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Preparations and Fluxional Behavior of some Tetrakis(1-pyrazolyl)boratopalladium(II) Complexes

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Dinuclear complexes $[Pd_2Cl_4L_2]$ *(L = neutral ligand) reacted with* $Na(BPz_4)$ *(Pz = 1-pyrazolyl) to yield* $[PdCl(BPz_4)L]$ *[(I) for L =* PEt_3 *and (II) for L =* $P(OEt)_3$*] and* $[(BPz_4)Pd(BPz_4)PdCl_2]\cdot\frac{1}{2}CH_2Cl_2$ *(III) for diethyl sulfide. In the* ^1H*-NMR spectra of I and II, fluxional behavior of the* BPz_4 *ligand was observed at high temperature leading to spectroscopic equivalence of all four pyrazolyl groups, and was studied in connection with* trans-*effects of other coexisting ligands. A reaction of* $[PdCl_2(en)]$ *(en = ethylenediamine) with* $Na(BPz_4)$ *gave a cationic complex of* $[Pd(BPz_4)(en)]ClO_4$ *(V), of which the* ^1H*-NMR spectra showed inversion of the Pd-(pyrazolyl)*$_2$*-B six-membered ring, dividing four pyrazolyl groups spectroscopically into two classes of coordinated and uncoordinated groups in a ratio of 2:2.*

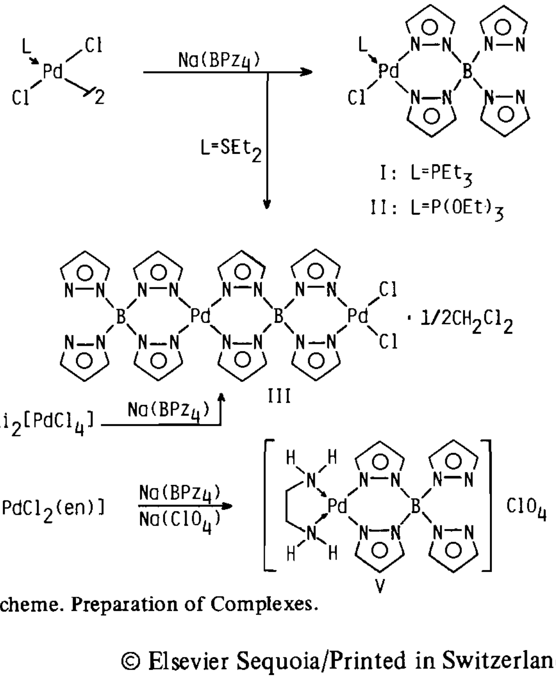
Introduction

Some kinds of fluxional behaviour of poly(1-pyrazolyl)borate ligands $[H_nBPz_{(4-n)}]^-$ (Pz = 1-pyrazolyl) were observed in many transition-metal complexes [1–5]. Some BPz_4 palladium(II) complexes exhibited a fast exchange of all four pyrazolyl groups, 'tumbling motion', in the ^1H-NMR spectra at high temperature [3–5]. In a stereochemically rigid state, the palladium(II) complexes were assumed to have square-planar structures about the central metal and a boat-form conformation of the Pd–$(N–N)_2$–B six-membered ring [4, 5]. The basic mechanism of the motion was proposed to involve coordination of an originally uncoordinated pyrazolyl group near palladium, accompanied instantaneously by dissociation of one of two previously coordinated groups and by inversion of the Pd–$(N–N)_2$–B ring [3,6].

In this paper, we deal with a few new BPz_4 palladium(II) complexes and their temperature-dependent ^1H-NMR spectra in connection with *trans*-effects of other ligands which occupy the coordination-site *trans* to the BPz_4 group.

Results and Discussion

Chloro-bridged dinuclear palladium(II) complexes $[Pd_2Cl_4L_2]$ {L = PEt_3, and $P(OEt)_3$} react with $Na(BPz_4)$ to yield stable mononuclear $[PdCl(BPz_4)L]$ complexes, whereas similar reactions of the dinuclear complexes and $Na(HBPz_3)$ do not yield the corresponding $[PdCl(HBPz_3)L]$ complexes. ^1H-NMR spectra of the mononuclear BPz_4 complexes were measured at various temperatures and the fluxional behavior of the BPz_4 ligand was observed at high temperature.



Scheme. Preparation of Complexes.

