Synthesis and Characterization of Palladium(II) and Platinum(II) Complexes Containing Monodentate Phosphorus Donating or Chelating 2-(Dimethylphosphino)pyridine (PMe_2py)

Takayoshi Suzuki, Masakazu Kita, Kazuo Kashiwabara, and Junnosuke Fujita*
Department of Chemistry, Faculty of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01
(Received June 7, 1990)

The complexes $[MX_2(PMe_2py\text{-}P)_2]$ (M=Pd(II), Pt(II); X=Cl, Br, and I) have been synthesized and characterized both in the solid state and in solution by their infrared and ^1H, ^{13}C, and ^{31}P NMR spectra, in addition to an X-ray crystallographic analysis of *cis*-$[PdCl_2(PMe_2py\text{-}P)_2]$. The latter complex exists as a cis-trans equilibrium mixture in solution, while only the cis isomer has been isolated in the solid state. The $[PdBr_2(PMe_2py\text{-}P)_2]$ complex which has been isolated as the trans isomer shows also the same isomerization in solution, in contrast to $[PdBr_2(PMe_2Ph)_2]$ which exists only as the trans isomer both in the solid state and in solution. Furthermore, PMe_2py has been found to have the ability for chelation via the nitrogen and phosphorus atoms to make a four-membered chelate ring. The chelate ring in the complexes $[PdX(PMe_2py)_2]Y$ (X=Cl, Br, and I; $Y=ClO_4^-$, PF_6^-) has been confirmed by infrared spectra and X-ray analysis of *cis*(*P,P*)-$[PdCl(PMe_2py\text{-}P,N)(PMe_2py\text{-}P)]ClO_4$. This is the first example in which PMe_2py is acting as a chelating ligand.

While the chemistry of metal complexes of 2-(diphenylphosphino)pyridine (PPh_2py) has been studied extensively,[1-6] no report has been published on metal complexes of analogous 2-(dimethylphosphino)pyridine (PMe_2py) except for the gold(I) complexes.[7] The PMe_2py ligand is less bulky and more basic than PPh_2py, and therefore its complexes are expected to have different properties from those of the PPh_2py complexes. This paper describes the synthesis and characterization of palladium(II) and platinum(II) complexes of the $[MX_2(PMe_2py)_2]$-type, in addition to an X-ray structure analysis of *cis*-$[PdCl_2(PMe_2py\text{-}P)_2]$. Also, the preparation of palladium(II) complexes, in which PMe_2py forms a four-membered chelate ring, is reported together with an X-ray structure analysis of *cis*(*P,P*)-$[PdCl(PMe_2py\text{-}P,N)(PMe_2py\text{-}P)]ClO_4$.

Experimental

The phosphine ligand was handled under an atmosphere of nitrogen until they formed air-stable metal complexes. All solvents used for the preparation of ligands and complexes were deoxygenated by bubbling nitrogen through them for 20 min immediately before use. Tetramethyldiphosphane[8] and $[PdCl_2(C_6H_5CN)_2]$[9] were prepared by the literature methods.

Preparation of 2-(dimethylphosphino)pyridine (PMe_2py). The method of Inoguchi et al.[7] was modified for the preparation of this ligand. A mixture of tetramethyldiphosphane (5.57 g, 45.6 mmol) and potassium metal (3.50 g, 91.3 mmol) in tetrahydrofuran (300 cm^3) was stirred for 1 day at 30 °C, and unreacted potassium metal was removed. To the yellow-orange solution of potassium dimethylphosphide was added deaerated 2-chloropyridine (10.37 g, 91.3 mmol) dropwise with stirring. The resulting dark brown-red solution was stirred for 2 h, and the solvent was evaporated under reduced pressure. The residue was extracted with diethyl ether (150 cm^3×3) to remove KCl. The reddish extract was distilled under reduced pressure (bp 60—72 °C, 1.07 kPa) to give a colorless oily product (5.41 g). It was an azeotropic mixture of PMe_2py and unreacted 2-chloropyridine, and the purity was determined from the ^1H NMR spectrum to be 90%.

Preparation of Complexes. *cis*-$[PdCl_2(PMe_2py\text{-}P)_2]$: To a dichloromethane solution (10 cm^3) of $[PdCl_2(C_6H_5CN)_2]$ (1.17 g, 3.06 mmol) was added a methanol solution (10 cm^3) of PMe_2py (852 mg, 6.12 mmol) with stirring. During the addition of the ligand a yellow precipitate appeared. (The product is nearly insoluble in water and common organic solvents and has the composition $PdCl_2(PMe_2py)$. Found: C, 26.57; H, 3.18; N, 4.43%. Calcd for $C_7H_{10}Cl_2NPPd$: C, 26.57; H, 3.19; N, 4.43%.) When the addition of the ligand was completed, the precipitate had dissolved to give an orange solution. The solution was evaporated to dryness under reduced pressure, the residue was washed with diethyl ether (50 cm^3), and dissolved in a mixture of dichloromethane and methanol (1 : 1). The solution was filtered, and the filtrate was allowed to stand. Pale yellow crystals were formed by slow evaporation of the solvent, collected by filtration and recrystallized from hot methanol. Yield: 1.26 g (90.4%). Found: C, 36.90; H, 4.44; N, 6.07%. Calcd for $C_{14}H_{20}Cl_2N_2P_2Pd$: C, 36.91; H, 4.42; N, 6.15%. The complex is very soluble in chloroform and dichloromethane and soluble in methanol, acetone, and acetonitrile.

***trans*-$[PdBr_2(PMe_2py\text{-}P)_2]$:** The complex was prepared by reaction of *cis*-$[PdCl_2(PMe_2py\text{-}P)_2]$ with KBr. To a dichloromethane solution (10 cm^3) of *cis*-$[PdCl_2(PMe_2py\text{-}P)_2]$ (700 mg, 1.54 mmol) was added a methanol solution (60 cm^3) of KBr (731 mg, 6.14 mmol). The mixture was stirred overnight at room temperature, and evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane (30 cm^3), and the extract was mixed with methanol (30 cm^3). The solution was allowed to evaporate slowly, yielding yellow crystals of *trans*-$[PdBr_2(PMe_2py\text{-}P)_2]$, which were collected by filtration and recrystallized from hot methanol. Yield: 795 mg (95.1%). Found: C, 30.72; H, 3.56; N, 5.10%. Calcd for $C_{14}H_{20}Br_2N_2P_2Pd$: C, 30.88; H, 3.70; N, 5.14%.

***trans*-$[PdI_2(PMe_2py\text{-}P)_2]$:** This complex was prepared by

a method similar to the dibromo complex using KI instead of KBr. Reddish orange crystals were obtained by recrystallization from a mixture of dichloromethane and methanol (1 : 1). Yield: 94.9%. Found: C, 26.24; H, 3.08; N, 4.42%. Calcd for $C_{14}H_{20}I_2N_2P_2Pd$: C, 26.34; H, 3.16; N, 4.39%.

These dibromo and diiodo Pd(II) complexes are soluble in chloroform, dichloromethane and benzene, and slightly soluble in methanol.

