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Palladium(II) Complexes Containing Both the Chelating β-Diketonato and σ-Pyridyl Ligands. Catalyzed Coordination-site Exchange Reactions

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A novel type of palladium(II) complexes, $[Pd(\beta\text{-dik})(pyridyl)(PPh_3)]$ and $[Pd(\beta\text{-dik})(pyridyl)]_2$ containing a chelating acetylacetonate, trifluoroacetylacetonate, or hexafluoroacetylacetonate anion and 2-, 3-, or 4-pyridyl radical as the coexisting ligands were prepared and characterized by elemental analysis and molecular weight determination as well as ^1H and ^{13}C NMR spectroscopy. $[Pd(acac)(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)]$ is stereochemically rigid in solution but undergoes the coordination-site exchange reaction catalyzed by nitrogen and phosphorus bases and donor solvents. Similar reaction of $[Pd(acac)(C_5H_4N\text{-}C^2)(PPh_3)]$ is catalyzed by triphenylphosphine liberated by the dinuclear-complex formation reaction (autocatalysis). Intact molecules of $[Pd(acac)(C_5H_4N\text{-}C^3$ and $\text{-}C^4)(PPh_3)]$ catalyze mutually their own coordination-site exchange (self-catalysis).

A stable dinuclear complex $[PdBr(C_5H_4N\text{-}C^2)(PPh_3)]_2$ (**3a**) was prepared by the reaction of $[Pd(PPh_3)_4]$ (**1**) with 2-bromopyridine in toluene at 90 °C[1,2] and was disclosed by X-ray analysis to have a novel structure in which two pyridyl ligands are bridging palladium atoms through the C^2 and N atoms.[2,3] A similar reaction of **1** with 2,6-dichloropyridine gave a mononuclear complex *trans*-$[PdCl(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)_2]$ (**2d**), which coexists in equilibrium with a minute amount of the dinuclear complex $[PdCl(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)]_2$ in solution and is completely converted into the latter by oxidation of freed triphenylphosphine with hydrogen peroxide.[1,2] On the other hand, the reactions of **1** with 3- and 4-bromopyridines in toluene at 90 °C afforded *trans*-$[PdBr(C_5H_4N\text{-}C^3)(PPh_3)_2]$ (**2b**) and *trans*-$[PdBr(C_5H_4N\text{-}C^4)(PPh_3)_2]$ (**2c**), respectively, and the corresponding dinuclear complexes have never been obtained.[4] Treatment of complexes **3a**, **2b**, and **2c** with triethylphosphine in diethyl ether at room temperature gave rise to a set of linkage isomers *trans*-$[PdBr(C_5H_4N\text{-}C^2, \text{-}C^3, \text{and } \text{-}C^4)(PEt_3)_2]$, of which properties and molecular structures were compared with each other.[4]

In the present investigation, a new type of palladium(II) complexes $[Pd(\beta\text{-dik})(pyridyl)(PPh_3)]$ containing an O,O'-chelated β-diketonate anion and a carbon-bonded pyridyl ligand have been derived from complexes **3a**, **2b**, **2c**, and **2d**. This paper reports the properties of these mixed-ligand complexes, laying emphasis on their dynamic behaviors in solution catalyzed by Lewis bases including donor solvents.[5]

Experimental

Preparation of Complexes. $[PdBr(C_5H_4N\text{-}C^2)(PPh_3)]_2$ (**3a**), *trans*-$[PdBr(C_5H_4N\text{-}C^3)(PPh_3)_2]$ (**2b**), *trans*-$[PdBr(C_5H_4N\text{-}C^4)(PPh_3)_2]$ (**2c**), and *trans*-$[PdCl(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)_2]$ (**2d**) were prepared by the methods reported previously.[2,4)

$[PdBr(C_5H_4N\text{-}C^3)(PPh_3)]_n$ *(3b)*: To a suspension of complex **2b** (6.35 g, 8.05 mmol) in acetone (50 cm³) was added 12 cm³ of 30% hydrogen peroxide solution (106 mmol) and the mixture was stirred at room temperature for 24 h. A white precipitate was filtered, washed with acetone and dietyl ether successively, and dried *in vacuo*. The yield was 4.15 g (97.9%).

$[PdBr(C_5H_4N\text{-}C^4)(PPh_3)]_n$ *(3c)*: White complex **3c** was obtained almost quantitatively (4.50 g, 98.8%) in a similar fashion by the reaction between **2c** (6.82 g, 8.64 mmol) and aqueous hydrogen peroxide (13 cm³ , 115 mmol).

$[PdCl(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)]_2$ *(3d)*: Yellow product **3d** from the reaction between **2d** (6.09 g, 7.82 mmol) and aqueous hydrogen peroxide (9 cm³, 79.4 mmol) was purified by dissolution in dichloromethane and reprecipitation on addition of diethyl ether. The yield was 3.98 g (98.5%).

$[PdClO_4(C_5H_4N\text{-}C^2)(PPh_3)]_2$ *(4a)*: A solution of silver perchlorate (2.00 g, 9.65 mmol) in methanol (10 cm³) was added to a dichloromethane (100 cm³) solution of **3a** (3.00 g, 2.85 mmol) and the mixture was stirred at room temperature for 2 h. A precipitate of silver bromide was filtered off and the filtrate was treated three times with deionized water (50 cm³ each) to extract residual silver perchlorate. The dichloromethane solution was passed through a column of anhydrous sodium sulfate and then concentrated to about 10 cm³ under reduced pressure. On addition of diethyl ether to the concentrate, a yellow precipitate appeared, which was filtered, washed with the ether, dried *in vacuo*, and purified by reprecipitation from dichloromethane–diethyl ether. The yield was 2.56 g (82.0%).

$\{[Pd(C_5H_4N\text{-}C^3)(PPh_3)(H_2O)]ClO_4\}_n$ *(4b)*: *Method A*; A solution of silver perchlorate (1.02 g, 4.93 mmol) in methanol (10 cm³) was added to a suspension of **3b** (2.03 g, 3.76 mmol when $n=1$) in dichloromethane (10 cm³) and the mixture was stirred at room temperature for 50 min. After filtration of silver chloride, the filtrate was concentrated to about 2 cm³. On scratching the wall of vessel with a glass rod after addition of methanol (20 cm³) to the concentrate, a white precipitate appeared, which was filtered, washed with diethyl ether, and dried *in vacuo*. The yield was 1.84 g (86.7%).

Method B; After the reaction of **2b** (0.653 g, 0.838 mmol) with silver perchlorate (0.209 g, 1.01 mmol) in a mixture of dichloromethane (5 cm³) and methanol (2 cm³) at room temperature for 1 h, work up similar to method A gave a white precipitate. The yield was 0.215 g (45.5%) after reprecipitation from dichloromethane–ethanol.