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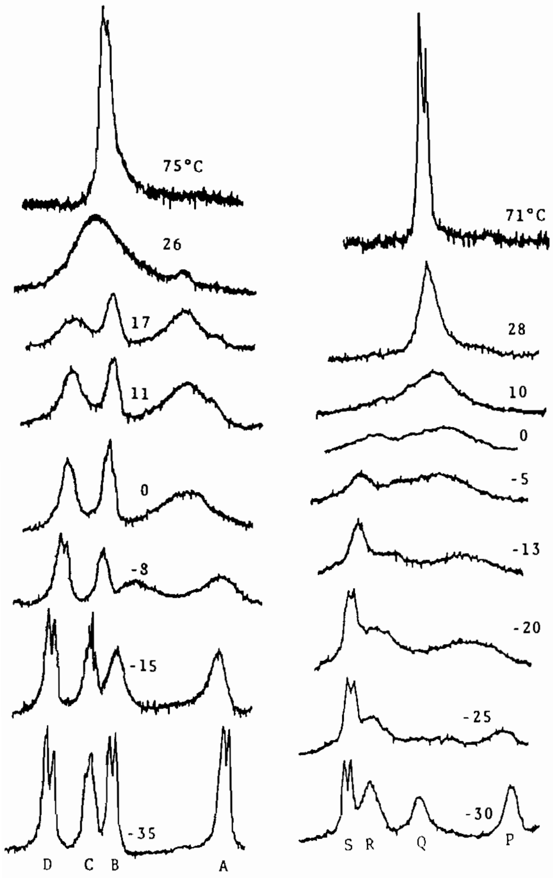

a) $[PdCl(BPz_4)(PEt_3)]$
b) $[PdCl(BPz_4)\{P(OEt)_3\}]$

Fig. 1. Temperature-dependent 3-H resonances of the BPz_4 groups in *I* and *II* (CD_3CN). The average chemical shifts of four 3-H resonances are slightly temperature-dependent, but the frequency scale of each spectrum is appropriately offset so that the average shifts are almost at the same position.

In the ^{1}H-NMR spectrum of $[PdCl(BPz_4)(PEt_3)]$ (I) at −35 °C, four 3-H protons in the four pyrazolyl groups gave four signals, A, B, C and D arranged from high to low fields, as shown in Fig. 1. At this temperature, coordination of the ligand to palladium was stereochemically rigid to give the four spectroscopically non-equivalent 3-H protons. As described previously [4, 5], the four signals of 3-H protons were distributed in wider fields in comparison with two sets of 4-H and 5-H protons.

Upon warming to *ca.* 0 °C, two doublets of A and B coalesced into one broad hump, indicating spectroscopic equivalence of two originally uncoordinated pyrazolyl groups (A and B) on boron, owing to the rapid inversion of the $Pd{-}(N{-}N)_2{-}B$ boat-form six-membered ring. Moreover, the signal D broadened at *ca.* 17 °C. This broadening was associated with cleavage of a comparatively weak palladium–pyrazolyl bond *trans* to PEt_3 with strong *trans*-effect. At temperatures such as 75 °C, the fourth pyrazolyl group began to participate in the fluxional motion and four 3-H protons became spectroscopically equivalent (*i.e.* tumbling motion). The palladium–pyrazolyl bond *trans* to the chlorine atom was comparatively strong owing to weak *trans*-effect of the atom. The signal C was assigned to the 3-H proton in the pyrazolyl group *trans* to the atom.

As a whole, temperature-dependent fluxional behavior of *I* consisted of three steps. The first step at low temperature was the inversion of the $Pd{-}(N{-}N)_2{-}B$ ring. The second step was coordination of one of two originally uncoordinated pyrazolyl groups and dissociation of the coordinated pyrazolyl group *trans* to PEt_3. At the third step, the pyrazolyl group *trans* to the chlorine atom dissociated from palladium and joined exchange motion of other three pyrazolyl groups to give spectroscopic equivalence of all pyrazolyl groups.

