Stereochemical Nonrigidity of {Poly(1-pyrazolyl)borato}palladium(II) Complexes Containing a Metal-1-Alkenyl or -Alkyl Bond†

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New{poly(1-pyrazolyl)borato}palladium(II) complexes, [Pd{CH=CCl–$CMe_2(NMe_2)$-1-*C,N*}(BPz_4)] (Pz= 1-pyrazolyl) **1**, [Pd{$CH_2CMe(OMe)–CH_2S$-*t*-Bu-1-*C,S*}(BPz_3Y)] (Y=Pz or H), and [Pd{$CH_2CMe(OMe)–CH_2NMe_2$-1-*C,N*}(BPz_3Y)] were prepared and characterized by means of elemental analysis and IR and ^{1}H-NMR spectroscopy. The stereochemical nonrigidity of these complexes was discussed on the basis of ^{1}H-NMR data. The fluxional behavior of the BPz_4 ligand in **1** was analyzed in detail by means of an approximate method based on the Bloch equation, and found to consist of three kinds of motions: inversion of the Pd–$(N–N)_2$–B boat-type six-membered ring, rotation of the BPz_4 ligand about the Pd-pyrazolyl nitrogen bond accompanying the inversion, and a tumbling process.

Stereochemical nonrigidity of a poly(1-pyrazolyl)-borate ligand of transition metal complexes has received considerable attention.[1–7] Fluxional motions of the tridentate poly(1-pyrazolyl)borate (BPz_3Y, Pz=1-pyrazolyl, Y=Pz or H) ligand in formally seven-coordinated molybdenum complexes, [Mo(1-3-η-CH_2CRCH_2)(BPz_3Y)$(CO)_2$][2] or in penta-coordinated platinum ones, [PtMe(BPz_3Y)L] (L=neutral ligand)[3] were analyzed by means of a simplified density matrix method. It is of interest to investigate the stereochemical nonrigidity of bidentate BPz_3Y ligands in square planar transition metal complexes, in comparison with that of the tridentate BPz_3Y ligands in molybdenum[1,2] or platinum complexes.[3]

Fluxional behavior has been reported for several {poly(1-pyrazolyl)borato}palladium(II) complexes which contain both metal-aryl and -nitrogen bonds.[6,7] ^{1}H-NMR spectra of these complexes involve fairly complicated aromatic protons, overlapping with some 1-pyrazolyl protons and it was difficult to analyze quantitatively the fluxional motion of the BPz_3Y ligands of the complexes.

We have prepared some {poly(1-pyrazolyl)borato}-palladium(II) complexes having a metal-1-alkenyl or -alkyl bond assisted by chelation with a nitrogen- or a sulfur donor site; the stereochemical nonrigidity of these complexes is discussed on the basis of ^{1}H-NMR spectra. The line shape analysis was carried out quantitatively as regards the fluxional motion of {2-chloro-3-(dimethylamino)-3-methyl-1-butenyl-1-*C,N*}{tetrakis(1-pyrazolyl)borato}palladium(II) [Pd(cdamb)(BPz_4)] {cdamb =CH=CCl–$CMe_2(NMe_2)$-1-*C,N*} (**1**).

Experimental

General Procedure. IR spectra were recorded and melting points determined according to the method given in the previous paper.[7] ^{1}H-NMR spectra at various temperatures were observed on a Japan Electron Optics Laboratory model MH-100 spectrometer (100 MHz), using $CDCl_3$, CD_2Cl_2, or CD_3CN as a solvent and tetramethylsilane as an internal standard. The temperature of the NMR samples was determined with methanol or 1,3-propanediol within an error of ±1 °C.

Sodium tetrakis(1-pyrazolyl)borate Na[BPz_4],[8] sodium hydrotris(1-pyrazolyl)borate Na[BPz_3H],[8] and starting dinuclear 1-alkenyl- or alkylpalladium(II) complexes, [{PdCl(cdamb)}$_2$],[9] di-μ-chloro-bis{3-(*t*-butylthio)-2-methoxy-2-methylpropyl-1-*C,S*}dipalladium(II) [{PdCl(btmmp)}$_2$] {btmmp=$CH_2CMe(OMe)–CH_2S$-*t*-Bu-1-*C,S*},[10] di-μ-chloro-bis{3-(dimethylamino)-2-methoxy-2-methylpropyl-1-*C,N*}dipalladium(II) [{PdCl(dammp)}$_2$] {dammp=CH_2-$CMe(OMe)–CH_2NMe_2$-1-*C,N*}[11] were prepared according to the reported methods.