$\{[Pd(C_5H_4N\text{-}C^4)(PPh_3)(H_2O)]ClO_4\}_n$ *(4c)*: Two preparative methods starting from **3c** and **2c** gave a light yellow powder of **4c** in 100 and 90.8% yields, respectively. The dichloromethane–benzene system was used for reprecipitation.

$[PdClO_4(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)]_2$ *(4d)*: Yellow complex **4d** was derived analogously from **3d** and **2d** in 89.0 and 81.6%

yields, respectively. Reprecipitation was performed from dichloromethane–diethyl ether.

Thus two methods were used for preparation of type-**4** complexes and method A was found better since products from method B were contaminated with a small amount of free triphenylphosphine. Analogously, the following type-**5** complexes were prepared by each of three methods: (method A) reactions of type-**2** complexes with thallium(I) β-diketonates, (method B) reactions of type-**3** complexes with thallium(I) β-diketonates, and (method C) reactions of type-**4** complexes with potassium β-diketonates. For brevity only the preferable methods are described here for each complex.

$[Pd(acac)(C_5H_4N\text{-}C^2)(PPh_3)]$ (5a1): Method B; Thallium(I) acetylacetonate, Tl(acac) (0.625 g, 2.06 mmol) was added to a solution of **3a** (0.986 g, 0.936 mmol) in dichloromethane (20 cm^3) and the mixture was stirred at room temperature for 30 min. After separation of thallium(I) bromide, the filtrate was concentrated to about 3 cm^3 under reduced pressure. A small amount of diethyl ether was added to the concentrate and crystallization was induced by scratching the flask. The product was filtered, washed with the ether, and recrystallized from dichloromethane–diethyl ether. The yield was 0.925 g (90.5%).

Method C; To a solution of **4a** (0.943 g, 0.863 mmol) in dichloromethane (30 cm^3) was added a methanol (10 cm^3) solution of potassium acetylacetonate (0.729 g, 5.28 mmol) and the mixture was stirred at room temperature for 20 min. After separation of potassium perchlorate by filtration, the solvent was evaporated to dryness under reduced pressure. Dichloromethane (30 cm^3) was added to the residue and insoluble material was filtered off. The filtrate was concentrated to about 2 cm^3 under reduced pressure. Crystallization was induced by scratching the flask after addition of diethyl ether (10 cm^3) to the concentrate. The product was filtered, washed with diethyl ether, and recrystallized from dichloromethane–diethyl ether. The yield was 0.802 g (85.2%).

$[Pd(tfac)(C_5H_4N\text{-}C^2)(PPh_3)]$ (5a2): The reaction of **3a** with thallium(I) trifluoroacetylacetonate, Tl(tfac) (method B) and that of **4a** with K(tfac) (method C) gave complex **5a2** in 68.7 and 46.9% yields, respectively. Petroleum ether (bp<60 °C) was used instead of diethyl ether for recrystallization.

$[Pd(hfac)(C_5H_4N\text{-}C^2)(PPh_3)]$ (5a3): Method B using **3a** and thallium(I) hexafluoroacetylacetonate, Tl(hfac), and method C using **4a** and K(hfac) afforded **5a3** in 51.9 and 44.3% yields, respectively.

$[Pd(acac)(C_5H_4N\text{-}C^3)(PPh_3)]$ (5b1), $[Pd(tfac)(C_5H_4N\text{-}C^3)(PPh_3)]$ (5b2), and $[Pd(hfac)(C_5H_4N\text{-}C^3)(PPh_3)]$ (5b5): These 3-pyridyl complexes were prepared by methods C,B, and B in 82.8, 78.6, and 53.2% yields, respectively.

$[Pd(acac)(C_5H_4N\text{-}C^4)(PPh_3)]$ (5c1), $[Pd(tfac)(C_5H_4N\text{-}C^4)(PPh_3)]$ (5c2), and $[Pd(hfac)(C_5H_4N\text{-}C^4)(PPh_3)]$ (5c3): The 4-pyridyl complexes were obtained in 63.9, 63.0, and 63.3% yields by methods C, B, and B, respectively.

$[Pd(acac)(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)]$ (5d1), $[Pd(tfac)(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)]$ (5d2), $[Pd(hfac)(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)]$ (5d3): Methods C, C, and B were used to prepare these complexes in 84.0, 78.4, and 65.8% yields, respectively.

$[Pd(acac)(C_5H_4N\text{-}C^2)]_2$ (6a1), $[Pd(tfac)(C_5H_4N\text{-}C^2)]_2$ (6a2), and *$[Pd(acac)(C_5H_3(6\text{-}Cl)N\text{-}C^2)]_2$ (6d1)*: To a suspension of complex **5a1** (0.356 g, 0.652 mmol) in acetone (10 cm^3) was added 2 cm^3 of aqueous hydrogen peroxide solution (10%, 5.8 mmol) and the mixture was stirred at room temperature for 2 h. A yellow precipitate of **6a1** was filtered, washed with diethyl ether and dried *in vacuo*. The yield was 0.147 g (76.2%). Complexes **6a2** and **6d1** were similarly prepared from **5a2** and **5d1** in 43.6% (0.103 g) and 28.1% (0.120 g) yields, respectively.

$[Pd(acac)(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PEt_3)]$ (7d1): Triethylphosphine (0.115 cm^3, 0.788 mmol) was added to a suspension of **6d1** (0.249 g, 0.392 mmol) in dichloromethane (5 cm^3) and the mixture was stirred at room temperature for 1 h. After evaporation of the solvent, the oily residue was treated with diethyl ether and the extract was concentrated to dryness. The yield was 0.198 g (57.9%).

Measurements. Infrared spectra were recorded in Nujol mull on a JASCO DS 701G spectrophotometer. The NMR spectra were taken with JEOL JNM-MH100 (for ^{1}H) and FX 60Q (for ^{13}C) spectrometers. The molecular weight was determined by vapor pressure osmometry with an instrument manufactured by Knauer in West Berlin, West Germany.

The ^{1}H NMR line shape simulation was carried out with a FACOM 230-60 computer according to the Nakagawa's equation.[6)]

Results and Discussion

Synthesis. The 2-, 3-, and 4-pyridyl complexes $[PdBr(C_5H_4N\text{-}C^2)(PPh_3)]_2$ (**3a**), $[PdBr(C_5H_4N\text{-}C^3)(PPh_3)_2]$ (**2b**), $[PdBr(C_5H_4(N\text{-}C^4)(PPh_3)_2]$ (**2c**), and $[PdBr(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)_2]$ (**2d**) were used as the starting materials for the present synthetic work, and the reaction sequences from **2b** and **2c** and also from **2d** are illustrated in Figs. 1 and 2, respectively. Hydrogen peroxide treatment of the mononuclear complexes **2b**, **2c**, and **2d** eliminated one of the two PPh$_3$ ligands in each complex to result in $[PdBr(C_5H_4N\text{-}C^3)(PPh_3)]_n$ (**3b**), $[PdBr(C_5H_4N\text{-}C^4)(PPh_3)]_n$ (**3c**), and $[PdCl(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)]_2$ (**3d**), respectively. The analytical and molecular weight data of **3d** indicate that the yellow complex is dinuclear. It may have the pyridyl-bridged dinuclear structure similar to that of **3a**.[2,3)] Complexes **3b** and **3c** are white and insoluble in usual organic solvents, suggesting that they may have polynuclear structures.