Figure 1 shows also similar fluxional behavior of the BPz_4 ligand in $[PdCl(BPz_4)\{P(OEt)_3\}]$ (*II*), but the behavior of *II* indicates continuous gradual transitions of three steps. It is notable that the coordinated pyrazolyl group (R* in Fig. 1) *trans* to $P(OEt)_3$ began to exchange with two uncoordinated pyrazolyl groups (P and Q) at the second step near −20 °C, and that the temperature was considerably lower than that of *I*. One of two uncoordinated pyrazolyl groups approached palladium through a vacant axial coordination-site to form a five-coordinated (quasi trigonal bipyramid) transition-state, and the coordinated pyrazolyl group dissociated simultaneously from the position *trans* to the phosphorus ligand. In a d^8 trigonal-bipyramidal system, all $d(\pi)$ orbitals of metal are filled, and π-*trans* effect theory [7] suggests that the trigonal-bipyramidal transition-state is fairly stabilized through π-interaction if the *trans* group possesses empty π-orbitals to accommodate the excess electronic charge added to the central metal by the entering group. Compared with the tertiary phosphine PEt_3, the phosphite $P(OEt)_3$ was a potentially better π-acceptor [8, 9] due to the electronegative OEt substituent, leading to lower overall activation energy for intramolecular bond-breaking substitution of the pyrazolyl groups.

A chloro-bridged complex $[Pd_2Cl_4(SEt_2)_2]$ was treated with $Na(BPz_4)$ in order to prepare a mononuclear one of $[PdCl(BPz_4)(SEt_2)]$. However, the mononuclear complex was not formed owing to weak coordination of diethyl sulfide to palladium, and the reaction mixture gave a pale-yellow powder (*III*). A reaction of *III* with PPh_2Me afforded both

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*The 3-H proton (R) in the coordinated Pz group *trans* to phosphorus ligand resonated at higher field than that (S) *trans* to Cl, in contrast to the case of *I*.

TABLE I. Analyses and Properties of the BPz_4 Palladium(II) Complexes.

Complex		Yield (%)	Analyses (%)[a]			M.p.[b] (°C)	Λ_M[c]
			C	H	N		
$[PdCl(BPz_4)(PEt_3)]$	*I*	62	40.39 (40.10)	5.02 (5.05)	20.84 (20.79)	194–197	0.60
$[PdCl(BPz_4)\{P(OEt)_3\}]$	*II*	35	36.87 (36.82)	4.65 (4.64)	19.32 (19.09)	118–127	0.72
$[(BPz_4)Pd(BPz_4)PdCl_2]\cdot\frac{1}{2}CH_2Cl_2$[d]	*III*	56	33.15 (33.27)	2.87 (2.85)	25.52 (25.34)	~273	4.51 2.03[e]
$[(BPz_4)Pd(BPz_4)PdBr_2]\cdot\frac{1}{2}CH_2Cl_2$[d]	*IV*	42	30.11 (30.24)	2.36 (2.59)	22.95 (23.03)	~235	
$[Pd(BPz_4)(en)]ClO_4$	*V*	10	30.88 (30.85)	3.63 (3.70)	25.87 (25.70)	269–273	117

[a] Calculated values in parentheses. [b] With decomposition. [c] Molar conductivity, Ω^{-1} cm^2 mol^{-1}. Determined for 1.0×10^{-3} *M* solution at 25 °C. In acetone, unless noted elsewhere. [d] Hemisolvation of CH_2Cl_2 was confirmed in the ^{1}H-NMR spectrum. [e] In dichloromethane.

TABLE II. Selected Spectroscopic Data of the BPz_4 Palladium(II) Complexes.

Complex	ν(Pd–Cl)[a]	δ Values of 3-H Protons in the BPz_4 Group[b]
I	330	7.06(d, 2.3, 1H), 6.91(bs, 1H), 6.80(d, 2.3, 1H), 6.34(d, 2.3, 1H)[c]
II	334	7.10(d, 2.3, 1H), 7.02(bs, 1H), 6.80(bs, 1H), 6.46(bs, 1H)[d]
III	339 330	7.41(d, 2.3, 2H), 7.28(c, 2H), 7.03(d, 2.3, 4H)[e]
IV		7.39(d, 2.3, 2H), 7.28(c, 2H), 7.01(d, 2.3, 4H)[e]
V		7.25(d, 2.5, 2H), 7.01(d, 2.5, 2H)[f]

[a] In cm^{-1} in KBr disk. [b] δ Value (ppm) from TMS. Signal shape, coupling constant (Hz), and proton number are given in parentheses. Abbreviations used: bs = broad singlet, d = doublet, c = complex. [c] At −35 °C in CD_3CN. [d] At −30 °C in CD_3CN. [e] At 25 °C in $CDCl_3$. [f] At 25 °C in CD_3OD.