Preparation of [Pd(cdamb)(BPz_4)]. A benzene suspension (25 ml) containing [{PdCl(cdamb)}$_2$] (0.61 mmol) and Na[BPz_4] (1.31 mmol) was stirred at room temperature for 16 h. The resulting solids were filtered off. The remaining solution was concentrated at a reduced pressure, followed by addition of hexane. On cooling, the mixture yielded pale yellow crystals, which were recrystallized from benzene–hexane to give [Pd(cdamb)(BPz_4)] (**1**).

Preparations of [Pd(btmmp)(BPz_4)] and [Pd(btmmp)(BPz_3H)]. A benzene suspension (20 ml) containing [{PdCl(btmmp)}$_2$] (0.63 mmol) and Na[BPz_4] (1.26 mmol) was stirred at room temperature for 2 h. The resulting supernatant solution was evaporated in a rotary evaporator to yield yellow oil. The oil was dissolved in diethyl ether, followed by addition of hexane at 5—8 °C. White needles precipitated, which were recrystallized from diethyl ether–hexane to afford [Pd(btmmp)(BPz_4)] (**2**).

Complex [Pd(btmmp)(BPz_3H)] (**3**) was prepared by a similar method, Na[BPz_3H] being used in place of Na[BPz_4].

Preparation of [Pd(dammp)(BPz_4)] and [Pd(dammp)(BPz_3H)]. A benzene suspension (20 ml) involving [{PdCl(dammp)}$_2$] (0.63 mmol) and Na[BPz_4] (1.26 mmol) was stirred at ambient temperature for 2 h. The resulting solid was filtered off and the remaining solution concentrated. On cooling, white solids precipitated gradually, which were collected and washed with diethyl ether and hexane to give [Pd(dammp)(BPz_4)] (**4**).

A white complex [Pd(dammp) (BPz_3H)] (**5**) was synthesized in a similar manner to the preparation of **2**.

Line Shape Analysis

Method of Approximation. Fluxional motion of the BPz_4 ligand corresponds to the exchange of four protons at a given position on the four pyrazolyl groups. Line shape analysis of **1** was performed for a spin system of

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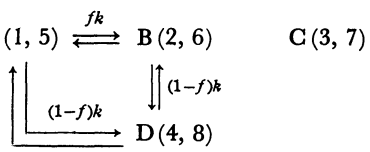
four pyrazolyl 3-H's of the BPz_4 ligand, since the 3-H's displayed well-resolved spectra of four doublets due to coupling to neighboring 4-H at low temperature, as shown in Fig. 2. In terms of spin notation, the process is an exchange of an ABCDXYZW spin system, since resonance frequencies of the 3-H's are far apart from those of the 4-H's. In a strict sense, complete line shape analysis of this spin system should be carried out by the density matrix method,[2,3,12,13] which is applicable to a spin-exchange system having spin-spin couplings. However, it needs too much computer-calculations to obtain theoretical spectra of the present exchanging system by this method. For a good approximation overcoming the difficulty, four doublets of the 3-H's were analyzed by means of the modified Bloch equation,[14] which should be applied to a spin system with no coupling, instead of the density matrix method, since the chemical shifts of the 4-H's are far apart from those of the 3-H's, and the mixing transition between spins of 3-H's and those of 4-H's might be small. A similar approximation has been reported on the NMR analysis of a restricted rotation of a tetrahedral carbon in 9-isopropyltriptycenes.[15]

Absorption intensity $I(\omega)$ at each frequency ω is derived from the modified Bloch equation:[14]

$$I(\omega) = \frac{1}{\pi}\mathrm{Re}[-P\cdot\{i(\Omega-\omega)+D\}^{-1}\cdot l]$$

where the notation of the matrices (P,Ω,ω,D,l) refer to the work of Johnson,[13] Re representing the real part of the matrix.

^{1}H-NMR spectra of three pyrazolyl 3-H's of the BPz_4 ligand showed remarkable temperature-dependency in the region 76——30 °C, while the doublet {at δ 7.49 (3 and 7) at −30 °C, in Fig. 2} corresponding to the fourth 3-H remained unchanged below 43 °C and showed temperature-dependent spectra only above 58 °C. The present analysis deals with the spin system of the four 3-H's appearing in the ^{1}H-NMR spectra in the range 43——30 °C. Concerning the former three pyrazolyl 3-H's, the exchange rate between two 3-H's {at δ 6.82 (1 and 5) and 7.25 (2 and 6) at −30 °C} differs from that between the former two 3-H's and the third one {at δ 7.59 (4 and 8) at −30 °C}. A parameter f was introduced in order to express these two different exchange rates. The terms fk and $(1-f)k$ denote the former and latter exchange rates, respectively.



This treatment is based on the assumption that activation energies for these two exchange processes are virtually equal, since it is very difficult for the present exchange system to detect a fine difference between the two activation energies.