The halide ligands in dinuclear complexes **3a** and **3d** were substituted by the perchlorate ion to result in **4a**

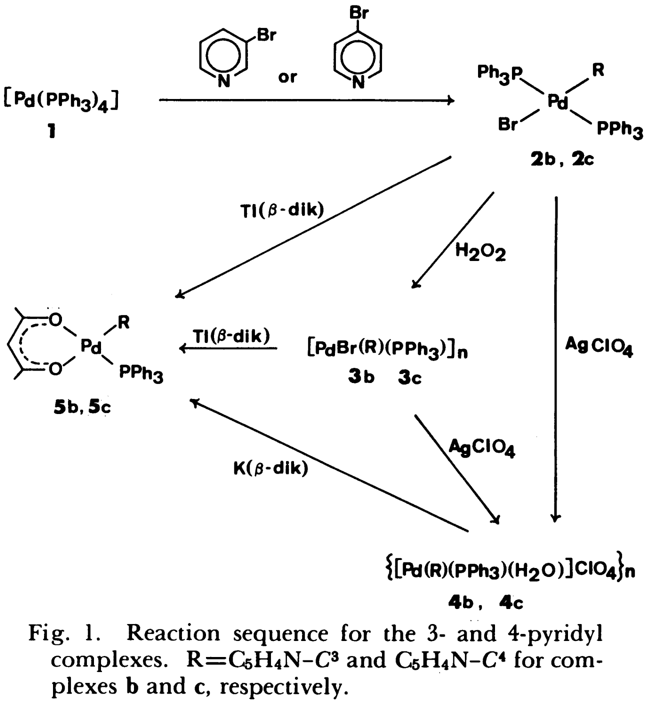


Fig. 1. Reaction sequence for the 3- and 4-pyridyl complexes. R=$C_5H_4N\text{-}C^3$ and $C_5H_4N\text{-}C^4$ for complexes **b** and **c**, respectively.

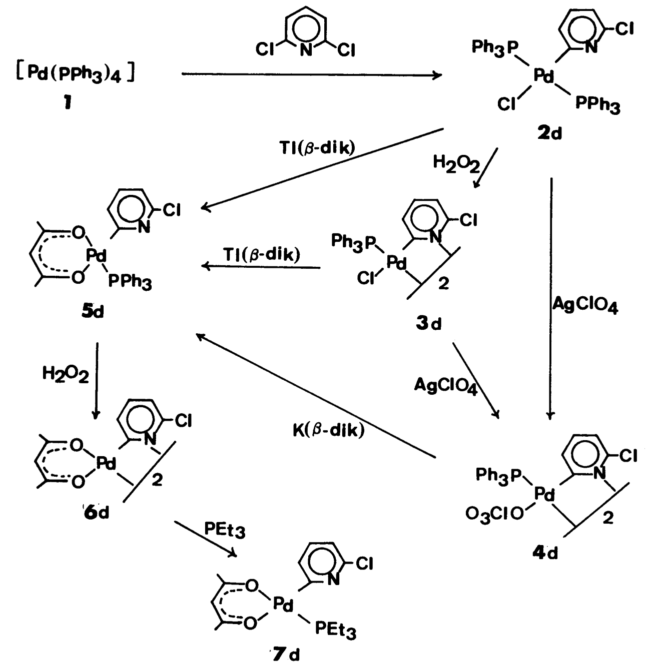


Fig. 2. Reaction sequence for the 6-chloro-2-pyridyl complexes.

and **4d**, respectively, which are yellow and retain the dinuclear structures as evidenced by the analytical and molecular weight data. Although silver perchlorate was again effective in displacing the bromide ligand from **3b** and **3c**, the perchlorate anion was not bound to the metal in these cases, but remained in the outer sphere and instead a water molecule contained in the organic solvents was accepted as a ligand. Silver perchlorate also reacted with mononuclear complexes **2b**, **2c**, and **2d** to remove not only the halide ion but also one phosphine molecule in either case and give rise to **4b**, **4c**, and **4d**, respectively. The molecular weights of **4b** and **4c** determined in dichloromethane at 27 °C are 2090 and 1500, respectively, and are much larger than the formula weight (548.2) calculated for the tight ion pair $[Pd(C_5H_4N)(PPh_3)(H_2O)]ClO_4$, indicating that **4b** and **4c** are polynuclear.

The tendency of the σ-carbon-bonded pyridyl ligands to bridge two metal atoms stems from the enhanced basicity of pyridine bound to palladium at either the C^2, C^3, or C^4 position.[4] It seems reasonable on the steric consideration that the 3- and 4-pyridyl ligands favor the polynuclear structure, while the 2-pyridyl ligand stabilizes the dinuclear form. However, it can not be readily rationalized why the perchlorate ion serves as a ligand in the dinuclear 2-pyridyl complexs but not in the polynuclear 3- and 4-pyridyl complexes. It is worth noting that **4a** and **4d** reacted with pyridine to give mononuclear complexes as exemplified by Eq. 1.

$$\underset{\textbf{4a}}{[PdClO_4(C_5H_4N\text{-}C^2)(PPh_3)]_2} + 2py \longrightarrow$$
$$2[PdClO_4(C_5H_4N\text{-}C^2)(PPh_3)(py)] \qquad (1)$$

Pyridine did not replace the perchlorate ligand, but cleaved the 2-pyridyl bridge. On the other hand, pyridine and even much more basic 4-dimethylaminopyridine in large excess did not split the polynuclear chain in **4b** and **4c**, but merely replaced the aqua ligand (Eq. 2).

$$\{[Pd(C_5H_4N\text{-}\underset{\textbf{4b}}{C^3}\text{ or -}\underset{\textbf{4c}}{C^4})(PPh_3)(H_2O)]ClO_4\}_n$$
$$+ nL(\text{py or 4-Me}_2\text{N-py}) \longrightarrow$$
$$\{[Pd(C_5H_4N\text{-}C^3\text{ or -}C^4)(PPh_3)L]ClO_4\}_n + nH_2O \qquad (2)$$

However, bidentate β-diketonate anions readily cleaved not only the dinuclear bridge in **4a** and **4d**, but also the polynuclear bridge in **4b** and **4c** to afford the mononuclear type-**5** complexes [Pd(β-dik)(pyridyl)-(PPh_3)], of which the analytical and molecular weight data are listed in Table 1 together with those for complexes **3** and **4**. The type-**5** complexes were also derived by the reactions with thallium(I) β-diketonates from the halogeno complexes **2b**, **2c**, **2d**, **3a**, **3b**, **3c**, and **3d** irrespective of their nuclearity (Figs.1 and 2).

