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Fluxional Behavior of Palladium(II) and Platinum(II) Complexes Containing both a Metal–Aryl Bond and a Pyrazole-derived Ligand†

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New (acetophenone oximato, 2-*C,N*)- and (benzophenone oximato, 2-*C,N*)palladium(II) complexes containing poly(1-pyrazolyl)borato ligand (BPz_4 or $HBPz_3$, Pz=1-pyrazolyl) or poly(1-pyrazolyl)methane (CPz_4 or $HCPz_3$) were prepared and investigated by means of ^{1}H-NMR spectroscopy. For the BPz_4 complexes, the tumbling motion of the BPz_4 ligand averaged the environments of all four pyrazolyl groups to give spectroscopic equivalence above 65 °C, and was virtually frozen at *ca.* −9 °C. With regard to the $HBPz_3$, CPz_4, and $HCPz_3$ complexes, all pyrazolyl groups were equivalent at high temperature exhibiting stereochemical nonrigidity. The well-defined slow-exchange limiting spectra were not obtained at *ca.* −34 °C. In addition, new (acetophenone oximato, 2-*C,N*)platinum(II) complexes involving the BPz_4 or $HBPz_3$ ligand were prepared. The bidentate coordination of the BPz_4 ligand in the BPz_4 platinum(II) complex was stereochemically rigid in the range of 29 to 110 °C in DMSO-d_6. Three pyrazolyl groups in the $HBPz_3$ platinum(II) complex were equivalent at 85 °C in DMSO-d_6, while the fluxional motion was fairly restricted at room temperature.

Trofimenko[1,2] synthesized π-allylpalladium(II) complexes, $[Pd(\pi\text{-}C_3H_5)(PBz_4)]$ (Pz=1-pyrazolyl) and $[Pd(\pi\text{-}C_3H_5)(CPz_4)]PF_6$, reported that each of the 3-, 4-, and 5-H's of the four pyrazolyl groups in these complexes showed only one signal in the ^{1}H-NMR spectra at room temperature, and explained the fluxional behavior in terms of a "tumbling process."[1]

It is interesting to compare the fluxional behavior of the pyrazole-derived chelate ligands in the other square-planar complexes with those of the π-allylpalladium(II) complexes[1,2] and related platinum(II) complexes.[3] In a previous paper,[4] the fluxional behavior has been reported for several polypyrazolylborato palladium(II) complexes, which were prepared from dimeric cyclopalladated complexes derived from *N,N*-dimethylbenzylamine, azobenzene, 2-phenylpyridine, and benzo[*h*]quinoline.

This paper will deal with several new polypyrazolylborato (BPz_4 or $HBPz_3$) and polypyrazolylmethane (CPz_4 or $HCPz_3$) palladium(II) complexes, derived from cyclopalladated complexes, di-μ-chloro-bis(acetophenone oximato, 2-*C,N*)dipalladium(II)[5] $[\{PdCl(apo)\}_2]$ {apo=$-C_6H_4-C(=NOH)CH_3$,2-*C,N*} or di-μ-chloro-bis(benzophenone oximato, 2-*C,N*)dipalladium(II)[5] $[\{PdCl(bpo)\}_2]$ {bpo=$-C_6H_4-C(=NOH)C_6H_5$, 2-*C,N*}, and with the fluxional behavior of the pyrazole-derived ligands in these complexes by means of ^{1}H-NMR spectroscopy.

New platinum(II) complexes, $[Pt(apo)(BPz_4)]$ and $[Pt(apo)(HBPz_3)]$ were also obtained and compared with the corresponding polypyrazolylborato palladium(II) complexes.

Experimental

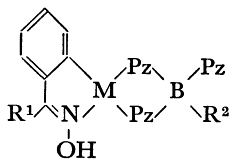
General Procedures. Melting points were determined on a Yanagimoto MP-S3 microstage apparatus and are uncorrected. IR spectra were recorded on a Hitachi model 285 spectrometer. ^{1}H-NMR spectra were run on a Japan Electron Optics Laboratory model JNM-MH-100 (100 MHz) spectrometer using tetramethylsilane as the internal standard. The temperatures of the NMR samples were determined with methanol or 1,3-propanediol.

$[\{PdCl(apo)\}_2]$,[5] $[\{PdCl(bpo)\}_2]$,[5] $[PtCl(apo)(Hapo)]$,[5] sodium tetrakis(1-pyrazolyl)borate $\{Na(BPz_4)\}$,[6] sodium hydrotris(1-pyrazolyl)borate $\{Na(HBPz_3)\}$,[6] CPz_4,[2] and $HCPz_3$[7] were prepared and purified according to the methods described in the literature.