***cis*-[PtCl$_2$(PMe$_2$py-*P*)$_2$]:** An aqueous solution (50 cm^3) of $K_2[PtCl_4]$ (1.55 g, 3.72 mmol) was added to an ethanol solution (50 cm^3) of PMe_2py (1.06 g, 7.59 mmol) with stirring. Immediate precipitation of a white product occurred. The mixture was heated at 50 °C for 10 min, and then the solvent was removed under reduced pressure. The residue was washed with water (10 cm^3) to remove KCl, and recrystallized from hot ethanol to give white crystals, which were collected by filtration and dried in vacuo. Yield: 1.27 g (62.7%). Found: C, 31.05; H, 3,76; N, 5.16%. Calcd for $C_{14}H_{20}Cl_2N_2P_2Pt$: C, 30.90; H, 3.70; N, 5.15%.

***cis*-[PtX$_2$(PMe$_2$py-*P*)$_2$] (X=Br, I):** These complexes were prepared from *cis*-[PtCl$_2$(PMe$_2$py-*P*)$_2$] by a method similar to that for *trans*-[PdBr$_2$(PMe$_2$py-*P*)$_2$]. By recrystallization of the crude products from a mixture of dichloromethane and methanol (1 : 1), pale yellow crystals of *cis*-[PtBr$_2$(PMe$_2$py-*P*)$_2$] and yellow crystals of *cis*-[PtI$_2$(PMe$_2$py-*P*)$_2$] were obtained in yields of 84.2 and 71.5%, respectively. Found for the dibromo complex: C, 26.56; H, 3.21; N, 4.40%. Calcd for $C_{14}H_{20}Br_2N_2P_2Pt$: C, 26.56; H, 3.18; N, 4.42%. Found for the diiodo complex: C, 23.13; H, 2.78; N, 3.85%. Calcd for $C_{14}H_{20}I_2N_2P_2Pt$: C, 23.12; H, 2.77; H, 3.85%.

These Pt(II) complexes are very soluble in chloroform and dichloromethane, and soluble in methanol, ethanol, and acetonitrile.

[PdX(PMe$_2$py-*P*,*N*)(PMe$_2$py-*P*)]ClO$_4$ (X=Cl, Br, and I): These complexes were obtained by reaction of [PdX$_2$(PMe$_2$py-*P*)$_2$] with an equimolar amount of $AgClO_4$. To a methanol solution (250 cm^3) of *cis*-[PdCl$_2$(PMe$_2$py-*P*)$_2$] (911 mg, 2.00 mmol) was added a methanol solution (50 cm^3) of $AgClO_4$ (415 mg, 2.00 mmol) with stirring. The mixture was stirred for 6 h in the dark, and AgCl was filtered off. Slow evaporation of the filtrate yielded yellow crystals, which were collected by filtration and recrystallized from hot methanol. Yield: 938 mg (90.2%). Found: C, 32.36; H, 3.86; N, 5.41%. Calcd for $C_{14}H_{20}Cl_2N_2O_4P_2Pd$: C, 32.36; H, 3.88; N, 5.39%.

Yellow crystals of [PdBr(PMe$_2$py-*P*,*N*)(PMe$_2$py-*P*)]ClO$_4$ and [PdI(PMe$_2$py-*P*,*N*)(PMe$_2$py-*P*)]ClO$_4$ were obtained by similar methods from the corresponding trans-dihalogeno complexes in yields of 85.9% and 73.3%, respectively. Found for the bromo complex: C, 29.81; H, 3.58; N, 5.00%. Calcd for $C_{14}H_{20}BrClN_2O_4P_2Pd$: C, 29.81; H, 3.57; N, 4.97%. Found for the iodo complex: C, 27.54; H, 3.22; N, 4.54%. Calcd for $C_{14}H_{20}ClIN_2O_4P_2Pd$: C, 27.52; H, 3.30; N, 4.58%. These halogeno complexes are soluble in nitromethane, slightly soluble in methanol, and hardly soluble in chloroform and dichloromethane.

[PdX(PMe$_2$py-*P*,*N*)(PMe$_2$py-*P*)]PF$_6$ (X=Cl, Br, and I): These complexes were prepared by methods similar to that for the above perchlorate salts. A methanol solution (30 cm^3) of $AgNO_3$ (1.86 mg, 1.01 mmol) was added to a methanol solution (100 cm^3) of *cis*-[PdCl$_2$(PMe$_2$py-*P*)$_2$] (500 mg, 1.01 mmol) with stirring. After stirring for 2 h in the dark, AgCl was filtered off, and the filtrate was evaporated to a volume of ca. 40 cm^3 under reduced pressure. To the concentrate was added a methanol solution of NH_4PF_6 (179 mg, 1.10 mmol). The solution was evaporated slowly, yielding a yellow precipitate together with a small amount of red product. The precipitate was collected by filtration, and treated with hot methanol (50 °C, 50 cm^3). The yellow precipitate was soluble, while the red one remained undissolved and was filtered off. Yellow crystals were deposited from the filtrate by slow evaporation, collected by filtration, and dried in vacuo. Yield: 353 mg (56.8%). Found: C, 29.72; H, 3.55; N, 5.01%. Calcd for $C_{14}H_{20}ClF_6N_2P_3Pd$: C, 29.76; H, 3.57; N, 4.96%.

Yellow crystals of [PdBr(PMe$_2$py-*P*,*N*)(PMe$_2$py-*P*)]PF$_6$ and [PdI(PMe$_2$py-*P*,*N*)(PMe$_2$py-*P*)]PF$_6$ were obtained by similar methods from the corresponding trans-dihalogeno complexes in yields of 52 and 79.2%, respectively. Found for the bromo complex: C, 27.71; H, 3.35; N, 4.79%. Calcd for $C_{14}H_{20}BrF_6N_2P_3Pd$: C, 27.59; H, 3.31; N, 4.60%. Found for the iodo complex: C, 25.61; K, 3.09; N, 4.23%. Calcd for $C_{14}H_{20}F_6IN_2P_3Pd$: C, 25.61; H, 3.07; N, 4.27%. These halogeno complexes are soluble in methanol and nitromethane and hardly soluble in chloroform and dichloromethane.

***cis*- and *trans*-[PdCl$_2$(PPh$_2$py-*P*)$_2$]:** [PdCl$_2$(PPh$_2$py-*P*)$_2$]·1.7CH$_2$Cl$_2$ was prepared according to the literature method.[2] The complex was dissolved in methanol, and the solution was kept in a desiccator over diethyl ether. Yellow crystals deposited. They were collected by filtration and dried in vacuo. The product was a mixture of nonsolvated *cis*- and *trans*-[PdCl$_2$(PPh$_2$py-*P*)$_2$] as confirmed by elemental analysis and NMR and IR spectra (ν(Pd-Cl): 315 and 292 cm^{-1} (cis), and 365 cm^{-1} (trans)). Found: C, 57.86; H, 4.13; N, 3.97%. Calcd for $C_{34}H_{28}Cl_2N_2P_2Pd$: C, 58.02; H, 4.01; N, 3.98%.

***trans*-[PdX$_2$(PPh$_2$py-*P*)$_2$](X=Br, I):** These complexes were prepared from a mixture of *cis*- and *trans*-[PdCl$_2$(PPh$_2$py-*P*)$_2$] and potassium bromide or iodide by methods similar to those for the PMe_2py complexes. The dibromo complex was obtained as yellow crystals in a yield of 90.7%. Found: C, 51.52; H, 3.76; N, 3.54%. Calcd for $C_{34}H_{28}Br_2N_2P_2Pd$: C, 51.51; H, 3.56; N, 3.53%. The diiodo complex was obtained as reddish orange crystals in a yield of 97.2%. Found: C, 45.49; H, 3.23; N, 3.14%. Calcd for $C_{34}H_{28}I_2N_2P_2Pd$: C, 46.06; H, 3.18; N, 3.16%.