Of the type-**5** complexes, **5a1**, **5a2**, and **5d1** gave the dinuclear complexes **6a1**, **6a2**, and **6d1**, respectively, on

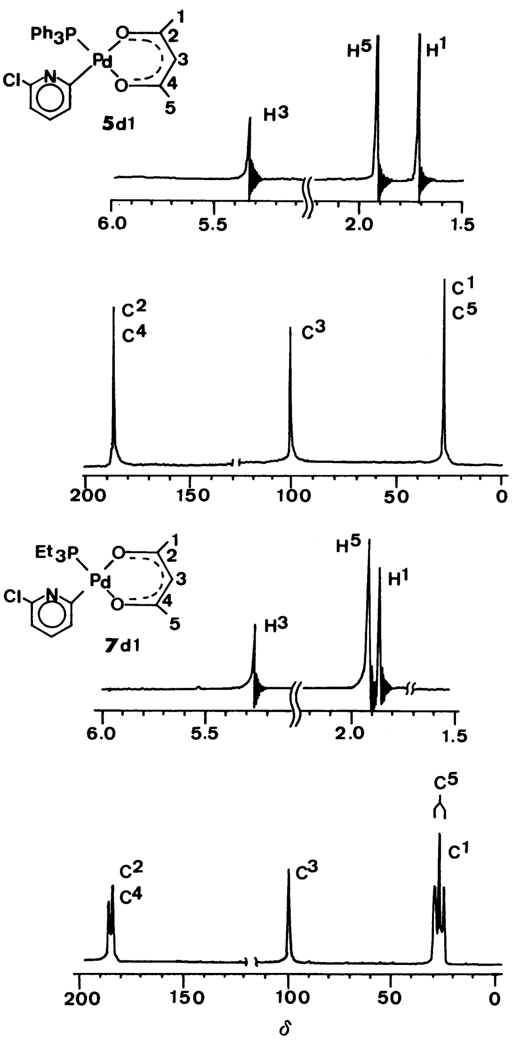


Fig. 3. ^1H and $^{13}C\{^1H\}$ NMR signals from the acetylacetonate ligand in $[Pd(acac)(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)]$ (**5d1**) and $[Pd(acac)(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PEt_3)]$ (**7d1**) in $CDCl_3$ at room temperature. Chemical shifts are shown in ppm from internal Me_4Si.

TABLE 1. ANALYTICAL DATA FOR THE $[PdBr(pyridyl)(PPh_3)]_n$ (**3b** AND **3c**), $[PdCl(pyridyl)(PPh_3)]_2$ (**3d**), $[PdClO_4(pyridyl)(PPh_3)]_2$ (**4a** AND **4d**), $\{[Pd(pyridyl)(PPh_3)(H_2O)]ClO_4\}_n$ (**4b** AND **4c**), [Pd(β-dik)(pyridyl)(PPh_3)] (**5**), [Pd(β-dik)(pyridyl)]$_2$ (**6**), AND [Pd(β-dik)(pyridyl)(PEt_3)] (**7**) COMPLEXES

Compd	β-dik	Pyridyl	Found (Calcd)			
			C(%)	H(%)	N(%)	Mol wt[a]
3b		C_5H_4N-C^3	51.96(52.45)	3.68(3.64)	2.65(2.66)	b)
3c		C_5H_4N-C^4	52.64(52.45)	3.59(3.64)	2.66(2.66)	b)
3d		C_5H_3(6-Cl)N-C^2	53.72(53.47)	3.55(3.51)	2.75(2.71)	1023(1033)
4a		C_5H_4N-C^2	50.75(50.75)	3.62(3.51)	2.57(2.56)	1058(1092)
4b		C_5H_4N-C^3	48.79(48.96)	3.87(3.75)	2.35(2.48)	2090(548.2)
4c		C_5H_4N-C^4	50.03(48.96)	3.98(3.75)	2.35(2.48)	1500(548.2)
4d		C_5H_3(6-Cl)N-C^2	47.50(47.57)	3.14(3.12)	2.40(2.41)	1119(1161)
5a1	acac	C_5H_4N-C^2	61.01(61.61)	4.83(4.80)	2.57(2.57)	535(545.9)
5a2	tfac	C_5H_4N-C^2	55.50(56.06)	3.98(3.86)	2.26(2.33)	600(599.9)
5a3	hfac	C_5H_4N-C^2	50.99(51.44)	3.07(3.08)	2.13(2.14)	620(653.8)
5b1	acac	C_5H_4N-C^3	61.42(61.61)	4.81(4.80)	2.56(2.57)	540(545.9)
5b2	tfac	C_5H_4N-C^3	55.15(56.06)	3.86(3.86)	2.11(2.33)	543(599.9)
5b3	hfac	C_5H_4N-C^3	51.73(51.44)	3.11(3.08)	2.11(2.14)	595(653.8)
5c1	acac	C_5H_4N-C^4	60.81(61.61)	4.81(4.80)	2.49(2.57)	538(545.9)
5c2	tfac	C_5H_4N-C^4	57.37(56.06)	3.98(3.86)	1.92(2.33)	535(599.9)
5c3	hfac	C_5H_4N-C^4	51.84(51.44)	3.09(3.08)	2.12(2.14)	634(653.8)
5d1	acac	C_5H_3(6-Cl)N-C^2	58.07(57.95)	4.35(4.34)	2.86(2.41)	580(580.3)
5d2	tfac	C_5H_3(6-Cl)N-C^2	52.75(53.02)	3.47(3.50)	2.33(2.21)	648(634.3)
5d3	hfac	C_5H_3(6-Cl)N-C^2	47.00(48.86)	2.66(2.64)	1.85(2.04)	692(688.3)
6a1	acac	C_5H_4N-C^2	42.32(42.35)	3.91(3.91)	4.96(4.94)	572(567.2)
6a2	tfac	C_5H_4N-C^2	35.86(35.58)	2.42(2.39)	4.11(4.15)	682(675.1)
6d1	acac	C_5H_3(6-Cl)N-C^2	37.76(37.76)	3.17(3.17)	4.39(4.40)	642(636.1)
7d1	acac	C_5H_3(6-Cl)N-C^2	44.56(44.06)	5.77(5.78)	3.35(3.21)	408(436.2)

a) Determined in dichloromethane at 27 °C. b) Insoluble in organic solvents.