Moreover, as regards the exchange of the three 3-H's in the temperature range 43——30 °C, upper-field signals (1, 2, and 4 in Fig. 2) of the three doublets were assumed to undergo exchange with each other, as well as the lower-field ones (5, 6, and 8). It is unlikely that the lower-field level of one 3-H doublet exchanges with a higher-field level of another doublet. A similar assumption has been reported by Suzuki *et al.*[15]

Accordingly, the matrix D of the probability of the spin transfer is given as follows.

$$D = \begin{vmatrix}
-k-\frac{1}{T_1}, & fk, & 0, & (1-f)k, & 0, & 0, & 0, & 0, \\
fk, & -k-\frac{1}{T_2}, & 0, & (1-f)k, & 0, & 0, & 0, & 0, \\
0, & 0, & -\frac{1}{T_3}, & 0, & 0, & 0, & 0, & 0, \\
(1-f)k, & (1-f)k, & 0, & -2(1-f)k-\frac{1}{T_4}, & 0, & 0, & 0, & 0, \\
0, & 0, & 0, & 0, & -k-\frac{1}{T_5}, & fk, & 0, & (1-f)k, \\
0, & 0, & 0, & 0, & fk, & -k-\frac{1}{T_6}, & 0, & (1-f)k, \\
0, & 0, & 0, & 0, & 0, & 0, & -\frac{1}{T_7} & 0, \\
0, & 0, & 0, & 0, & (1-f)k, & (1-f)k, & 0, & -2(1-f)k-\frac{1}{T_8}
\end{vmatrix}$$

Full width in Hz at half height of the i-th peak is $(\pi T_i)^{-1}$ in the absence of exchanging broadening, and the parameter T_i is a transverse relaxation time modified by some effects, such as long-range coupling to 5-H, mechanical fluctuation of resolving power, and mixing transition. ^{1}H-NMR spectrum at −30 °C was actually a slow-exchange limiting one, and the parameters T_i's were obtained readily from line widths of respective peaks. Above this temperature, T_i's were estimated from the values at −30 °C, using observed line widths of signals of 1,1,2,2-tetrachloroethane as a reference.

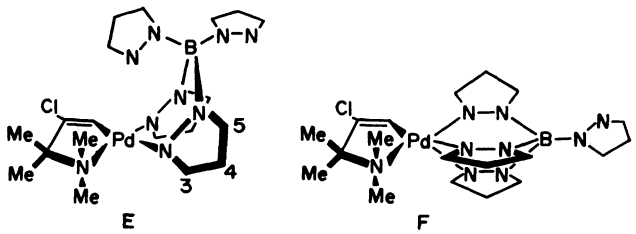
Calculations. For the given parameter f and the rate constant k together with chemical shifts and line widths in the absence of the exchanging broadening, calculations of the theoretical spectra were carried out with a FACOM 270-20 computer. The spectra were accomodated in order to get the best visual fitting with

the observed spectra by varying both f and k. The theoretical spectra were checked up as regards 1/2, 3/4, 4/5, and 6/7 of f.

Results and Discussion

General Properties. The chloro-bridging dinuclear cyclopalladated complexes reacted fairly smoothly with $Na[BPz_3Y]$ in the suspension of a non-polar solvent, such as benzene, to afford the corresponding new {poly(1-pyrazolyl)borato}palladium(II) complexes **1**—**5**. Yields, analytical data, and some physical properties of the new palladium(II) complexes are summarized in Table 1. Complexes **1**—**5** are stable in a solid state in the air, and soluble in the usual organic solvents except saturated hydrocarbons. Complexes **2**—**5** are soluble even in diethyl ether, and can not easily be purified by recrystallization. The compositions of **1**—**5** were confirmed by elemental analysis (Table 1), IR data (Table 2), and ^{1}H-NMR evidence (Table 3). ^{1}H-NMR spectra of these five complexes showed considerable temperature-dependency in the region 85——36 °C.

Two coordination types of the BPz_3Y ligands are possible for **1**—**5**. Possible structures for **1** are shown in Fig. 1, as a typical example. The definite structure in the solid phase should be determined by X-ray analysis. The BPz_3Y ligands of **1**—**5** in solution were assumed to serve as a bidentate chelate (structure **E**) for the following reasons.



E F

Fig. 1. Possible structures of **1**.

(1) The bidentate coordination of the BPz_3Y ligands was found in (acetophenone oximato-2-*C*,*N*){tetrakis(1-pyrazolyl)borato}platinum(II)[7] similar to **1**, **4**, and **5**, in $[Pd(1\text{-}3\text{-}\eta\text{-}C_3H_5)(BPz_4)]$,[1] and in $[PtMe(BPz_3H)(CO)]$ in the solid phase.[16]

(2) The relatively electron-rich palladium atom in **1**—**5** presumably prevents the third 1-pyrazolyl group of the BPz_3Y ligand from being coordinated to the palladium atom, in contrast with $[PtMe(BPz_4)(CO)]$ in solution[3] or $[PtMe(BPz_3H)(un)]$ {un=$F_3C\text{-}C{\equiv}C\text{-}CF_3$[17] or $F_2C{=}CF_2$[3]}, each of which possesses a considerably strong π-back-bonding ligand, CO or un.