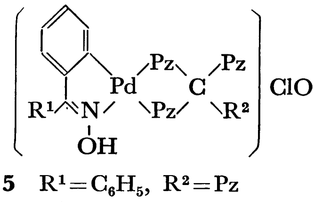
Syntheses of the BPz_4 Palladium(II) Complexes. $[\{PdCl(bpo)\}_2]$ (1.6 g) and $Na(BPz_4)$ (1.5 g) were mixed in ethanol (80 ml) and the suspension stirred at room temperature for *ca.* 20 h. The precipitate was extracted with hot benzene, the solvent evaporated, and the residue recrystallized from ethanol to give yellow crystals of $[Pd(bpo)(BPz_4)]\cdot C_2H_5OH$, 0.9 g. This complex was converted into the non-solvated complex (**1**), by recrystallization from benzene.

The acetophenone oxime analogue, (**2**) and the ethanol monosolvate were obtained by a similar method.

Syntheses of the $HBPz_3$ Palladium(II) Complexes. A solution of $Na(HBPz_3)$ (0.9 g) in ethanol (20 ml) was added dropwise to a stirred suspension of $[\{PdCl(bpo)\}_2]$ (1.3 g)



1 $R^1=C_6H_5$, $R^2=Pz$, M=Pd
2 $R^1=CH_3$, $R^2=Pz$, M=Pd
3 $R^1=C_6H_5$, $R^2=H$, M=Pd
4 $R^1=CH_3$, $R^2=H$, M=Pd
9 $R^1=CH_3$, $R^2=Pz$, M=Pt
10 $R^1=CH_3$, $R^2=H$, M=Pt



5 $R^1=C_6H_5$, $R^2=Pz$
6 $R^1=CH_3$, $R^2=Pz$
7 $R^1=C_6H_5$, $R^2=H$
8 $R^1=CH_3$, $R^2=H$

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Table 1. Properties and elemental analyses of the new complexes

	Yield^a)^ (%)	Color	Mp^b)^ (°C)	Found (Calcd) (%) C	H	N
1	21	Pale yellow	167—169	51.82(51.62)	3.90(3.81)	21.39(21.67)
2	28	Pale yellow	181—184	45.88(46.23)	3.89(3.88)	23.93(24.26)
3	55	Pale yellow	170—173^c)^	51.09(51.24)	3.90(3.91)	18.95(19.01)
4	25	Pale yellow	159—162^c)^	44.71(45.02)	3.94(4.00)	21.59(21.62)
5	36	Yellow	183—215	46.14(45.76)	3.31(3.25)	18.63(18.47)
6	44	Pale yellow	197—200	40.59(40.66)	3.12(3.25)	20.05(20.32)
7	41	Yellow	142—152	44.54(44.82)	3.20(3.27)	15.83(15.91)
8	41	Pale yellow	209—212	39.13(39.01)	3.24(3.27)	17.58(17.69)
9	40	Orange	230—233	39.59(39.49)	3.21(3.31)	20.73(20.72)
10	50	Orange	218—220	37.70(37.65)	3.29(3.35)	18.17(18.08)

a) Based on the starting palladium(II) or platinum(II) complexes. b) All complexes decomposed without melting.
c) Measured in dinitrogen atmosphere.

in ethanol (10 ml). After stirring for *ca.* 20 h, the suspension was filtered and the precipitate washed with dichloromethane and methanol to yield a pale yellow powder of [Pd(bpo)(HBPz$_3$)] (**3**), 1.1 g: IR (Nujol) 2410 and 2425 cm^{-1} (ν_{BH}).

The complex [Pd(apo)(HBPz$_3$)] (**4**) was prepared similarly except the washing was conducted with dichloromethane: IR (Nujol) 2425 and 2440 cm^{-1} (ν_{BH}).

Syntheses of the CPz$_4$ Palladium(II) Perchlorate Complexes. A mixture of CPz$_4$ (0.1 g) and [{PdCl(bpo)}$_2$] (0.12 g) in methanol–water (35 ml) (1:3), was stirred for *ca.* 20 h at room temperature.

The mixture was filtered and a solution of sodium perchlorate in methanol–water added to the filtrate. The resulting precipitate was recrystallized from methanol to give a yellow solid of [Pd(bpo)(CPz$_4$)]ClO$_4$ (**5**), 0.09 g.

The complex [Pd(apo)(CPz$_4$)]ClO$_4$ (**6**) was prepared in a similar method as described for **5**, where the corresponding precipitate was washed with benzene, dichloromethane, and water in place of recrystallization.