These dihalogenobis(PPh_2py) complexes are soluble in chloroform, dichloromethane, methanol, and benzene.

Measurements. Infrared spectra in the range 700—200 cm^{-1} were obtained with a HITACHI EPI-L spectrometer by the Nujol mull method using polyethylene films. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at 90.02, 22.66, and 36.46 MHz, respectively, on a HITACHI R90-HS spectrometer. ^1H NMR spectra at 399.8 MHz were obtained with a JOEL JMX GW-400 spectrometer. Chemical shifts for ^{31}P are relative to an external standard, 85% H_3PO_4, and those for ^1H and ^{13}C to an internal standard, TMS. Conductivity measurements were carried out on a TOA CM-6A conductometer with 1 mmol dm^{-3} nitromethane solutions at room temperature.

X-Ray Analyses. Structures of *cis*-[PdCl$_2$(PMe$_2$py-*P*)$_2$] and *cis(P,P)*-[PdCl(PMe$_2$py-*P*,*N*)(PMe$_2$py-*P*)]ClO$_4$ were determined by the X-ray diffraction method. Crystal data and experimental details are given in Table 1. Diffraction

data were collected on a Rigaku AFC-5R diffractometer with graphite monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å). Within the range of $2\theta<60°$, 4582 and 4522 independent reflections ($|F_o|>3\sigma(|F_o|)$) were obtained for *cis*-[$PdCl_2$-(PMe_2py-*P*)$_2$] and *cis*(*P*,*P*)-[$PdCl(PMe_2py$-*P*,*N*)(PMe_2py-*P*)]-ClO_4, respectively. No absorption correction was applied. All the calculations were performed on a HITAC M-180 computer at the Computer Center of the Institute for Molecular Science using the Universal Crystallographic Computation Program System UNICS III.[10] The structures were

Table 1. Crystal Data, Experimental Details, and Final *R* Factors

Compound	*cis*-[$PdCl_2(PMe_2py$-*P*)$_2$]	*cis*(*P*,*P*)-[$PdCl(PMe_2py$-*P*,*N*)-(PMe_2py-*P*)]ClO_4
Formula	$C_{14}H_{20}Cl_2N_2P_2Pd$	$C_{14}H_{20}Cl_2N_2O_4P_2Pd$
Formula weight	455.599	519.597
Crystal color	Pale yellow	Pale yellow
Crystal size/mm^3	0.30×0.225×0.20	0.75×0.225×0.20
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/a$
a/Å	9.070(2)	18.496(2)
b/Å	23.789(8)	12.796(1)
c/Å	8.922(3)	8.720(2)
β/°	107.42(2)	98.10(2)
U/Å^3	1836.8(9)	2037.5(6)
Z	4	4
D_c/g cm^{-3}	1.647	1.691
D_m/g cm^{-3}	1.622	1.682
μ(Mo $K\alpha$)/cm^{-1}	14.575	13.379
$2\theta_{max}$/°	60	60
No. of unique data	4582	4522
Scan type	ω	θ-2θ
Scan speed/° min^{-1}	5	4
Scan range/°	1.1+0.5 tan θ	1.2+0.5 tan θ
Background constant/s^{-1}	5	5
R	0.0388	0.0450
R_w	0.0464	0.0640

Table 2. Positional Parameters (×10^4; ×10^5 for Pd, Cl, and P in *cis*-[$PdCl_2(PMe_2py$-*P*)$_2$] and for Pd in *cis*(*P*,*P*)-[$PdCl(PMe_2py$-*P*,*N*)(PMe_2py-*P*)]ClO_4) and Equivalent Isotropic Temperature Factors (Å^2) of *cis*-[$PdCl_2(PMe_2py$-*P*)$_2$] and *cis*(*P*,*P*)-[$PdCl(PMe_2py$-*P*,*N*)(PMe_2py-*P*)]ClO_4

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
	cis-[$PdCl_2(PMe_2py$-*P*)$_2$]					*cis*(*P*,*P*)-[$PdCl(PMe_2py$-*P*,*N*)(PMe_2py-*P*)]ClO_4			
Pd	59441(2)	13297(1)	22341(3)	2.3	Pd	39854(3)	13552(4)	46804(5)	3.0
Cl1	84541(9)	15924(5)	22783(12)	4.7	Cl1	4089(1)	822(2)	7279(2)	4.7
Cl2	68683(12)	10772(6)	48919(11)	5.5	Cl2	6595(1)	3517(2)	3047(2)	5.2
P1	35996(8)	10267(4)	22220(9)	2.6	P1	4002(1)	1527(1)	2127(2)	3.1
P2	52472(9)	16189(4)	−2791(10)	3.1	P2	3856(1)	3032(1)	5328(2)	3.5
N1	3224(4)	349(1)	−188(4)	4.2	O1	7204(4)	4176(7)	3034(12)	10.3
N2	2483(3)	2070(1)	−655(4)	3.7	O2	6176(6)	3617(9)	4200(11)	12.8
C11	2413(3)	709(1)	399(4)	2.7	O3	6054(7)	3929(11)	1770(13)	16.0
C12	849(4)	789(2)	−257(4)	3.2	O4	6683(6)	2548(8)	2489(16)	14.2
C13	81(4)	496(2)	−1593(5)	4.3	N1	3972(3)	−150(4)	3608(6)	3.4
C14	913(5)	124(2)	−2192(5)	5.2	N2	4135(4)	4011(6)	2792(8)	5.1
C15	2470(5)	58(2)	−1467(6)	5.1	C11	3913(4)	105(5)	2084(7)	3.4
C16	2483(4)	1559(2)	2811(4)	4.2	C12	3799(4)	−635(6)	947(8)	4.3
C17	3610(5)	461(2)	3569(5)	5.4	C13	3731(5)	−1674(6)	1354(9)	4.7
C21	3211(4)	1717(1)	−1363(4)	3.0	C14	3790(4)	−1928(6)	2889(9)	4.6
C22	2504(4)	1473(2)	−2803(4)	4.0	C15	3914(4)	−1152(6)	4024(9)	4.2
C23	952(5)	1601(2)	−3541(5)	5.2	C16	3261(4)	2053(6)	779(8)	4.3
C24	191(5)	1961(2)	−2826(5)	4.9	C17	4844(4)	1846(7)	1399(9)	4.6
C25	1009(5)	2180(2)	−1402(5)	4.6	C21	3614(4)	3927(5)	3717(7)	3.6
C26	5989(5)	2312(2)	−527(6)	6.3	C22	2951(4)	4469(7)	3469(10)	5.1
C27	6027(5)	1143(3)	−1429(5)	6.1	C23	2835(6)	5125(8)	2222(11)	6.8
					C24	3352(6)	5230(7)	1286(10)	6.9
					C25	4004(6)	4665(8)	1576(10)	6.3
					C26	4666(5)	3627(7)	6399(10)	5.7
					C27	3127(6)	3157(8)	6520(11)	6.8

solved by the usual heavy-atom method. The positions of all hydrogen atoms of *cis(P,P)*-[PdCl(PMe_2py-*P,N*)(PMe_2py-*P*)]ClO_4 and ten of the twenty in *cis*-[$PdCl_2$(PMe_2py-*P*)$_2$] were identified in the subsequent difference Fourier maps. The final positional parameters and the corresponding isotropic thermal parameters with their estimated standard deviations for non-hydrogen atoms are given in Table 2. The positional parameters of hydrogen atoms, the anisotropic parameters for all non-hydrogen atoms, and the complete list of $|F_o|$ and $|F_c|$ are deposited at the office of the Chemical Society of Japan (Document No. 9089 for *cis*-[$PdCl_2$(PMe_2py-*P*)$_2$] and *cis(P,P)*-[PdCl(PMe_2py-*P,N*)(PMe_2py-*P*)]ClO_4).