(3) As regards the ^{1}H-NMR spectrum of **1** at −30 °C, both the chemical shift difference between two 3-methyl groups and that between two *N*-methyl ones are considerably large (Table 3). It seems unlikely that the conformation of the uncoordinated 1-pyrazolyl group in structure **F** would cause these large differences in **1**.

*^{1}H-NMR Spectra of $[Pd(cdamb)(BPz_4)]$ **1**.* At −30 °C, **1** exhibited the limiting slow exchange ^{1}H-NMR spectrum (Table 3). At this temperature, the four pyrazolyl groups are spectroscopically unequal, the BPz_4 ligand being coordinated to the central metal in a spectroscopically rigid state. In this state, it is expected that the differences in environments and chemical shifts among the four 3-H's are larger than those among the 5-H's, by considering the proposed

Table 1. Yields and elemental analyses of the new complexes

	Complex	Yield[a] %	Mp[b] °C	Found (Calcd) (%) C	H	N
1	$[Pd(cdamb)(BPz_4)]$	57	164—166	42.58 (42.88)	4.74 (4.73)	23.61 (23.69)
2	$[Pd(btmmp)(BPz_4)]$	17	130—138	45.13 (44.98)	5.63 (5.57)	20.08 (19.98)
3	$[Pd(btmmp)(BPz_3H)]$	16	108—126	43.69 (43.70)	6.00 (5.91)	17.13 (16.99)
4	$[Pd(dammp)(BPz_4)]$	23	155—170	43.98 (44.24)	5.46 (5.48)	24.56 (24.45)
5	$[Pd(dammp)(BPz_3H)]$	15	96—99	42.58 (42.73)	5.80 (5.84)	21.90 (21.81)

a) Based on the starting palladium(II) complexes. b) All complexes decomposed without melting.

Table 2. Characteristic IR bands of the complexes[a]

Complex	The BPz_3Y ligand ν(CH)	ν(BH)	The other ligand ν(C–O)	δ(Me)	δ(CH_2,Me)
1[b]	3085sh, 3110m	—	—	1380s	1470w
2	3090sh, 3130sh 3110w	—	1075s	1370m	1455m
3	3090sh, 3100m 3140w	2420m 2440w	1090s	1365m	1455m
4	3090sh, 3110sh 3130w	—	1075s	1385s	1462m
5	3080sh, 3100sh 3130sh	2440w 2480m	1070s	1380m	1462m

a) Measured in KBr disk, values in cm^{-1}. b) The other characteristic bands were observed at 660 cm^{-1} [ν(C–Cl), m] and 1580 cm^{-1} [ν(C=C), m].

Table 3. H-NMR data of the poly(1-pyrazolyl)borate complexes[a]

Complex	Temp °C	Pyrazolyl protons[b]			The other chelate				
		3-H	4-H	5-H	1-CH_2 (1-CH)[d]	2-Me[c]	OMe[c]	3-CH_2 (3-Me)[d]	NMe[c] (*t*-Bu)[e]
1	−30	6.82(d), 7.25(d)	6.41(t), 6.44(t)	7.74(d), 7.76(d)	6.10[d]	—	—	1.10[d]	2.34
		7.49(d), 7.59(d)	6.47(t), 6.53(t)	7.95(d), 8.00(d)				1.41[d]	2.83
2[f]	−36	6.35(d), 6.77(d)	6.20(t, 3)	7.53(d), 7.56(d)	2.0[g]	1.30,[h]	3.32[h]	2.78[i]	0.96[e,h]
		6.85(d), 7.33(d)	6.30(t)	7.68(d), 7.84(b)		1.57,[j]	3.19[j]	2.90[i]	1.02[e,j]
3[f]	−36	7.6(b, 3)	6.24(b, 3)	7.7(b, 3)	2.1[g]	1.36,[h]	3.32[h]	2.63[i]	1.06[e,h]
						1.58,[j]	3.24[j]	2.80[i]	1.14[e,j]
4[k]	−31	6.6[l], 6.7[l], 7.0(b)	6.19(t), 6.34(b)	7.45(b), 7.56(b)	1.72[i]	1.10	3.24	2.5[g]	2.40
		7.12(d), 7.27(b)	6.24(t, 2)	7.68(b, 2)	1.86[i]				2.95
5	−36	7.33(d), 7.40(b)	6.19(t)	7.56(d), 7.59(b)	1.90[c]	1.13	3.17	2.5[g]	2.4
		7.50(b)	6.24(t, 2)	7.73(b)					2.76