TABLE 2. ^1H NMR SIGNALS FROM THE β-DIKETONATE LIGAND IN THE [Pd(β-dik)(pyridyl)(PPh_3)] (**5**) AND [Pd(β-dik)(pyridyl)]$_2$ (**6**) COMPLEXES AND [Pd(acac)(C_5H_3(6-Cl)-N-C^2)(PEt_3)] (**7d1**)[a]

Compd	CH_3	CH
5a1	1.82, 2.02, 2.05	5.30
5b1	1.82	5.41
5c1	1.82	5.36
5d1	1.70, 1.92	5.33
5d2	1.87, 2.07	5.72
6a1	2.02, 2.05	5.44
6d1	1.94, 2.03	5.44
7d1	1.87, 1.91	5.27

a) Chemical shifts in ppm from internal Me_4Si in $CDCl_3$ at room temperature.

being treated with hydrogen peroxide. Isolation of similar products from the other 2-pyridyl complexes **5a3**, **5d2**, and **5d3** was unsuccessful. The reactions of type-**5** complexes containing the 3- and 4-pyridyl ligands with hydrogen peroxide resulted in decomposition of complexes. Complexes **6** may return to **5** by virtue of the bridge-splitting reactions with triphenylphosphine, and will also react with other Lewis bases to afford similar mononuclear complexes. Table 1 includes the analytical data for one of these complexes [Pd(acac)(C_5H_3(6-Cl)N-C^2)(PEt_3)] (**7d1**) following those for type-**6** complexes.

NMR Spectra. The ^1H NMR signals from the β-diketonate ligands in the [Pd(β-dik)(pyridyl)(PPh_3)] (**5**) and [Pd(β-dik)(pyridyl)]$_2$ (**6**) complexes as well as [Pd(acac)(C_5H_3(6-Cl)N-C^2)(PEt_3)] (**7d1**) are collected in Table 2, and the ^{13}C NMR data for complexes **5d1**, **5d2**, **5d3**, and **7d1** are listed in Table 3. Figure 3 also compares the ^1H and $^{13}C\{^1H\}$ NMR signals from the acac ligand in **5d1** and **7d1**. Complex **5d1** exhibits two methyl proton signals at δ 1.72 and 1.92 reflecting unequal environments of the two methyl groups. The higher-field signal is assigned to the methyl group which is positioned cis to triphenylphosphine and experiences the anisotropic shielding effect of the phenyl ring.[7] In the case of complex **7d1** two methyl signals lie close to each other, of which the lower-field one (δ 1.91) coincides with that from **5d1** and is assigned to the methyl group trans to the phosphine. Methyl protons situated cis to PEt_3 resonate in much lower field than those cis to PPh_3 in **5d1**.

Complex **5d1** shows only three ^{13}C signals at δ 27.7, 99.6, and 186.7 which are assigned to the CH_3, CH, and CO carbons of the acac ligand, respectively, indicating similarity in the magnetic influences of the 6-chloro-2-pyridyl and PPh_3 ligands on both halves of acac. On the other hand, the pyridyl and PEt_3 ligands in **7d1** exert slightly different influences on the carbonyl carbons, exhibiting two signals at δ 186.7 and 186.9 which can not be separately assigned. Both of the methyl carbons in **7d1** resonate at δ 28.0, one as a singlet and the other as a doublet (J(P–C)=6 Hz). The latter is attributed to C^5 positioned trans to PEt_3.

As is seen in Fig. 4, methyl protons of the tfac ligand

TABLE 3. $^{13}C\{^1H\}$ NMR DATA FOR THE 6-CHLORO-2-PYRIDYL COMPLEXES, $[Pd(\beta\text{-dik})(R)(PPh_3)]$ (**5**) AND $[Pd(acac)(R)(PEt_3)]$ (**7dl**) IN $CDCl_3$ AT ROOM TEMPERATURE[a)]

Complex	β-dik					R=$C_5H_3(6\text{-}Cl)N\text{-}C^2$					PPh3 or PEt3			
	CH_3	CF_3	CH	$CH_3\underline{C}O$	$CF_3\underline{C}O$	C^2	C^3	C^4	C^5	C^6	C^1	C^2	C^3	C^4
5dl	27.7		99.6	186.7		174.4 br	129.5 (4)	134.4	117.5	147.4	131.0 (21)	134.2 (12)	127.9 (11)	130.1
5d2	29.0	118.6 [284]	95.0	194.5	167.9 [33]	171.9 br	129.2 br	134.8	118.1	147.4	130.1 (29)	134.1 (12)	128.0 (10)	130.5
5d3		117.7 [286]	89.7		175.2 [34]	168.1 br	126.9 br	135.0	118.8	147.5	130.0 (21)	134.1 (12)	128.4 (12)	130.9
7dl	28.0		99.6	186.7		174.2 (4)	129.9 (5)	134.6	118.0	148.0	14.2 (31)	7.9 (3)		
	28.0 (6)			186.9										

a) β-dik=acac, tfac, and hfac for complexes **1**, **2**, and **3**, respectively. Chemical shifts are given in ppm from internal Me_4Si. Figures in parentheses and brackets give J(C–P) and J(C–F) in Hz.

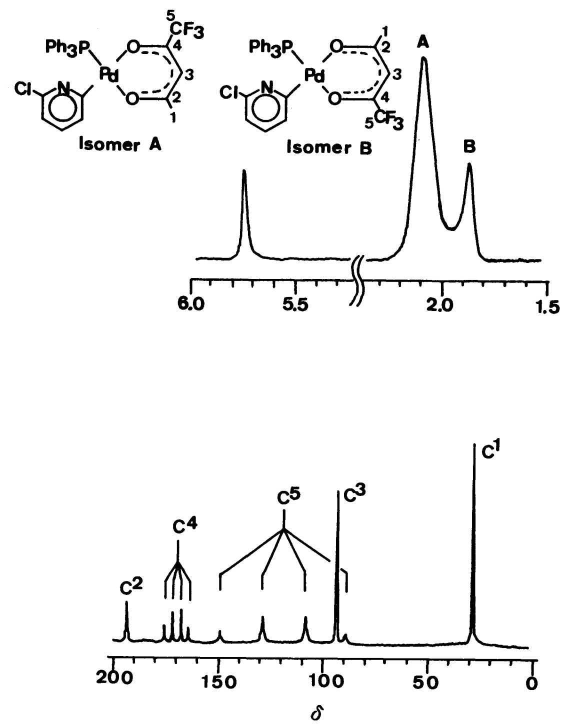


Fig. 4. ^1H and $^{13}C\{^1H\}$ NMR signals from the trifluoroacetylacetonate ligand in $[Pd(tfac)(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)]$ (**5d2**) in $CDCl_3$ at room temperature. Chemical shifts are shown in ppm from internal Me_4Si.