Results and Discussion

Preparation of Complexes. The monodentate phosphorus donating PMe_2py complexes, [MX_2(PMe_2py-*P*)$_2$] (M=Pd(II), Pt(II); X=Cl, Br, I) have been prepared by methods similar to those for dihalogenobis(phosphine)palladium(II) and platinum(II) complexes. All of the complexes are neutral in solution as confirmed by conductivity measurements (Table 3).

Since it is posible for PMe_2py to chelate via nitrogen and phosphorus making a four-membered chelate ring, we have examined the syntheses of palladium(II) complexes with chelating PMe_2py. The chelate ring formed by this ligand is anticipated to have large strain. While a diphosphinomethane ligand (P-P), such as dppm[11] ($Ph_2PCH_2PPh_2$) or Medppm[12] ($Ph_2PCH(CH_3)PPh_2$), by reaction of a stoichiometric amount of ligand with [$PdCl_2$(C_6H_5CN)$_2$] easily forms 1 : 1 neutral complexes, [$PdCl_2$(P-P)], which have P-P type four-membered chelate rings, PMe_2py did not form such a neutral chelate complex by a similar procedure. In fact, by the addition of an equimolar amount of PMe_2py to a dichloromethane solution of [$PdCl_2$(C_6H_5CN)$_2$], an insoluble yellow precipitate whose composition is $PdCl_2(PMe_2py)$ was obtained. However, the infrared spectrum of the precipitate shows a band at 256 cm^{-1} assignable to the stretching for bridging Pd-Cl-Pd, and does not show Pd-Cl stretching bands around 300 cm^{-1} expected for a monomeric cis-dichloro complex. The cationic chelate complex, however, was obtained by halogen elimination from the dihalogeno complexes with an equimolar amount of silver ion;

$$[PdX_2(PMe_2py\text{-}P)_2] + Ag^+ \rightarrow [PdX(PMe_2py\text{-}P,N)(PMe_2py\text{-}P)]^+ + AgX \quad (X=Cl, Br, I)$$

The chelate complexes have been crystallized as perchlorate and hexafluorophosphate salts which contain no solvent of crystallization. The presence of chelating PMe_2py in these salts is suggested by the infrared spectra (vide infra) and by conductivity measurements which show that the complexes are 1 : 1 electrolytes in solution (Table 3), and is confirmed by X-ray analysis on the chloro complex (vide infra).

The PMe_2py ligand is possible to act as a monodentate via nitrogen and a bidentate bridging two metal ions. However, neither of them was formed with Pd(II) and Pt(II). No such Pd(II) and Pt(II) complexes of PPh_2py are known either, although dinu-

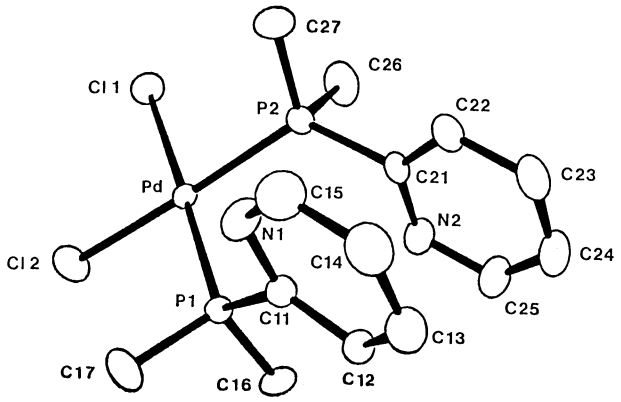

Fig. 1. A perspective view and the atom-numbering scheme for *cis*-[$PdCl_2$(PMe_2py-*P*)$_2$].

Table 3. Conductivity Measurements and Far-Infrared Spectral Data

Compound	Λ_m[a]	ν(py)	ν(M-X)	ν(M-P)	Geometry
	$cm^2 mol^{-1} \Omega^{-1}$	cm^{-1}	cm^{-1}	cm^{-1}	
[$PdCl_2$(PMe_2py-*P*)$_2$]	1.83	617	305, 283	394, 358	cis
[$PdBr_2$(PMe_2py-*P*)$_2$]	0.06	618	286	340	trans
[PdI_2(PMe_2py-*P*)$_2$]	0.01	617	b)	339	trans
[$PtCl_2$(PMe_2py-*P*)$_2$]	2.43	619	316, 290	393, 363	cis
[$PtBr_2$(PMe_2py-*P*)$_2$]	9.76	617	202, b)	394, 362	cis
[PtI_2(PMe_2py-*P*)$_2$]	19.4	617	b)	393, 357	cis
[PdCl(PMe_2py)$_2$]ClO_4	87.2	645, b)	325		
[PdBr(PMe_2py)$_2$]ClO_4	88.3	646, b)	200		
[PdI(PMe_2py)$_2$]ClO_4	91.6	645, b)	b)		
[PdCl(PMe_2py)$_2$]PF_6	86.1	643, 617	326		
[PdBr(PMe_2py)$_2$]PF_6	87.7	648, 618	200		
[PdI(PMe_2py)$_2$]PF_6	88.4	642, 619	b)		

a) 1 mmol dm^{-3} in CH_3NO_2. b) Not observed.

clear Pd(I) and Pt(I) complexes with bridging PPh_2py are well known.[1,2] We have obtained the same dinuclear complexes with PMe_2py. The results will be reported elsewhere.

Crystal Structures of *cis*-[$PdCl_2(PMe_2py$-*P*)$_2$] and *cis*(*P,P*)-[$PdCl(PMe_2py$-*P,N*)(PMe_2py-*P*)]ClO_4. Figure 1 shows the X-ray structure of *cis*-[$PdCl_2(PMe_2py$-*P*)$_2$] together with the numbering scheme. The bond distances and angles are listed in Table 4. The complex molecule forms a square plane with two monodentate phosphorus donating PMe_2py and two chloride ions. The largest displacement of an atom from the least-square plane around the Pd center is 0.080(2) Å. The complex is a cis isomer and has approximately C_2 symmetry in the crystal, while in solution it exists as a cis and trans mixture (vide infra). The structure including the conformation of two Pd-PMe_2py moieties is similar to the one found for *cis*-[$PdCl_2(PMe_2Ph)_2$][13] except for small differences in bond distances and angles. Both the Pd-P (2.242(1), 2.248(1) Å) and the Pd-Cl (2.350(1), 2.344(1) Å) lengths in the PMe_2py complex are slightly shorter than the corresponding lengths in the PMe_2Ph complex (Pd-P: 2.260(2), Pd-Cl: 2.362(3) Å). The angle between two bulky PMe_2py ligands, Pl-Pd-P2 (96.35(3)°) is also slightly smaller than that of the PMe_2Ph complex (97.85(9)°). The nitrogen atoms of two PMe_2py are oriented above and below the coordination plane with distances, Pd-N1: 3.607(3) and Pd-N2: 3.841(3) Å. These distances are so long that any interaction is not recognized. Such orientations of two pyridyl groups will reduce steric interactions between the two bulky phosphine ligands in the cis positions.