Syntheses of the HCPz$_3$ Palladium(II) Perchlorate Complexes. A mixture of [{PdCl(bpo)}$_2$] (0.37 g) and HCPz$_3$ (0.24 g) in methanol–water (30 ml) (1:3) was stirred for 5 h at room temperature and the reaction mixture filtered. Sodium perchlorate was added to the filtrate, and the resulting precipitate was recrystallized from methanol to afford a yellow solid of [Pd(bpo)(HCPz$_3$)]ClO$_4$ (**7**) 0.28 g: IR (KBr) 3000 cm^{-1} (ν_{CH} of $\underline{H}CPz_3$).

The complex [Pd(apo)(HCPz$_3$)]ClO$_4$ (**8**) was prepared similarly: IR (KBr) 2990 cm^{-1} (ν_{CH} of $\underline{H}CPz_3$).

Syntheses of [Pt(apo)(BPz$_4$)] and [Pt(apo)(HBPz$_3$)]. After a mixture of Na(BPz$_4$) (0.3 g) and [PtCl(apo)(Hapo)] (0.41 g) was stirred for *ca.* 20 h in benzene (20 ml), the solvent was removed. The residue was extracted with dichloromethane and the extract evaporated to dryness. The resulting solid was washed with diethyl ether and ethanol to yield an orange powder of [Pt(apo)(BPz$_4$)] (**9**), 0.2 g.

The complex [Pt(apo)(HBPz$_3$)] (**10**) was obtained similarly, and recrystallized from methanol: IR(Nujol) 2430 and 2410 cm^{-1} (ν_{BH}).

Results and Discussion

Physical Properties. The analytical data and the physical properties of the new palladium(II) and platinum(II) complexes are summarized in Table 1. The BPz$_4$ palladium(II) complexes, **1** and **2** were soluble in chloroform and DMSO, and slightly soluble in ethanol and benzene. The HBPz$_3$ palladium(II) complexes, **3** and **4**, were less soluble than the corresponding BPz$_4$ complexes, **1** and **2**, respectively. The ^{1}H-NMR spectrum of **3** was not obtainable. The complexes were stable in the solid state. However, complex **4** decomposed slowly in dichloromethane to give metallic palladium. The cationic palladium(II) complexes, **5**, **6**, **7**, and **8** involving polypyrazolylmethane were insoluble in common organic solvents except for acetonitrile and methanol. The polypyrazolylmethane complexes were thermally more stable than the corresponding polypyrazolylborato ones in the solid

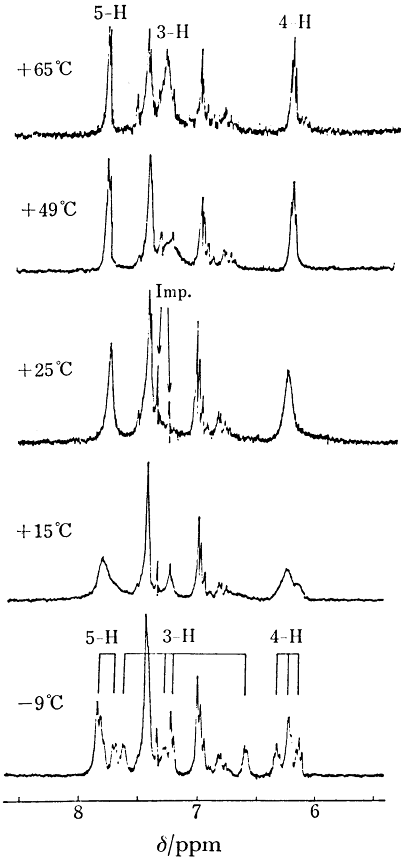

Fig. 1. ^{1}H-NMR spectra of **1** in CDCl$_3$. Two impurities are CHCl$_3$ and C$_6$H$_6$.

Table 2. Solvent effects on the chemical shifts of pyrazolyl protons[a)]

Proton	[Pd(bpo)(BPz$_4$)]			[Pd(apo)(BPz$_4$)]		
	DMSO-d_6	C_6D_6	$CDCl_3$[b)]	DMSO-d_6	C_6D_6	$CDCl_3$[b)]
3-H	7.19	7.49	7.28	7.01	7.46	7.27
4-H	6.38	6.08	6.22	6.21	6.10	6.24
5-H	7.84	7.80	7.76	7.70	7.75	7.71

a) δ-Values relative to TMS, at 76 °C unless noted elsewhere. b) At 65 °C.

