-H) = ca. 8.5 Hz. d) 1 : 4 : 6 : 4 : 1 quintet with J = ca. 4.0 Hz. s: singlet, d: doublet, t: triplet, quin: quintet, m: multiplet.

Table 4. ^{13}C NMR Data for Complex **1b** and Uncoordinated Triphenylphosphine and Pyridine

Compound	Chemical shift (ppm)					Coupling constant (Hz)
$P(C_6H_5)_3$	C^1 138.3	C^2 134.4	C^3 129.2	C^4 129.3		J(P-C^1) = 21, J(P-C^2) = 20 J(P-C^3) = 7, J(P-C^4) < 1
C_5H_5N	C^2, C^6 149.7	C^3, C^5 123.6	C^4 135.5			
1b						
Phenyl carbon	C^1 138.6	C^2 143.0	C^3 135.3	C^4 139.7		J(P-C^1) = 49, J(P-C^2) = 11.7 J(P-C^3) = 10.7, J(P-C^4) = 0
Pyridyl carbon	C^2 200.5	C^3 124.5	C^4 140.3	C^5 124.4	C^6 161.7	

On the other hand, there was no significant up-field shift observed for the pyridine-ring proton resonances in the 2-pyridyl complexes containing triethylphosphine such as **5**, rhenium carbonyls,[5] and osmium clusters.[7b] Thus the up-field shift of pyridine-ring proton resonances seems to be caused by an anisotropic shielding effect of the triphenylphosphine ligand through space[20] as well as by the back-donation from palladium to the pyridine ring via the carbon atom. In fact, according to X-ray analysis of **1b**,[11] the pyridine-ring protons at the 3, 4, and 5 positions lie in the vicinity of a benzene ring of the triphenylphosphine ligand, whereas the proton at the 6 position is far from it.

Table 4 shows the ^{13}C NMR data for **1b** together with those for uncoordinated triphenylphosphine[21] and pyridine.[22] Assignment of the phenyl carbons in **1b** was readily made on the basis of J(P-C) values and also by reference to the data for the uncoordinated phosphine. It is worth noting that the J(P-C^1) value (49 Hz) is more than twice larger than the value (21 Hz) for the free ligand and that (20 Hz) for the corresponding nickel(II) complex.[8] Assignment of the pyridyl carbons in **1b** was based on

the results for *trans*-PdBr(C_5H_4N-C^2)(PEt_3)$_2$ which were obtained by the proton off-resonance and selective decoupling experiments.[9b] Pyridyl carbons are more or less deshielded on bonding to palladium(II) through C^2, and the down-field shift of C^2 is astonishingly large. The effect of coordination is quite different from the nickel(II) complexes where both the ^{13}C and ^1H signals showed up-field shifts probably due to the back donation from the metal atom. No reasonable rationalization of the palladium(II) case is possible at the present stage of investigation.

Characterization of the Pseudohalogeno σ-Pyridyl Complexes. The dinuclear pseudohalogeno complexes **8a—d** and **10a-c** were prepared by simple metathesis reactions of **1a** and **3a**, respectively, with the pseudohalides in good yields. It should be noted that the bridge-splitting reactions to give rise to anionic pyridyl complexes did not occur, but simple substitution of the halide ligands was resulted.

As is seen in Table 3, the patterns of ^1H NMR spectra for **8a—c** and the chemical shifts of pyridine and benzene-ring protons in these complexes are quite similar to each other. Compounds **10a—c** also exhibit a close resemblance to **8a—c** in the spectral patterns except for lacking of the pyridine H^6 resonance. These facts strongly suggest that all these complexes have a common bridging mode.

Complex **10c** containing the ^{15}NCS ligand (95% ^{15}N) was prepared and the ^{15}N NMR spectrum was measured in CD_2Cl_2. As Fig. 2 shows, a single doublet with J(P—N)=ca. 3.2 Hz is observed at −235.61 ppm up-field from external $NH_4{}^{15}NO_3$. The coupling constant of ^{15}N to ^{31}P situated at the trans position in *cis*-PtNCS(SCN){$P(OEt)_3$}$_2$[23] and PtNCS(SCN)($Ph_2PCH_2C(CF_3)$=CHPPh_2)[24] was found to be 91 and 53.71 Hz, respectively, whereas that of ^{15}N to the cis ^{31}P in either complex was too small to be detected. The small value of ^{31}P–^{15}N coupling constant in **10c** indicates that the N-bonded thiocyanate ligand occupies the coordination site cis to the phosphine.