A drawing of the complex cation in *cis(P,P)*-[$PdCl(PMe_2py$-*P,N*)(PMe_2py-*P*)]ClO_4 is shown in Fig. 2 together with the numbering scheme. Selected bond distances and angles are listed in Table 4. The complex ion has a distorted square planar structure with a chelating PMe_2py, a monodentate phophorus donating PMe_2py and a chloride ion. The largest displacement of an atom from the best coordination plane is 0.237(6) Å. The two phosphorus atoms are cis to each other. The nitrogen atom of monodentate PMe_2py is oriented above the coordination plane with the distance of 3.803(7) Å. The structure is similar to the one found for *cis(P,P)*-[$PtCl(PPh_2py$-*P,N*)(PPh_2py-*P*)]$^+$.[3]

The two different Pd-P bond distances are the same within the standard deviation (av. 2.241(2) Å), which is slightly longer than the average Pt-P bond distance (2.228(6) Å) in *cis(P,P)*-[$PtCl(PPh_2py$-*P,N*)(PPh_2py-*P*)]$^+$. The Pd-N distance of 2.140(6) Å is long com-

Table 4. Selected Bond Distances (l/Å) and Angles (ϕ/°) for *cis*-[$PdCl_2(PMe_2py$-*P*)$_2$] and *cis*(*P,P*)-[$PdCl(PMe_2py$-*P,N*)(PMe_2py-*P*)]ClO_4

cis-[$PdCl_2(PMe_2py$-*P*)$_2$]				*cis*(*P,P*)-[$PdCl(PMe_2py$-*P,N*)(PMe_2py-*P*)]ClO_4			
Pd-Cl1	2.350(1)	Pd-Cl2	2.344(1)	Pd-Cl1	2.348(2)	Pd-P1	2.242(2)
Pd-P1	2.242(1)	Pd-P2	2.248(1)	Pd-P2	2.240(2)	Pd-N1	2.140(6)
P1-C11	1.824(3)	P2-C21	1.825(4)	P1-C11	1.827(7)	P2-C21	1.819(7)
P1-C16	1.795(5)	P2-C26	1.820(5)	P1-C16	1.806(7)	P2-C26	1.817(9)
P1-C17	1.803(5)	P2-C27	1.807(6)	P1-C17	1.809(8)	P2-C27	1.822(11)
N1-C11	1.333(5)	N2-C21	1.337(5)	N1-C11	1.358(8)	N2-C21	1.346(10)
N1-C15	1.336(6)	N2-C25	1.330(6)	N1-C15	1.341(9)	N2-C25	1.346(11)
C11-C12	1.376(5)	C21-C22	1.380(5)	C11-C12	1.366(10)	C21-C22	1.399(11)
C12-C13	1.376(5)	C22-C23	1.397(6)	C12-C13	1.385(11)	C22-C23	1.366(13)
C13-C14	1.372(6)	C23-C24	1.372(7)	C13-C14	1.368(11)	C23-C24	1.349(16)
C14-C15	1.374(7)	C24-C25	1.368(7)	C14-C15	1.397(10)	C24-C25	1.398(15)
Cl1-Pd-C12	89.99(5)	Cl1-Pd-P2	85.24(4)	Cl2-O1	1.409(9)	Cl2-O2	1.360(11)
Cl1-Pd-P1	176.61(4)	Cl2-Pd-P2	174.91(4)	Cl2-O3	1.485(12)	Cl2-O4	1.350(11)
Cl2-Pd-P1	88.51(4)	P1-Pd-P2	96.35(3)	Cl1-Pd-P1	167.46(7)	Cl1-Pd-P2	91.86(7)
Pd-P1-C11	116.3(1)	Pd-P2-C21	120.4(1)	Cl1-Pd-N1	98.9(2)	P1-Pd-P2	99.97(6)
Pd-P1-C16	112.9(2)	Pd-P2-C26	113.3(2)	P1-Pd-N1	69.8(2)	P2-Pd-N1	167.8(1)
Pd-P1-C17	114.9(2)	Pd-P2-C27	109.5(2)	Pd-P1-C11	84.8(2)	Pd-P2-C21	115.6(2)
C11-P1-C16	108.6(2)	C21-P2-C26	99.9(2)	Pd-P1-C16	124.6(3)	Pd-P2-C26	114.9(3)
C11-P1-C17	99.8(2)	C21-P2-C27	106.6(2)	Pd-P1-C17	120.2(2)	Pd-P2-C27	110.0(3)
C16-P1-C17	102.8(2)	C26-P2-C27	106.1(3)	C11-P1-C16	107.4(3)	C21-P2-C26	103.2(4)
C11-N1-C15	117.9(4)	C21-N2-C25	116.9(3)	C11-P1-C17	107.3(4)	C21-P2-C27	105.3(4)
P1-C11-N1	111.6(3)	P2-C21-N2	113.2(3)	C16-P1-C17	107.5(4)	C26-P2-C27	107.1(4)
P1-C11-C12	125.5(3)	P2-C21-C22	123.7(3)	Pd-N1-C11	101.9(4)	Pd-N1-C15	137.6(5)
N1-C11-C12	122.7(3)	N2-C21-C22	123.1(3)	C11-N1-C15	119.8(6)	C21-N2-C25	117.2(7)
C11-C12-C13	119.3(3)	C21-C22-C23	118.0(4)	P1-C11-N1	103.0(4)	P2-C21-N2	113.2(5)
C12-C13-C14	118.0(4)	C22-C23-C24	119.5(4)	P1-C11-C12	135.2(5)	P2-C21-C22	123.2(6)
C13-C14-C15	119.9(4)	C23-C24-C25	117.5(4)	N1-C11-C12	121.8(6)	N2-C21-C22	123.7(7)
N1-C15-C14	122.3(4)	N2-C25-C24	125.1(4)	C11-C12-C13	119.3(7)	C21-C22-C23	117.6(8)
				C12-C13-C14	118.8(7)	C22-C23-C24	120(1)
				C13-C14-C15	120.5(7)	C23-C24-C25	120(1)
				N1-C15-C14	119.9(7)	N2-C25-C24	121(1)

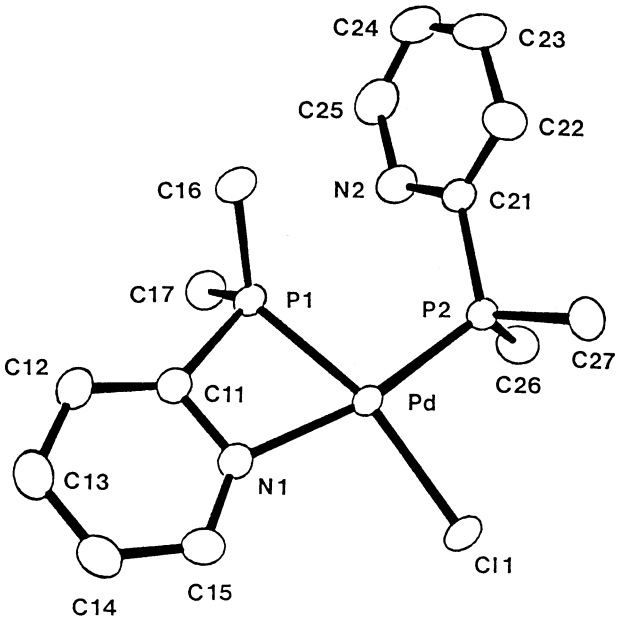

Fig. 2. A perspective view and the atom-numbering scheme for *cis(P,P)*-[PdCl(PMe_2py-*P,N*)(PMe_2py-*P*)]$^+$.