a) δ value (ppm) from TMS. In $CDCl_3$, unless stated otherwise. Abbreviations used: b=broad, d=doublet, t=triplet. b) An intensity for two or three protons is given in parentheses. See notes h), j), and l) about the isomers. c) Appearing as a singlet. d) For **1**. Appearing as a singlet. e) For **2** and **3**. f) In CD_3CN. g) Overlapping with solvent signal or the other signal. h) For the main isomer. i) Appearing as an AB type quartet. $^2J_{AB}$=10—12 Hz. j) For the minor isomer. See the text. k) In CD_2Cl_2.l) With an intensity of about 1/2.

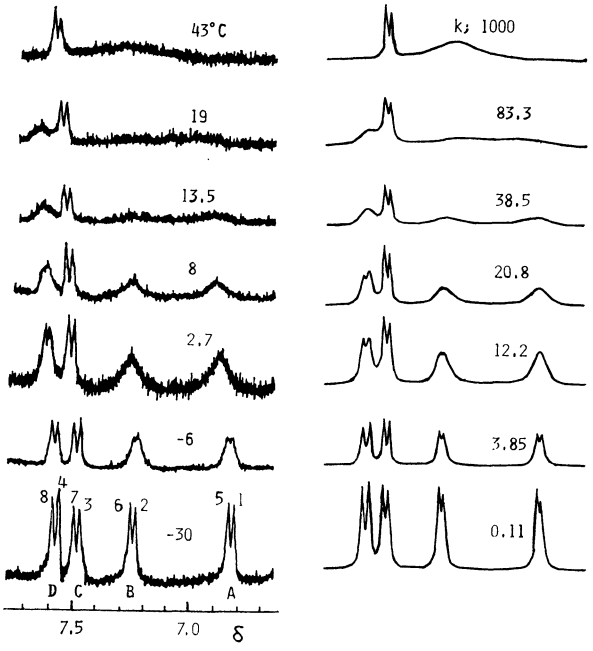


Fig. 2. ^{1}H-NMR spectra of 3-H's of the 1-pyrazolyl groups in **1** in $CDCl_3$. Left; Observed spectra. Right; Calculated spectra. See the text.

arrangement **E** shown in Fig. 1.

Two higher-field 3-H doublets (A and B at −30 °C, in Fig. 2)[18] broadened at −6 °C, apparently disappearing at 19 °C. Above −6 °C, the third 3-H doublet at the lowest field (D in Fig. 2) broadened more gradually as compared with the former two. These three 3-H signals coalesced into a very broad hump at 43 °C, its height increasing slowly with rise in temperature. The fourth 3-H doublet (C in Fig. 2) remained actually unchanged below 43 °C, beginning to broaden only near 58 °C.

Two sharp 3-methyl singlets observed at −30 °C broadened near −6 °C, coalesced at 10 °C, turning into a sharp singlet at δ 1.29 at 43 °C. The 4-H's and 5-H's of the BPz_4 ligand and *N*-methyl signals of the cdamb moiety changed, corresponding to the 3-H's and the 3-methyl protons upon warming from −30 °C. Complex **1** in CD_3CN gave no limiting fast-exchange spectrum even at 79 °C.

There is a clear difference between the collapsing rates of the signals corresponding to the three pyrazolyl groups upon warming from −30 °C; the signals of the two pyrazolyl groups collapse more readily than that of the third pyrazolyl one. The former two pyrazolyl groups are reasonably associated with two uncoordinated ones at low temperature. Upon warming, an inversion of a Pd–$(N\text{–}N)_2$–B boat-type six-membered ring is expected to take place readily with no rupture of palladium-pyrazolyl nitrogen bond, accompanied by a simultaneous fluttering of two coordinated pyrazolyl groups. A similar inversion has been reported as for $[Mo(\eta^5\text{-}C_5H_5)(BPz_3Y)(CO)_2]$[4,5] and $[Mo(\eta^5\text{-}C_5H_5)(BPz_2Et_2)(CO)_2]$.[5]

The third pyrazolyl group was assigned to the one coorrdinated at a *trans* position to a carbon-palladium σ-bond of the cdamb moiety, since comparatively strong *trans* influence of the 1-alkenyl group possibly gave rise to a moderately weak binding of the palladium-pyrazolyl nitrogen bond *trans* to the 1-alkenyl-palladium σ-bond. Above −6 °C, the third pyrazolyl group participated gradually in the fluxional motion, *viz.*, in a rotation of the three pyrazolyl groups around a palladium-nitrogen bond located at a *trans* position to a dimethylamino group, accompanied by a more rapid inversion of the Pd–$(N\text{–}N)_2$–B ring. Above 58 °C, the fourth pyrazolyl group began to participate in the fluxional motion of all pyrazolyl groups, *i.e.* in a "tumbling process."