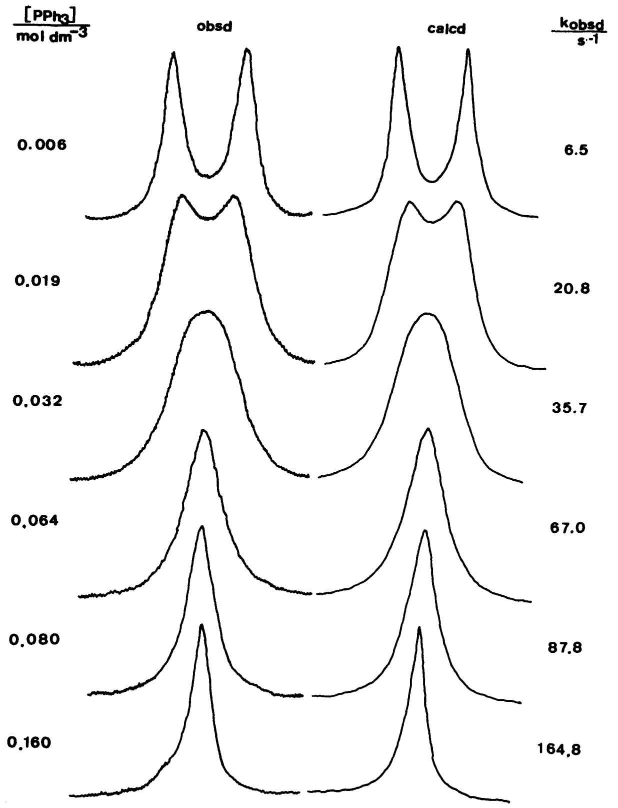


Fig. 5. Methyl proton signals from $[Pd(acac)(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)]$ (**5dl**) in the presence of various concentrations of triphenylphosphine in dichloromethane at −80 °C. [Complex]=0.1 mol dm^{-3}.

in **5d2** exhibit two very broad signals at δ 1.87 and 2.07 with the area ratio of 1:3. There seems to exist two geometrical isomers in solution (Eq. 3) and the minor higher-field signal is assigned to the isomer **B**, in which the methyl group lies at the position cis to PPh_3, and the major one to the other isomer **A**. Similarly to the case of complex **5dl** (Fig. 3), the ^{13}C NMR spectrum of **5d2** involves only one set of signals attributable to the tfac carbons, indicating again that the 6-chloro-2-pyridyl and PPh_3 ligands exert similar trans influences. The hfac ligand in complex **5d3** also shows one set of ^{13}C signals (Table 3).

Coordination-site Exchange Reaction of $[Pd(acac)(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)]$ (5dl) Catalyzed by Lewis Bases. As mentioned already, the acac ligand in complex **5dl** exhibits two sharp methyl signals at δ 1.70 and 1.92 in $CDCl_3$ at room temperature. When an increasing amount of Lewis base such as triphenylphosphine, tri-*o*-tolylphosphine, pyridine, and 2,6-lutidine is added to the solution, these signals become progressively broader to merge into a sharp singlet at δ 1.82. On decreasing temperature of the solution in dichloromethane, the signal again becomes broader and broader to split into two signals. During these events ^{1}H signals other than those from the acac-methyls remain unaltered except appearance of peaks due to the added base. These results indicate that **5dl** is stereochemically rigid in noncoordinating solvents but undergoes the coordination-site exchange as shown by Eq. 3 (X=Cl) catalyzed by Lewis bases (L) and that the fluxional motion is depressed at lower temperatures.

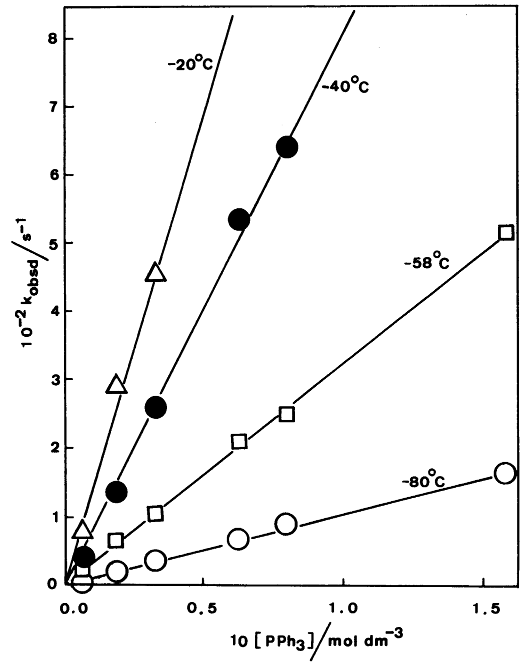


Fig. 6. Pseudo first order rate constant for the coordination-site exchange reaction of complex **5dl** in $CDCl_3$ as a function of triphenylphosphine concentration.

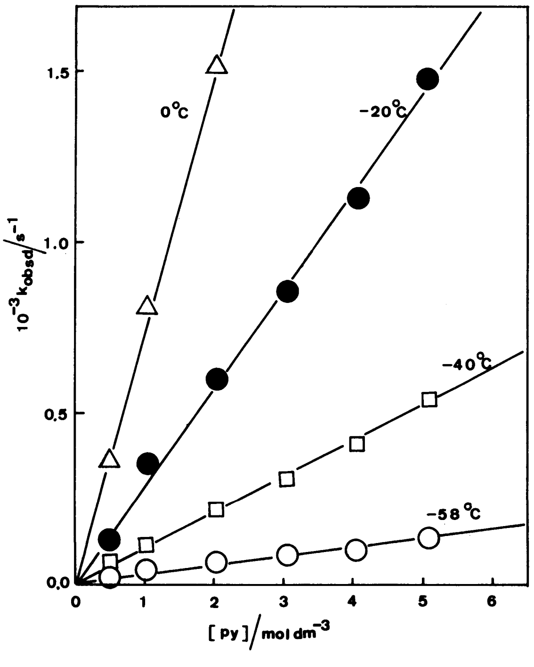
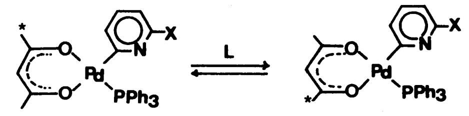


Fig. 7. Pseudo first order rate constant for the coordination-site exchange reaction of complex **5dl** in $CDCl_3$ as a function of pyridine concentration.