pared with those of other Pd(II)-pyridine complexes such as *trans*-[$PdCl_2$(2-NH_2-py)$_2$] (2.024(4) Å)[14] and the Pt-N distance (2.07(2) Å) of *cis(P,P)*-[PtCl(PPh_2py-*P,N*)(PPh_2py-*P*)]$^+$, but is similar to the Pd-N distance (2.155(5) Å) in *trans*-[$PdCl_2$(PEt_3)(2-NH_2-3-Me-py)],[15] in which the pyridyl nitrogen occupies at the position trans to PEt_3. All the bond angles within the four-membered chelate ring are largely reduced from the ideal values as seen from Table 4. The bite angle of chelating PMe_2py is reduced to 69.8(2)° from the ideal value of 90°. The Pd-P1-C11 angle of 84.8(2)° is the largest reduction from the tetrahedral angle (109.5°). The corresponding M-P-C angles in *cis(P,P)*-[PtCl(PPh_2py-*P,N*)(PPh_2py-*P*)]$^+$ and *trans(P,C1)*, *trans(N,C)*-[$RuCl_2$(PPh_2py-*P,N*)-$(CO)_2$][4] also show the largest reduction in bond angles of the chelate ring. Despite the large deviation in bond angles of Pd-P1-C11 (C16, C17) from the ideal value, three C-P1-C angles are nearly the tetrahedral angle. The two pyridyl rings are highly planar. The dihedral angle between the pyridyl ring of the chelating ligand and the Pd coordination plane is 13.6(1)°.

Geometrical Structures of Other Complexes in the Solid States. On the basis of the structures determined by X-ray analyses, the solid state structures of other complexes prepared in this study have been assigned by their infrared spectra. All [MX_2(PMe_2py)$_2$] (M=Pd, Pt; X=Cl, Br, I) show a band due to the in-plane ring deformation of pyridine in the range 617—620 cm^{-1}.[16] Thus it is concluded that none of the pyridyl nitrogens are coordinated to the metal in these complexes. On the other hand, *cis(P,P)*-[PdCl(PMe_2py-*P,N*)(PMe_2py-*P*)]ClO_4 shows a band at a higher frequency 645 cm^{-1}. This band can be assigned as the same deformation band of pyridine of chelating PMe_2py, since it is known that the deformation band is shifted to higher frequencies when the nitrogen atom is bound to a metal.[16] The band due to monodentate phosphorus donating PMe_2py is hidden by the strong band of ClO_4^- at 620 cm^{-1}. [PdX(PMe_2py)$_2$]ClO_4 (X=Br and I) also give the band around 645 cm^{-1}. For [PdX(PMe_2py)$_2$]PF_6 (X=Cl, Br, and I), two bands with similar intensities are observed around 645 and 618 cm^{-1}. Thus all the complexes contain both nitrogen-bound and non-nitrogen-bound PMe_2py.

Geometries of [MX_2(PMe_2py-*P*)$_2$] are characterized from comparisons of their spectra with that of *cis*-[$PdCl_2$(PMe_2py-*P*)$_2$] in the metal-ligand stretching region. The assignments of the bands were carried out by reference to the spectral data of [PdX_2(PMe_3)$_2$].[17] The results are given in Table 3. Three [PtX_2(PMe_2py-*P*)$_2$] (X=Cl, Br, and I) show spectra similar to that of *cis*-[$PdCl_2$(PMe_2py-*P*)$_2$], giving two bands due to ν(M-P) at ca. 394 and 360 cm^{-1}. For ν(M-Cl), two bands were observed at 305 and 283 cm^{-1} for M=Pd(II) and at 316 and 290 cm^{-1} for M=Pt(II), although one of two ν(Pt-Br) and two ν(Pt-I) were not detected in the measurable region. Thus all the Pt(II) complexes have the cis configuration. However, the spectra of [PdX_2(PMe_2py-*P*)$_2$] (X=Br and I) are similar but different from that of *cis*-[$PdCl_2$(PMe_2py-*P*)$_2$]. These bromo and iodo complexes show a relatively strong and sharp band due to ν(Pd-P) band at ca. 340 cm^{-1}. The bromo complex gives a strong and sharp band at 286 cm^{-1} assignable to ν(Pd-Br), the ν(Pd-I) band for the iodo complex being not detected in the region measured. These results indicate that the bromo and iodo complexes are the trans isomer. The structures of [MX_2(PMe_2py-*P*)$_2$] in the solid state, which depend on the kinds of metal and halide ions, are the same as those of the corresponding PMe_2Ph complexes.[18]

The spectra of [PdX(PMe_2py-*P,N*)(PMe_2py-*P*)]Y (X=Cl, Br, I; Y=ClO_4, PF_6) are too complicated to allow assignment of the bands except for the pyridyl ring deformation parts described above. However, all the complexes show spectra similar to one another except the bands due to ClO_4^- and PF_6^-, and can be assigned as the same isomer as *cis(P,P)*-[PdCl(PMe_2py-*P,N*) (PMe_2py-*P*)]ClO_4.

Structures of the Complexes in Solution. Several [MX_2(phosphine)$_2$]-type complexes (M=Pd(II), Pt(II); X=halide or pseudohalide ions) are known to undergo cis-trans isomerization in solution.[19] The structures in solution and cis-trans isomerization of [MX_2(PMe_2py-*P*)$_2$] have been examined by ^{1}H and ^{13}C as well as ^{31}P NMR spectra. In general, a P-CH_3 resonance in ^{1}H and ^{13}C NMR spectra appears as a doublet peak for *cis*-[MX_2P_2] (P=methylphosphines),

while for the trans isomer it appears as a triplet peak.[20] For the analogous Pt(II) complexes, each of these peaks becomes a triplet owing to the coupling with ^{195}Pt, and ^{1}J(Pt-P) values for cis isomers (ca. 3500 Hz) are, in general, larger than the ones for trans isomers (ca. 2500 Hz).[21] On the basis of these empirical features, the structures of the complexes in solution were assigned as shown in Table 5.