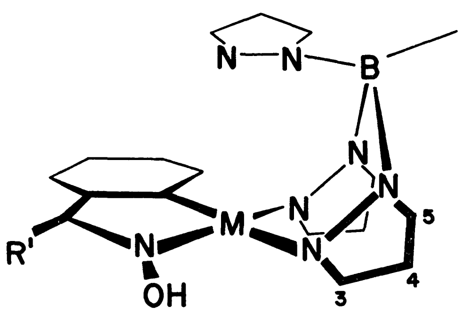

Fig. 2. The proposed geometrical arrangement.

state, complexes, **5** and **6** decomposing in acetonitrile at 80 °C.

The polypyrazolylborato platinum(II) complexes, **9** and **10** were stable in the solid state, slightly soluble in DMSO at room temperature, and insoluble in other common organic solvents.

Each of the ν(BH) bands in the $HBPz_3$ complexes consisted of two peaks, which were associated with ν(^{10}BH) and ν(^{11}BH) corresponding to the natural abundance of boron isotopes.

^{1}H-NMR Spectra of the BPz$_4$ Palladium(II) Complexes. Figure 1 shows the ^{1}H-NMR spectra of **1** in $CDCl_3$ at several temperatures between −9 and 65 °C. The line shapes of the three signals at δ 7.44 (5H), 7.01 (3H), and 6.80 (1H) were independent of temperature, and were unaffected by the exchange process. The first signal was assigned to the phenyl protons, and the remaining two to the metallated *o*-phenylene group. The protons of the four pyrazolyl groups showed signals which were remarkably temperature-dependent. At 65 °C, a signal at δ 6.22 (4H) exhibited a triplet and was ascribed to 4-H's. Signals at δ 7.28 (4H) and 7.76 (4H) were associated with 3-H's and 5-H's, respectively, on the basis of the temperature-dependency of each signal (*vide infra*). At this temperature, each of the three kinds of protons belonging to the four pyrazolyl groups exhibited spectroscopic identity, indicating a tumbling motion of the BPz_4 group as observed for [Pd(π-C_3H_5)(BPz_4)].[1)]

The signal for the 5-H's became gradually broader on cooling and separated into two signals at δ 7.79 (3H) and 7.66 (1H) at −9 °C. The signal for the 3-H's was apparently missing at 25 °C, and reappeared at δ 7.56, 7.26, 7.21, and 6.64 at −9 °C. These facts indicate that at this temperature the four pyrazolyl groups are spectroscopically unequal, and the BPz_4 ligand is coordinated to the central metal in a stereochemically rigid state. In this state, one can expect that the differences in environments and chemical shifts among the four 3-H's are larger than those among the 5-H's, respectively, by considering the proposed arrangement shown in Fig. 2. At 45 °C, a broad peak at δ 5.15 was observed in $CDCl_3$ and ascribed to an oxime proton, since it disappeared with the addition of D_2O.

Table 2 shows the NMR data of the pyrazolyl protons of **1** recorded at 76 °C in C_6D_6 and DMSO-d_6, and indicates an appreciable degree of solvent effect on the chemical shifts of the 3-H's, in contrast to that of the 5-H's. This confirms the above-mentioned assignment of the 3-H's.

At −16 °C, complex **2** exhibited a low-temperature limiting spectrum, in which a signal at δ 7.58 was attributed to two protons overlapping each other, assignable to one of the 3-H's and one of the 5-H's. The other signals of **2** exhibited very similar patterns to those of **1**.

In the BPz_4 complexes, the tumbling motion averages the environments of all four pyrazolyl groups to give spectroscopic equivalence at high temperature. The motion is thought to involve the coordination of one uncoordinated pyrazolyl group to the axial site of palladium accompanied instantaneously by the dissociation of one previously coordinated group and the inversion of the Pd–(N–N)$_2$–B boat-type six-menbered ring. In consideration of the proposed conformation shown in Fig. 2, it is reasonably expected that one uncoordinated pyrazolyl group easily approaches the axial site of the palladium atom. The tumbling motion is probably restricted to an appreciable degree in these aromatic oximato complexes, in which the *trans* positions of the BPz_4 ligand are coordinated with nitrogen donor and aryl group, in contrast to the π-allyl analogue. The comparatively weak *trans* influence of the nitrogen donor in the cyclometallated moiety of **1** and **2** possibly resulted in a moderately strong binding of Pd–Pz bond *trans* to the nitrogen donor and in an easy fixation of tumbling motion of the BPz_4 ligand.