 (3)

Pyridine or triphenylphosphine was added in various amounts to a solution (0.1 mol dm^{-3}) of **5dl** in dichloromethane and the rate of coordination-site exchange was determined at 0 °C and lower temperatures by means of the line-shape simulation method. Figure 5 exemplifies the change of methyl signals with the concentration of added triphenylphosphine at −80 °C. The values of cal-

Table 4. THE SECOND ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE COORDINATION-SITE EXCHANGE REACTION OF $[Pd(acac)(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)]$(**5dl**) CATALYZED BY PYRIDINE AND TRIPHENYLPHOSPHINE

	T/°C	py	PPh_3
$10^{-2}k$/dm^{3}mol^{-1}s^{-1}	0	8.05±0.17	
	−20	2.83±0.08	158±2
	−40	1.03±0.03	82.5±0.6
	−58	0.23±0.02	32.1±0.3
	−80		10.3±0.2
$\Delta H^{\neq}$/kJ mol^{-1}		25.6±0.8	16.8±0.6
$\Delta S^{\neq}$/J K^{-1} mol^{-1}		−94.9±3.0	−96.2±2.4

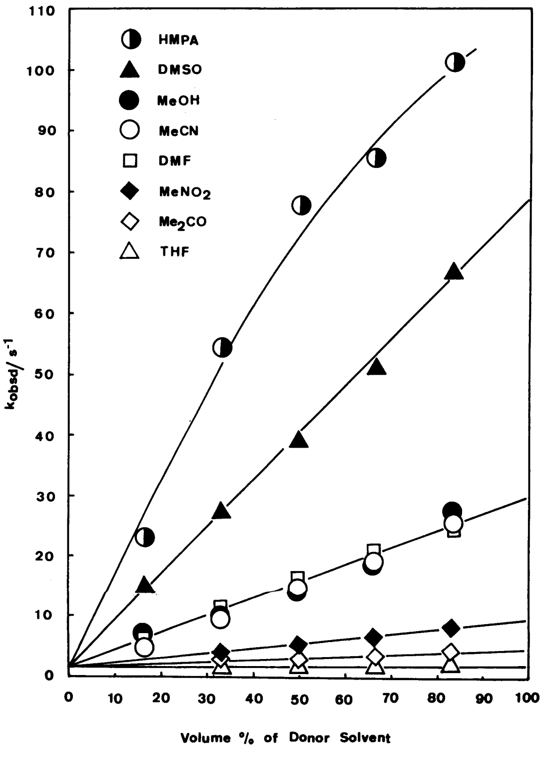
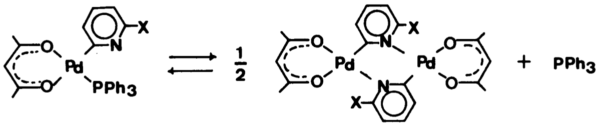


Fig. 8 Pseudo first order rate constant for the coordination-site exchange reaction of complex **5dl** in a mixture of $CDCl_3$ and a donor solvent at 50 °C.

culated pseudo first order rate constant k_{obsd} are also included. As is seen in Fig. 6, the plots of k_{obsd} obtained at several temperatures against the concentration of triphenylphosphine afford straight lines passing through the origin. Similar plots in Fig. 7 show the results obtained with pyridine as a catalyst. Slopes of these straight lines gave the second order rate constants which are listed in Table 4. The activation parameters calculated from the Eyring plots are also included in the table. The catalyzed coordination-site exchange reaction has a rather small $\Delta H^{\neq}$ and a large negative $\Delta S^{\neq}$ in either case, suggesting the associative nature of reaction mechanism as is the case for the ligand substitution reactions of square planer complexes.[8] Triphenylphosphine is much more effective as a catalyst than pyridine, the second order rate constants differing by two orders of magnitude.

Various coordinating solvents were also found to stimulate the coordination-site exchange of **5dl** although their catalytic activities are much weaker than those of pyridine and triphenylphosphine. The following eight solvents were examined: hexamethylphosphoric triamide (HMPA), dimethyl sulfoxide (DMSO), methanol, acetonitrile, *N*,*N*-dimethylformamide (DMF), nitromethane, acetone, and tetrahydrofuran (THF). The pseudo first order rate constant was determined at 50 °C by the same way in a mixture of $CDCl_3$ and a perdeuterated donor solvent containing **5dl** at a constant concentration (0.06 mol dm^{-3}). Complex **5dl** is hardly soluble in these solvents and k_{obsd}'s determined in mixed solvents were plotted against the volume percent of donor solvent (Fig. 8). Fortunately all data except those for HMPA lie on straight lines, giving a common intercept at $k_0=2.0\ s^{-1}$. Extrapolation of these lines to 100% gives rates (k_1) in neat donor solvents which can not be determined directly. Tetrahydrofuran is practically ineffective and the rate value 2.0 s^{-1} given by the intercept corresponds to an intrinsic reaction which is not assisted by donor solvents. It is not certain whether the reaction proceeds truly noncatalytically or is promoted by a trace of triphenylphosphine liberated by reaction 4 (X=Cl). It should be noted that straight lines in Figs. 6 and 7 which show the catalytic effects of pyridine and triphenylphosphine, respectively, do not give intercepts, but go through the origin. Reaction 4 might be endothermic and liberate a trace amount of the phosphine at 50 °C (*vide infra*), although the possibility may not be excluded that some other unimolecular mechanism (*e.g.* transformation *via* a tetrahedral transition state), which is not effective below 0 °C, makes the observed minor contribution at 50 °C.



(4)

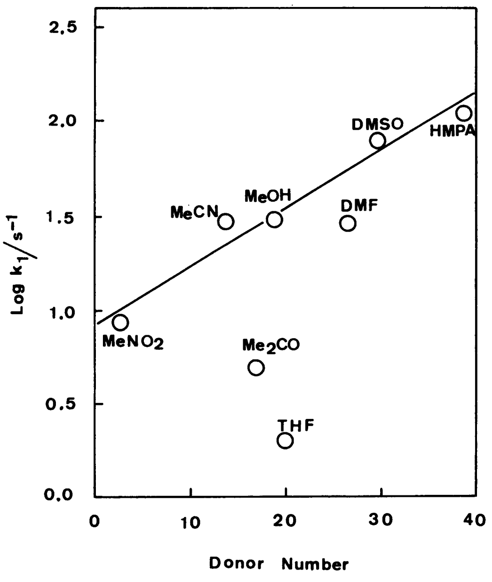
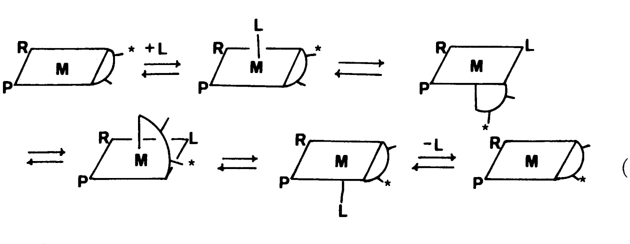


Fig. 9. Relation between the estimated pseudo first order rate constants for the coordination-site exchange reaction of complex **5dl** and donor number of solvents.