As shown in Table 5, some complexes show spectra implying the existance of both cis and trans isomers, although they are isolated as a single isomer in the solid state as indicated by the infrared spectra. Relative intensities for the cis and trans isomers in the NMR spectra are not changed with time, but changed with temperature and the kind of solvent. Figure 3 shows the ^{1}H NMR spectra of [$PdBr_2$(PMe$_2$py-*P*)$_2$] in $CDCl_3$ and $C_6D_5NO_2$ at various temperatures. From the relative intensities of either the P-CH_3 or the py-6H proton resonance, the equilibrium constants (K_{eq}=[*trans*-isomer]/[*cis*-isomer]) for cis-trans isomerization (at 33 °C) were obtained (Table 6). The table shows that the cis isomer is predominant when the coordinated halide ion becomes small, and when the dielectric constant of the solvent becomes high. The Pt(II) complexes favor the cis isomer compared with the corresponding Pd(II) complexes. The temperature dependent spectra of [$PdBr_2$(PMe$_2$py-*P*)$_2$] in Fig. 3 show that the cis isomer is predominant at a low temperature. In the spectra of a $C_6D_5NO_2$ solution coalescence of peaks due to the cis and trans isomers has been observed at temperatures higher than 100 °C. At 177 °C the spectrum shows a single sharp peak for the P-CH_3 protons.

The PMe$_2$py complexes seem to be stabilized in the cis isomer a little more than the corresponding PMe$_2$Ph complexes. In $CDCl_3$ at 32—34 °C, the iso-

Table 5. Selected NMR Data (Solvent: $CDCl_3$ for [MX_2(PMe$_2$py-*P*)$_2$] and CD_3NO_2 for [PdX(PMe$_2$py)$_2$]Y (X=Cl, Br, I; Y=ClO_4, PF_6); at 33 °C)[a]

Complex (geometry)	^{31}P	^{1}H		^{13}C
		P-C<u>H</u>$_3$	py-6<u>H</u>	P-<u>C</u>H$_3$
(Free ligand)	−40.11	1.28, d (2.9)	8.54, d	
[$PdCl_2$(PMe$_2$py-*P*)$_2$] (*cis*)	10.98	1.84, d (11.2)	8.52, d (4.2)	15.0, d (38.0)
(*trans*)	0.73	1.79, t (5.6)	8.67, d	10.9, t (5.6)
[$PdBr_2$(PMe$_2$py-*P*)$_2$] (*cis*)	9.58	1.77, d (13.2)	8.52, d	16.7, d (37.7)
(*trans*)	−4.18	1.95, t (3.5)	8.69, d (4.6)	13.5, t (16.9)
[PdI_2(PMe$_2$py-*P*)$_2$] (*trans*)	−14.06	2.22, t (3.5)	8.69, d (4.6)	18.7, t (17.5)
[$PtCl_2$(PMe$_2$py-*P*)$_2$] (*cis*)	−9.79 [3482]	1.86, d (11.2) [34.9]	8.54, d (4.8)	14.2, m
[$PtBr_2$(PMe$_2$py-*P*)$_2$] (*cis*)	−9.97 [3437]	1.92, d (11.0) [35.6]	8.53, d (4.6)	15.7, m
[PtI_2(PMe$_2$py-*P*)$_2$] (*cis*)	−12.63 [3304]	2.00, d (10.7) [35.8]	8.53, d	
(*trans*)	−16.23 [2316]	2.22, t (3.7) [24.8]	8.80, d	
[PdCl(PMe$_2$py)$_2$]ClO_4	18.3, br −52.9, br			
[PdBr(PMe$_2$py)$_2$]ClO_4	17.5, br −56.7, br	2.11, br 1.96, br		
[PdI(PMe$_2$py)$_2$]ClO_4	15.6, br −67.9, br			
[PdCl(PMe$_2$py)$_2$]PF_6	17.3, br −53.2, br	2.04, br 1.89, br		
[PdBr(PMe$_2$py)$_2$]PF_6	17.5, br −55.3, br	2.07, br 1.92, br		
[PdI(PMe$_2$py)$_2$]PF_6	15.8, br −68.0, br			

a) d, t, and m denote doublet, triplet, and multiplet, respectively. br denotes a broad peak. Coupling constants (J/Hz) are shown in the round parentheses. The squared ones show coupling constants with ^{195}Pt (J/Hz).

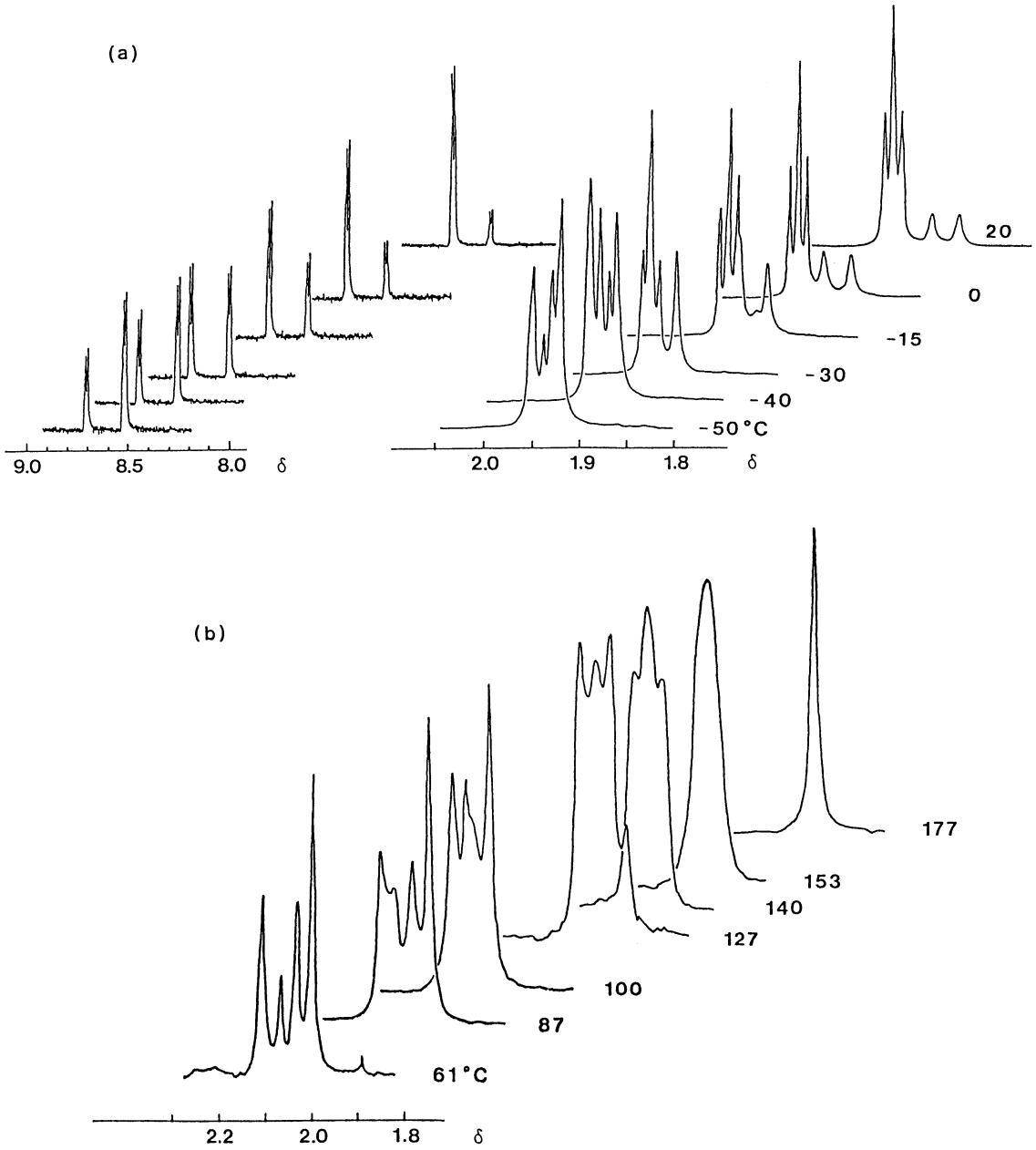

Fig. 3. Temperature dependence of the ^{1}H NMR spectra of [$PdBr_2$(PMe2py-*P*)$_2$] in (a) $CDCl_3$ and (b) $C_6D_5NO_2$. The spectra show only the P-CH_3 and py-6H regions (for (b) only the P-CH_3 region).