^{1}H-NMR Spectra of the Other Palladium(II) Complexes. In the NMR spectra of [Pd(apo)($HBPz_3$)], the three pyrazolyl groups were spectroscopically equivalent at 36 °C, indicating the fluxional motion of the $HBPz_3$ ligand. The peaks for pyrazolyl groups began to broaden at −24 °C. At *ca.* −34 °C, a new peak appeared near δ 6.5, which was tentatively ascribed to one proton of 3-H's. However, a slow-exchange limiting spectrum was not obtained even at this temperature. The fluxional motion of the $HBPz_3$ complex was more hardly fixed than that of the corresponding BPz_4 complex.

Each signal for the 3-, 4-, and 5-H's of the CPz_4

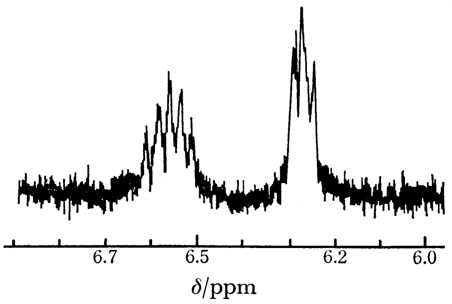

Fig. 3. 4-H's signals in ^{1}H-NMR spectrum of **9** in DMSO-d_6 at 30 °C.

complexes, **5** and **6**, showed only one signal at *ca.* 50 °C in CD_3CN, demonstrating the spectroscopic equivalence of all four pyrazolyl groups and the tumbling motion of the CPz_4 ligand. The signals for the 3- and 5-H's of the pyrazolyl groups became broad at temperatures below −10 °C, and began to separate at *ca.* −30 °C. In contrast to the polypyrazolylborate ligands, the fixation of the fluxional motion of the polypyrazolylmethane ligands was comparatively difficult.

The $HCPz_3$ complexes, **7** and **8**, at room temperature gave well-defined fast-exchange limiting spectra, showing spectroscopic equivalence of the three pyrazolyl groups and stereochemical nonrigidity.

^{1}H-NMR Spectra of Platinum(II) Complexes. Coordination of the BPz_4 ligand in the platinum(II) complex **9** was stereochemically rigid even at 110 °C on the basis of the ^{1}H-NMR spectra, and the compound decomposed at *ca.* 130 °C in DMSO-d_6. No fluxional behavior was observed. The 4-H's resonances showed a triplet at δ 6.28 and a multiplet at δ 6.55 in the ratio of 2:2, as shown in Fig. 3. The apparent multiplet was assigned to the 4-H protons with attendant ^{195}Pt satellites in two coordinated pyrazolyl groups, indicating that the BPz_4 ligand acted as a bidentate ligand and the complex was four-coordinated. For the ^{1}H-NMR spectra of methyl(polypyrazolylborato)platinum(II) complexes, similar ^{195}Pt satellites were observed for the 4-H protons of the pyrazolyl groups coordinated to platinum.[3)]

In the $HBPz_3$ platinum(II) complex **10**, three signals, a slightly broad peak (3H) at δ 7.89, a doublet (3H) at δ 7.74, and a triplet (3H) at δ 6.37 were observed for the pyrazolyl protons at *ca.* 85 °C and the triplet was assigned to the 4-H's. Three pyrazolyl groups were spectroscopically equivalent at this temperature showing stereochemical nonrigidity of the $HBPz_3$ ligand. At room temperature, the 4-H's signal separated into two signals in a 2:1 intensity ratio and the coordination of the $HBPz_3$ ligand became comparatively rigid on the NMR time scale. The slow-exchange limiting spectrum was not obtained due to poor solubility of **10** below room temperature. The fluxional motion of the $HBPz_3$ platinum(II) complex was easily fixed in contrast to that of the corresponding palladium(II) complexes.

TABLE 3. FAST-EXCHANGE LIMITING ^{1}H-NMR SPECTRA[a)] OF PYRAZOLYL GROUPS IN THE $HBPz_3$, CPz_4, AND $HCPz_3$ COMPLEXES

Complex	Temp (°C)	4-H	3-H or 5-H	
4[b)]	36	6.28(t, 2.0)	7.68(d, 1.9)[c)]	
5	61	6.76[d)]	7.52(d, 3.0)	8.19[d)]
6	75	6.80(t, 2.5)	7.58(d, 2.8)	8.22[d)]
7	28	6.73(t, 2.5)	8.09(d, 2.1)	8.27(d, 3.0)
8	29	6.63(t, 2.5)	7.96(d, 2.0)	8.13(d, 2.7)

a) δ-Values relative to TMS; multiplicities and coupling constants in Hz are given in parentheses; in CD_3CN, unless noted elsewhere; s=singlet, d=doublet, t=triplet. b) In CD_2Cl_2. c) Overlapping occurred. d) Coupling constants could not be detected.

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