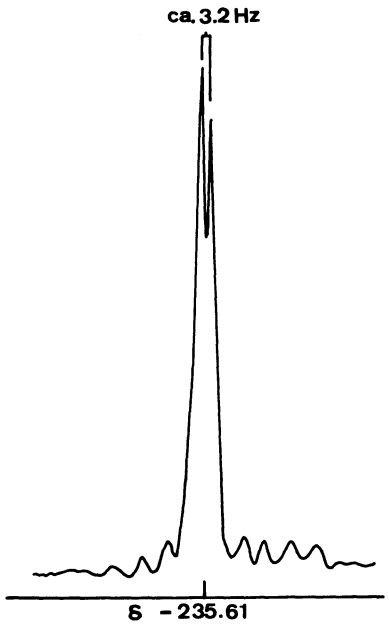

Fig. 2. ^{15}N NMR spectrum of diisothiocyanatobis(6-chloro-2-pyridyl)bis(triphenylphosphine)dipalladium(II) (**10c**) in CD_2Cl_2 by 3000 times scan at 9.04 MHz. The chemical shift is measured from external $NH_4{}^{15}NO_3$ (up-field negative).

Compounds **9a—c** were also prepared by the ligand substitution reactions of **2a**, and **11** was obtained from the reaction between **9b** and excess triethylphosphine. The trans mononuclear structure of these complexes is evidenced by the analytical and molecular-weight data in Table 1 and by the single ν(Pd–P) band around 350 cm^{-1} (Table 5). The quintet resonance at 1.09 ppm exhibited by the methyl protons of triethylphosphine in **11** (Table 3) also supports the trans structure of this complex.[17]

Infrared spectra are frequently useful in distinguishing the linkage mode of the pseudohalides in metal complexes.[25] Frequencies of the ν(CN) and ν(CS) vibrations observed for **8c**, **9c**, **10c**, and **12d** indicate that each NCS ligand in these complexes is N-bonded. Similarly the ν(CN), ν(CO), and δ(NCO) frequencies for the cyanate ligand in **8b**, **9b**, **10b**, and **11** (Table 5) are in the range assigned to N-bonding.[25] A related compound *trans*-PdNCS(C_5H_4N-C^3)(PPh_3)$_2$ was confirmed by X-ray analysis to have the N-bonded thiocyanato ligand.[26]

Reactions of the 2-Pyridylpalladium(II) Complexes. The pyridyl-palladium(II) bond is very strong and is not cleaved by methyl iodide and elementary iodine. Thus compound **2a** was merely

Table 5. Characteristic IR Data for the Pseudohalogeno Complexes[a]

Complex	ν(CN) or ν_a(NNN)	ν(CY) or ν_s(NNN)	δ(NCY) or δ(NNN)	ν(Pd-P)
8a	2044 s	1339 m	590 w	420 m
8b	2230 s	1330 m	605 m	425 m
8c	2090 s	810 w	b)	420 m
8d	2100 s	b)	b)	425 m
9a	2070 s	1337 m	597 w	347 m
9b	2220 s	1330 m	606 m	336 m
9c	2053 s	816 w	b)	353 w
10a	2050 s	1342 m	595 w	380 m
10b	2220 s	1336 m	604 m	381 m
10c	2053 s	815 w	b)	378 w
11	2240 s	1328 m	603 m	354 m
12d	2054 s	812 w	b)	b)

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

converted to **2c** and **3c**, respectively. Iodine seems to have shifted the mononuclear-dinuclear equilibrium analogous to Eq. 1 to right by oxidizing the freed phosphine. Benzoyl chloride did not react with **2a** in dichloromethane at room temperature. On the other hand gaseous chlorine cleaved the Pd–C bond to afford 2,6-dichloropyridine.