As regards line shape analysis, agreement between the observed spectra and the theoretical ones was excellent, when the parameter f was 6/7, *viz.*, the inversion rate was six times greater than the exchange rate between the two pyrazolyl groups and the third one. Figure 3 shows the relationship between (log k) and $10^3/T$, obtained from the line shape analysis of **1**. From the results and Arrhenius' and Eyring's equations,

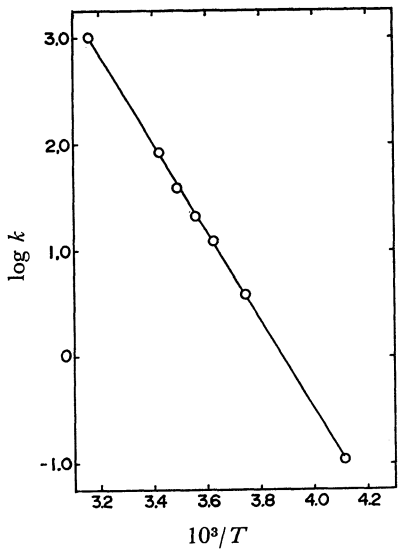


Fig. 3. The relationship between (log k) and $10^3/T$, obtained for **1**.

we find that $E_a=17.8\pm1.7$ kcal/mol, $\Delta G^{\ddagger}_{298}=14.5$ kcal/mol, $\Delta H^{\ddagger}_{298}=17.2$ kcal/mol, and $\Delta S^{\ddagger}=9.1$ cal/deg·mol for the fluxional motion of the three pyrazolyl groups. The value $\Delta G^{\ddagger}_{298}$ is considerably greater than $\Delta G^{\ddagger}_{198}$ for an internal rotation of the uncoordinated pyrazolyl ring and that for the exchange among the three coordinated pyrazolyl rings in [PtMe(BPz_4)(CO)],[3] being comparable with $\Delta G^{\ddagger}_{298}$ for the exchange among the three coordinated pyrazolyl rings in [PtMe(BPz_3H)(CO)].[3] The positive value of the $\Delta S^{\ddagger}$ for **1** is in contrast with the negative values of the $\Delta S^{\ddagger}$'s for [PtMe(BPz_3Y)(CO)],[3] suggesting that the palladium-pyrazolyl nitrogen bonds are elongated, becoming loose in the transition states for the fluxional motion of **1**.

It is noteworthy that the fluxional motion of the BPz_4 ligand in **1** actually consists of three kinds of motion, *i.e.* inversion of the Pd–(N–N)$_2$–B ring, rotation of the three pyrazolyl rings accompanying a more rapid inversion, and the tumbling process, shifting from the former to the latter continuously upon warming from −30 °C. A similar behavior was observed also for **2** and **4**.

^{1}H-NMR Spectra of [Pd(btmmp)(BPz_3Y)] 2 and 3. As regards the BPz_3H ligand of **3** in CD_3CN, each of 3-H's and 5-H's gave a doublet at 28 °C, which turned into a broad signal at −36.5 °C. This indicates that the BPz_3H ligand is stereochemically non-rigid above −36.5 °C, the exchange rate decreasing moderately on cooling. The ^{1}H-NMR spectrum of the btmmp moiety at 28 °C contained three sharp singlets at δ 1.12 (9H, *t*-Bu), 1.40 (3H, 2-Me), and 3.32 (3H, OMe). Each of these singlets broadened near 8 °C and separated into a fairly sharp singlet and a small broad one with an intensity ratio *ca.* 8: 1 at −0.5 °C, Thus, the signals of the btmmp moiety separated into the two sets at this temperature, but not each of the pyrazolyl protons even at −36.5 °C. This indicates that an exchange of the two configurations of the *t*-butyl group takes place above −0.5 °C, independent of the stereochemically nonrigid motion of the BPz_3H ligand. Four conformational isomers were expected to be present owing to asymmetric 2-carbon and boron atoms, when the motion of the BPz_3H ligand was quenched at low temperature (Fig. 4), but could not be detected at −36.5 °C.