The k_1 values (s^{-1}) decreases in the sequence, HMPA (109.5)>DMSO (78.0)>MeOH (30.3)≈MeCN (29.8)≈DMF (29.1)>$MeNO_2$ (8.8)>Me_2CO (4.9). The tendency may be related to the coordination ability of the solvent. In fact the plot of log k_1 against the donor number[9] of solvent gave a straight line although a few data lie far from this line (Fig. 9).

Geometrical isomerization of square-planar complexes has been the subject of extensive investigations.[10] Although some complexes such as *cis*-[PtCl(aryl)$(PEt_3)_2$] isomerize spontaneously in polar solvents,[11] most of the isomerization reactions proceed in the presence of neutral or ionic free ligands as catalysts,[12] and two mechanisms, consecutive displacement and intramolecular rearrangement of five-coordinate intermediates, are well documented.[10] Although the catalytic role of a solvent molecule coordinated to a complex as the fifth ligand has been suggested in some cases,[13] no conclusive evidence for solvent catalysis has yet been reported.

The consecutive displacement mechanism is not applicable to the present reaction, since a readily removable unidentate ligand such as halide is not contained in **5dl** and dissociation of the acetylacetonate ligand to give rise to [Pd(pyridyl)$(PPh_3)L_2$](acac) is not conceivable. By the analogy with the case of five-coordinate square-pyramidal complexes $[M(hfac)_2(PR_3)]$ (M=Pd^{II} and Pt^{II}, R=*o*-tolyl and cyclohexyl),[14] the intramolecular rearrangement such as illustrated by Eq. 5 is proposed, where R and P denote the pyridyl and phosphine ligands, respectively, and the trigonal-bipyramidal transition state involved in each step is omitted for the sake of brevity.



(5)

If the addition reaction to form the five-coordinate intermediate, $\mathbf{5dl}+\mathrm{L}\overset{K}{\rightleftharpoons}[\mathrm{Pd(acac)(R)(PPh_3)L}]$, attains equilibrium rapidly and the following intramolecular transformation is the rate-determining step (k_{tr}), the observed first order rate constant should be expressed by Eq. 6.

$$k_{\mathrm{obsd}}=\frac{k_{\mathrm{tr}}K[\mathrm{L}]}{1+K[\mathrm{L}]} \tag{6}$$

The linear dependence of k_{obsd} on the fraction of a donor solvent other than HMPA (Fig. 8) indicates that the equilibrium constants are very small for these solvent molecules even in the neat state. The second order rate law also holds for the reaction catalyzed by pyridine and triphenylphosphine, indicating that K[L] in the denominator of Eq. 6 is much smaller than one even for these strong ligands in the concentration regions examined, $[\mathrm{py}]<5.0$ mol dm^{-3} and $[\mathrm{PPh_3}]<0.15$ mol dm^{-3} against [**5dl**]$=0.1$ mol dm^{-3}. Although K and k_{tr} cannot be estimated separately at the present stage of investigation, the nature of L may influence not only on K but also on k_{tr}, since k_{obsd} spans over many orders of magnitude.

Coordination-site Exchange Reactions of Acetylacetonate Complexes Containing the 2-, 3-, or 4-Pyridyl Ligand. Methyl protons of the acetylacetonate ligand in the 2-pyridyl complex **5al** show a singlet at δ 1.82 accompanied by two minor signals at δ 2.02 and 2.05. The chemical shifts of the latter signals exactly coincide with those from the dinuclear complex **6al**, suggesting attainment of the equilibrium shown by Eq. 4 (X=H). Liberated triphenylphosphine may serve as a catalyst for the coordination-site exchange of **5al** as expressed by Eq. 3 (X=H), exhibiting a single methyl-proton resonance at δ 1.82. This effect may be called autocatalysis, since the catalyzing species is produced by the reacting species. The δ 1.82 signal becomes broader with decreasing temperature, collapses at −20 °C and gives rise to two signals at −60 °C.

The equilibrium constant of Eq. 4 (X=H) was determined to be 0.01 mol dm^{-3} at 37 °C based on the relative intensities of signals from **5al** and **6al**. Oxidation of liberated triphenylphosphine with hydrogen peroxide shifts the equilibrium completely to right and the δ 1.82 signal disappears. On the other hand, the ^{1}H NMR spectrum of **5dl** shows no sign of coexistence of **6dl**, indicating that the dinuclear bridging is less favorable for the 6-chloro-2-pyridyl ligand than for the 2-pyridyl group. However, treatment of **5dl** with hydrogen peroxide yields **6dl** under the preparative condition, supporting existence of the equilibrium, Eq.4 (X=Cl). It is worth noting that 2,6-dichloropyridine does not catalyze the coordination-site exchange of **5dl** (Eq. 3) although 2,6-dimethylpyridine is effective as a catalyst. The steric requirements of the chloro and methyl substituents are quite similar, and their electronic effects may be responsible for the difference in basicities. Similarly the weaker basicity of the 6-chloro-2-pyridyl ligand than that of the 2-pyridyl ligand seems to make the dinuclear structue in **6dl** less favorable than that in **6al**.

Each of complexes **5bl** and **5cl** containing the 3- and 4-pyridyl ligands, respectively, shows a broad methyl singlet at δ 1.82 in $\mathrm{CDCl_3}$ at room temperature. The signal becomes broader with decreasing concentration and temperature, and is converted into two broad signals at δ 1.74 and 1.92 at −60 °C. Thus the singlet at room temperature seems to be caused by the rapid coordination-site exchange catalyzed by some species. No spectroscopic evidence is observed which suggests liberation of triphenylphosphine to form the dinuclear species from **5bl** and **5cl**. Treatment of these complexes with hydrogen peroxide do not afford type-**6** complexes.

These observations allow the presumption that when two molecules of the reacting species encounter with each other, one is coordinated with the metal atom of the other *via* the nitrogen atom of the pyridyl ligand, forming a five-coordinate intermediate which undergoes the coordination-site exchange. Such a catalysis has no precedent and may be termed "self-catalysis" or "mutual catalysis", since molecules of the reacting species mutually serve as the catalyst. Complexes **5bl** and **5cl** are also effective as catalysts for the coordination-site exchange reaction of **5dl**. The carbon-bonded pyridyl ligand shows higher basicity than free pyridine$^{4)}$ and tends to interact with another metal atom, stabilizing the dinuclear structure of the 2-pyridyl complexes and the polynuclear linkage in the 3- and 4-pyridyl complexes. The enhanced basicity of the pyridyl ligand is origin of the self-catalysis.

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