Complexes **2a—c** and **9c** readily reacted with carbon monoxide to afford the pyridylcarbonyl complexes **12a—d**, which have the trans mononuclear structure as evidenced by the analytical and molecular-weight data as well as the existence of a single ν(Pd–P) band. Each of these complexes shows two ν(CO) bands in the frequency region reasonable for the acyl complex:[27] **12a**, 1661 and 1639 cm^{-1}; **12b**, 1663 and 1640 cm^{-1}; **12c**, 1672 and 1640 cm^{-1}, **12d**, 1673 and 1650 cm^{-1}. Compound **12b** reacted with methanol to produce methyl 6-chloropicolinate in a good yield. The reaction proceeded in the absence of base and the nucleophilic attack by the methanol molecule on the acyl carbon seems to have occurred. A proton must have been freed in this event, but the picolinate nitrogen is not protonated. Although ^{1}H NMR assay at low temperature (−40 to −60 °C) failed to detect a hydrido complex, the following sequence might be responsible for the overall reaction.

$$[PdBr(COR)(PPh_3)_2]+CH_3OH \rightarrow [PdBr(H)(PPh_3)_2]+RCOOCH_3$$

$$2[PdBr(H)(PPh_3)_2] \rightarrow [PdBr_2(PPh_3)_2]+Pd^0+2\,PPh_3+H_2.$$

The azide ligand in **8a** reacted with carbon monoxide to afford **8b**, which is the stable end product and did not react further with CO to give rise to an acyl complex, although carbonylation of the terminal azide ligand to isocyanate has been reported to occur readily for a number of metal complexes.[28] On the other hand, the mononuclear complex **9a** reacted with CO in two steps, a limited amount of CO converting the azide ligand to the isocyanate to result in **9b** and an additional amount of CO carbonylating the pyridyl ligand. The CO insertion into the Pd–pyridyl bond is appreciably slower than the reaction of the azide ligand with CO, and a small amount of $Pd_3(PPh_3)_3(CO)_3$[29] was produced by partial decomposition. Unfortunately, the product acyl complex analogous to **12d** could not be isolated in a satisfactory purity, but was characterized by the IR spectra (ν(CO)=1680 cm^{-1}).

It should be noted that only the pyridyl ligand in mononuclear complexes reacts with CO, while that in dinuclear complexes does not. The palladium–carbon bond in the latter complexes may be strengthened synergistically by the bridging of the pyridyl ligand to another metal atom through nitrogen so as to prevent CO insertion.

Cross Coupling Reactions. In recent years cross coupling reactions between organic halides and Grignard reagents have been found to be catalyzed by the nickel(II) and palladium(II) phosphine complexes.[30,31] Although $[\{NiCl(C_5H_4N\text{-}C^2)(PPh_3)\}_2]$ selectively catalyzes the cross coupling of 2-chloropyridine with methylmagnesium bromide in THF at room temperature,[8] the palladium(II) complex **1a** does not work as a catalyst under the same conditions. In refluxing THF, the catalytic coupling reaction does occur with **1a**, but the yield of 2-methylpyridine was as low as 13% when 1/100 molar amount of **1a** was added to 2-chloropyridine. Complex **3a** is more effective as a catalyst for the reaction of 2,6-dichloropyridine with methylmagnesium bromide in refluxing THF to give 2-methyl-6-chloropyridine in a 58% yield, reflecting the lability of **3a** compared with **1a**. In the presence of excess triphenylphosphine to prevent transformation of **2a** to **3a**, the mononuclear complex **2a** similarly attains the 53% yield of the product. On the other hand, the yield of 2,6-dimethylpyridine from 2,6-dichloropyridine was only 4% in the case of **3a** and was negligibly small when **2a** was used, although the nickel(II) catalyst was reported to promote the Grignard coupling of organo dihalides at both the reaction sites.[30] It is worth noting that the palladium(II) catalysts are less active but are more selective than the nickel(II) complexes for the synthesis of 2-methyl-6-chloropyridine. The selectivity of palladium(II) catalysts shown in the alkylation is analogous to that observed in the cross coupling reactions of 2,6-dihalopyridines with $PhCH_2ZnBr$ in the presence of $Pd(PPh_3)_4$ as a catalyst.[32]

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