Table 6. Equilibrium Constants for the Cis-Trans Isomerization of [MX_2(PMe2py-P_2] (M=Pd, Pt; X=Cl, Br, and I) in Some Deuterated Aprotic Solvents

Solvent	Dielectric constant[b]	Dipole moment	K_{eq}[a]					
			[PdX_2(PMe2py-*P*)$_2$]			[PtX_2(PMe2py-*P*)$_2$]		
	$J^{-1}C^2m^{-1}$	Debye	X=Cl	X=Br	X=I	X=Cl	X=Br	X=I
C_6D_6	2.28	0	—	All trans	All trans	—	—	All trans
$CDCl_3$	4.81	1.01	0.25	6.0	All trans	All cis	All cis	1.4
CD_2Cl_2	7.77[c]	1.60	<0.1	1.5	All trans	—	—	0.83
$(CD_3)_2CO$	20.7[d]	2.88	All cis	1.2	—	—	—	—
$C_6D_5NO_2$	34.8[d]	4.22	All cis	0.88	—	—	—	—
CD_3NO_2	35.9[e]	3.46	All cis	All cis	All trans	—	—	<0.3
CD_3CN	37.5	3.92	All cis	All cis	All trans	—	—	—

a) K_{eq}=[*trans*-isomer]/[*cis*-isomer]. b) Measured at 20 °C with exception of c) measured at 10 °C, d) measured at 25 °C, and e) measured at 30 °C.

mer distribution of $[PdCl_2(PMe_2py\text{-}P)_2]$ is ca. 80% cis and ca. 20% trans isomers, and that of $[PdCl_2(PMe_2Ph)_2]$ ca. 65% cis and ca. 35% trans isomers.[20] While $[PdBr_2(PMe_2py\text{-}P)_2]$ is a mixture of ca. 15% cis and ca. 85% trans isomers, $[PdBr_2(PMe_2Ph)_2]$ exists only as the trans isomer.[18] For this type of complex, the stability of the cis isomer will increase when the phosphine ligand is less bulky and more basic.[21] It is not clear that which ligand is more basic, but PMe_2py which lacks a hydrogen atom on the nitrogen atom is less bulky than PMe_2Ph and will be favorable for the formation of cis isomers.

The data of ^1H and ^{31}P NMR spectra of $[PdX(PMe_2py\text{-}P,N)(PMe_2py\text{-}P)]Y$ (X=Cl, Br, I; Y=ClO_4, PF_6) are listed in Table 5. In the ^{31}P spectra, the complexes show two broad peaks around 17 and −55 ppm, the PF_6^- ion showing a very sharp peak. The ^{31}P resonance of phosphine ligands which form a four-membered chelate ring is known to shift to a higher field upon chelate coordination.[22] Thus the two broad peaks around 17 and −55 ppm can be assigned as monodentate and bidentate PMe_2py, respectively. The P-CH_3 protons also exhibit two broad peaks in the ^1H NMR spectra. The spectra of the chloro complex in CD_3NO_2 measured at −50 °C remained almost unchanged to give broad peaks. We have no clear explanation for these broad peaks at present. However, they would be attributable to rapid breaking and binding reactions between the nitrogen atom of PMe_2py and the Pd(II) ion in a complex ion. The X-ray structure of *cis(P,P)*-$[PdCl(PMe_2py\text{-}P,N)(PMe_2py\text{-}P)]$ ClO_4 shows that the four-membered chelate ring is largely strained, but the Pd-P bond length of the ring is normal and nearly the same as that of the monodentate PMe_2py ligand. On the contrary, the Pd-N bond is considerably long. Therefore, such breaking and binding reactions between the nitrogen donor and Pd(II), that is, the exchange between the coordination modes of monodentate and bidentate PMe_2py ligands, would occur very easily to make the resonance peaks broad.

This work was supported by a Grant-in-Aid for Scientific Research No. 61430013 from the Ministry of Education, Science and Culture. We wish to thank the Institute for Molecular Science (Okazaki) for the use of X-ray and computation facilities. We also wish to thank Dr. Frode Galsbøl (University of Copenhagen) for helpful discussions.

References

1) J. P. Farr, F. E. Wood, and A. L. Balch, *Inorg. Chem.*, **22**, 3387 (1983).
2) A. Maisonnet, J. P. Farr, M. M. Olmstead, C. T. Hunt, and A. L. Balch, *Inorg. Chem.*, **21**, 3961 (1982).
3) J. P. Farr, M. M. Olmstead, F. E. Wood, and A. L. Balch, *J. Am. Chem. Soc.*, **105**, 792 (1983).
4) M. M. Olmstead, A. Maisonnat, J. P. Farr, and A. L. Balch, *Inorg. Chem.*, **20**, 4060 (1981).
5) L. J. Tortoralli, C. A. Tucker, C. Woods, and J. Bordner, *Inorg. Chem.*, **25**, 3534 (1986).
6) V. K. Jain, V. S. Jakkal, and R. Bohra, *J. Organomet. Chem.*, **389**, 417 (1990).
7) Y. Inoguchi, B. Milewski-Mahrla, and H. Schmidbaur, *Chem. Ber.*, **115**, 3085 (1983).
8) *Inorg. Synth.*, Vol. XV, p. 185.
9) *Inorg. Synth.*, Vol. VI, p. 218.
10) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).
11) W. L. Steffen and G. J. Palenic, *Inorg. Chem.*, **15**, 2432 (1976).
12) C. Lee, Y. Yang, S. J. Retting, B. R. James, D. A. Nelson, and M. A. Lilga, *Organometallics*, **5**, 2220 (1986).
13) L. L. Martin and R. A. Jacobson, *Inorg. Chem.*, **10**, 1795 (1971).
14) M. C. N. Ranninger, S. Martinez-Carrera, and S. Garcia-Blanco, *Acta Crystallogr., Sect. C*, **41**, 21 (1985).
15) A. Albinati, C. Arz, and P. S. Pregosin, *Inorg. Chem.*, **26**, 508 (1987).
16) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 4th ed, John Wiley & Sons Inc., New York (1986), p. 206.
17) P. J. D. Park and P. J. Hendra, *Spectrochim. Acta, Part A*, **25**, 227 (1969); **25**, 909 (1969).
18) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, **1966**, 770.
19) R. A. Redfield and J. H. Nelson, *Inorg. Chem.*, **12**, 15 (1973); J. A. Rahn, M. S. Holt, M. O'Neil-Johnson, and J. H. Nelson, *ibid.*, **27**, 1316 (1973).
20) D. A. Redfield, L. W. Cary, and J. H. Nelson, *Inorg. Chem.*, **14**, 50 (1975).
21) A. W. Verstuyft and J. H. Nelson, *Inorg. Chem.*, **14**, 1501 (1975).
22) P. E. Garren, *Chem. Rev.*, **81**, 229 (1981).