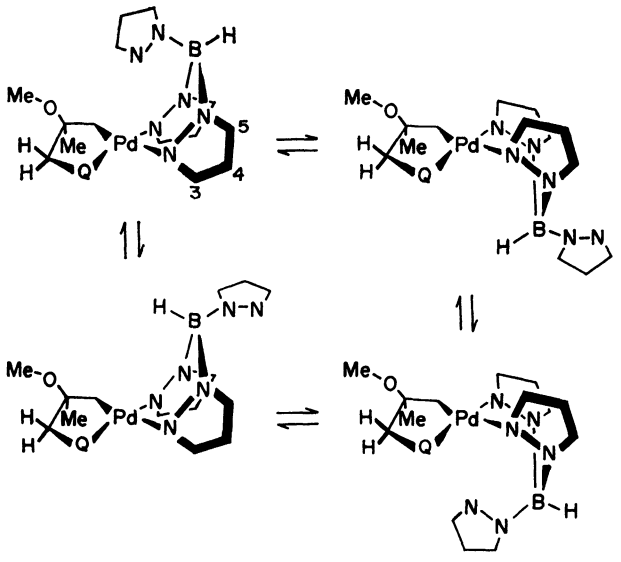


Fig. 4. Conformations of **3** and **5**.

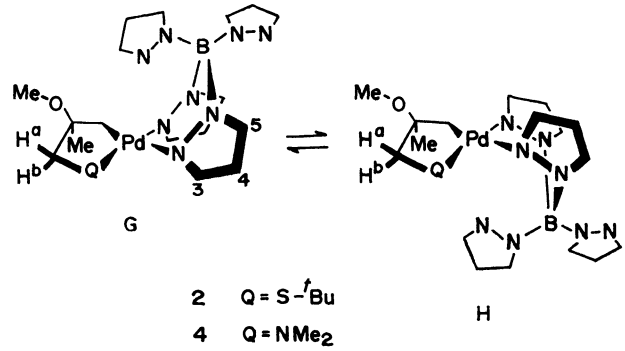


Fig. 5. Conformations of **2** and **4**.

At 85 °C, the ^{1}H-NMR spectrum of the btmmp moiety of **2** in CD_3CN showed three sharp singlets at δ 1.10 (9H, *t*-Bu), 1.44 (3H, 2-Me), and 3.38 (3H, OMe). Each of these singlets separated into a fairly sharp singlet and a small broad one with an intensity ratio *ca.* 6: 1 at −0.5 °C. In consideration of the very similar ^{1}H-NMR spectra of **2** to those of **3**, the two sets of the btmmp-signals are also associated with two configurations of the *t*-butyl group, which undergo exchange with each other rapidly at high temperature. Although two conformational isomers (**2G** and **2H** in Fig. 5) occur owing to an asymmetric 2-carbon atom when the stereochemically nonrigid motion of the BPz_4 ligand is quenched at low temperature, it seems unlikely that these isomers cause the two sets of the btmmp-signals.

The BPz_4 ligand of **2** exhibited a limiting slow exchange ^{1}H-NMR spectrum at −36 °C. It appears that the two configurational isomers due to the *t*-butyl group and the conformational isomers due to the quenching of the motion of the BPz_4 ligand show virtually identical signals as for the 3-H protons of the BPz_4 ligand. Three high-field 3-H doublets broadened at −21 °C and coalesced near −0.5 °C, whereas the fourth 3-H doublet remained unchanged below this temperature and began to collapse near 20 °C. These four 3-H signals united to a broad one near 47 °C and exhibited a slightly broad signal at 85 °C, while four pyrazolyl 5-H's resonated at δ 7.76 as a well-resolved doublet, indicating a fairly fast tumbling motion of the BPz_4 ligand on the NMR time scale. From the results it seems that the pyrazolyl groups in **2** move also in a similar mode to the case of **1** in the range −36—85 °C.

*^{1}H-NMR Spectra of [Pd(dammp)(BPz_3Y)] **4** and **5**.* At 85 °C, the ^{1}H-NMR spectrum of **4** in CD_3CN contained four sharp methyl singlets in the dammp moiety and three slightly broad pyrazolyl proton resonances at δ 6.4 (4H, 4-H's), 7.2 (4H, 3-H's), and 7.8 (4H, 5-H's). This spectrum did not correspond to a fast exchange limit, whereas the tumbling motion of the BPz_4 ligand was fairly fast on the NMR time scale.

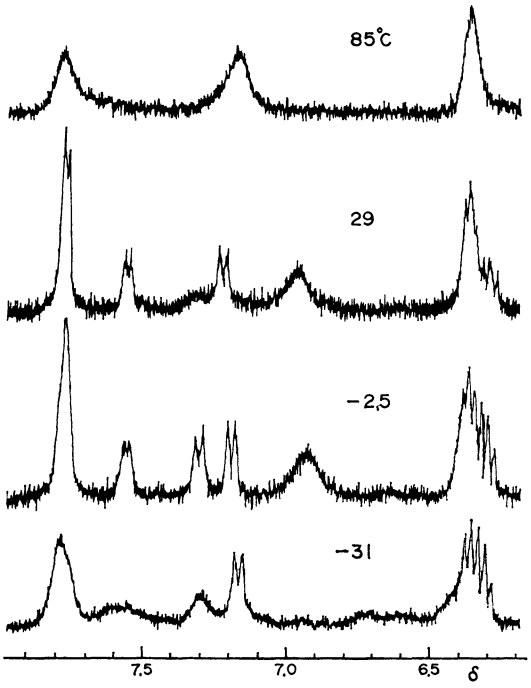


Fig. 6. ^{1}H-NMR spectra of the BPz_4 region of **4** in CD_3CN.

At 29 °C, the pyrazolyl 3-H resonance separated into a doublet at δ 7.18 (1H) and two broad signals at δ 6.9 (2H) and 7.3 (1H). The last broad signal turned into a doublet at −2.5 °C and broadened again at −31 °C. The larger broad signal at δ 6.9 separated into very broad humps near δ 6.6, 6.7, and 7.1 (overlapping with the doublet at δ 7.18) (Fig. 6). These broad humps were observed more obviously in CD_2Cl_2 (Table 3), and are tentatively ascribed to 3-H's of two conformational isomers (**4G** and **4H** in Fig. 5), which were distinguishable owing to the slowdown of the inversion of the Pd–$(N–N)_2$–B ring at low temperature. The broadening of the doublet at δ 7.3 at −31 °C might be due to the exchange between these two conformers. Each of the four methyl singlets also broadened considerably at this temperature, but did not separate into two signals expected for the two conformers. Complex **4** exhibited the three stages of the stereochemically non-rigid motion of the BPz_4 ligand, similar to **1**, no slow exchange limiting spectrum for **4** being obtained.

Concerning the BPz_3H group of **5** in $CDCl_3$ at 60.5 °C, each of 3-H's and 5-H's gave a doublet at δ 7.56 and 7.67, respectively, corresponding to a fast exchange limiting spectrum. The 3-H signal broadened at 25 °C, and separated into three broad ones of an equal intensity at −2.5 °C. The highest-field 3-H signal changed into a doublet at δ 7.33 at −36 °C, indicating that one of the three pyrazolyl groups is fixed and the others undergo exchange with each other at a slow rate. Above 25 °C, each of four methyl protons of the dammp moiety resonated as a sharp singlet, which broadened considerably with no separation at −36 °C, corresponding to the 3-H signals.

The BPz_3H ligand in **3** and **5** was more stereochemically non-rigid as compared with the BPz_4 ligand in **2** or **4**, analogous to the case of (acetophenone oximato-2-*C,N*){poly(1-pyrazolyl)borato}palladium(II) complexes.[7]

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References

1) S. Trofimenko, *J. Am. Chem. Soc.*, **91**, 3183 (1969).
2) P. Meakin, S. Trofimenko, and J. P. Jessom, *J. Am. Chem. Soc.*, **94**, 5677 (1972).
3) L. E. Manzer and P. Z. Meakin, *Inorg. Chem.*, **15**, 3117 (1976).
4) J. L. Calderon, F. A. Cotton, and A. Shaver, *J. Organomet. Chem.*, **37**, 127 (1972).
5) J. L. Calderon, F. A. Cotton, and A. Shaver, *J. Organomet. Chem.*, **38**, 105 (1972).
6) M. Onishi, Y. Ohama, K. Sugimura, and K. Hiraki, *Chem. Lett.*, **1976**, 955.
7) M. Onishi, K. Sugimura, and K. Hiraki, *Bull. Chem. Soc. Jpn.*, **51**, 3209 (1978).
8) S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 3170 (1967).
9) T. Yukawa, *Inorg. Chem.*, **7**, 1458 (1968).
10) Y. Takahashi, A. Tokuda, S. Sakai, and Y. Ishii, *J. Organomet. Chem.*, **35**, 415 (1972).
11) A. C. Cope, J. M. Kliegman, and E. C. Friedrich, *J. Am. Chem. Soc.*, **89**, 289 (1967).
12) J. L. Kaplan, *J. Chem. Phys.*, **28**, 278 (1958); **29**, 462 (1958).
13) C. S. Johnson, Jr., "Advances in Magnetic Resonance," Academic Press, New York (1965), Vol. 1, p. 33.
14) a) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953); b) H. M. McConnell, *ibid*, **28**, 430 (1958). c) H. Nakanishi, *Kagaku No Ryoiki*, **31**, 226 (1977).
15) F. Suzuki, M. Oki, and H. Nakanishi, *Bull. Chem. Soc.*

Jpn., **47**, 3114 (1974).
16) P. E. Rush and J. D. Oliver, *J. Chem. Soc., Chem. Commun.*, **1974**, 996.
17) B. W. Davies and N. C. Payne, *Inorg. Chem.*, **13**, 1848 (1974).
18) Coupling constants $^3J_{34}$ and $^3J_{45}$ of the BPz_3Y ligands are actually 1.6—2.5 Hz as for **1**—**5**.