$[PdCl_2(PPh_2Me)_2]$ and $[Pd(BPz_4)_2]$. In addition, ν(Pd–Cl) bands in a far-IR spectrum of *III* were observed at 339 and 330 cm^{-1}, and assigned to a terminal *cis*-$PdCl_2$ moiety [10]. These data and elemental analyses suggested *III** to have a structure of $[(BPz_4)Pd(BPz_4)PdCl_2]\cdot\frac{1}{2}CH_2Cl_2$. Complex *III* and its bromo analogue (*IV*) were also prepared from reactions of $Li_2[PdX_4]$ (X = Cl, Br) and $Na(BPz_4)$ in a ratio of 1:1 in ethanol. Similar bis-bidentate coordination of the BPz_4 ligand was previously reported for $[(\text{substituted } \pi\text{-allyl})Pd(BPz_4)Pd(\text{substituted } \pi\text{-allyl})]^+$ complexes [11].

An ethylenediamine (en) complex $[Pd(BPz_4)(en)]ClO_4$ (*V*) was derived from $Na(BPz_4)$ and $[PdCl_2(en)]$. In the ^{1}H-NMR spectrum in CD_3OD at 25 °C, 4-H protons in the pyrazolyl groups resonated at δ 6.47 (4H) as a complex signal, whereas 3-H protons gave two doublets at δ 7.01 (2H) and 7.25 (2H), and 5-H protons gave two doublets at δ 7.71 (2H) and 7.80 (2H). No significant spectral change was observed in the range of 60 °C to −33 °C. In this range, inversion of the $Pd\text{–}(N\text{–}N)_2\text{–}B$ ring occurred quickly to divide four 3-H protons into two classes of those in coordinated and uncoordinated pyrazolyl groups, and the motion was not fixed, even at −33 °C. Lack of fluxional motion including cleavage of the palladium–pyrazolyl bonds was probably attributed both to weak *trans*-effect of ethylenediamine and to cationic charge on the central metal. Thus, fluxional behavior of all BPz_4 complexes described in this paper confirmed the important role of *trans*-effect of other ligands *trans* to the BPz_4 group.

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*Molecular weight-determination of *III* was not performed owing to its poor sublimation and low solubility.

Experimental

^{1}H-NMR spectra were run on a JEOL model MH-100 spectrometer (100 MHz) with tetramethylsilane as an internal standard. Temperatures of NMR samples were determined with methanol or 1,3-propanediol. IR spectra were obtained using a Hitachi 285 grating spectrometer and a Shimadzu IR-450 spectrometer. Melting points were observed on a Yanagimoto MP-S3 microstage apparatus in capillary tubes and are uncorrected.

Sodium tetrakis(1-pyrazolyl)borate $Na(BPz_4)$ [1], sodium hydrotris(1-pyrazolyl)borate $Na(HBPz_3)$ [1], and starting complexes, $[Pd_2Cl_4L_2]$ [L = PEt_3, $P(OEt)_3$, and SEt_2] [12] and $[PdCl_2(en)]$ [13] were prepared according to the reported methods.

Preparation of $[PdCl(BPz_4)(PEt_3)]$ I

An ethanol solution of $Na(BPz_4)$ (0.44 g, 1.46 mmol) was added to an ethanol suspension of $[Pd_2Cl_4(PEt_3)_2]$ (0.40 g, 0.68 mmol) and the mixture was stirred for 3 h at ambient temperature. After removal of the solvent, recrystallization of the residue from dichloromethane and hexane yielded yellow microcrystals of *I*, 0.45 g (0.84 mmol); Molecular weight Found: M^+ 538. Calcd for $C_{18}H_{27}B^{35}ClN_8P^{106}Pd$: M, 538.1.

Preparation of $[PdCl(BPz_4)\{P(OEt)_3\}]$ II

A THF suspension of $Na(BPz_4)$ (0.30 g, 0.99 mmol) was mixed with a THF solution of $[Pd_2Cl_4\{P(OEt)_3\}_2]$ (0.30 g, 0.44 mmol), and the mixture was stirred for 3 h at room temperature. THF was removed under vacuum and the resulting solid was recrystallized from benzene and hexane to give pale-yellow powder of *II*, 0.18 g (0.31 mmol); Molecular weight, Found: M^+ 586. Calcd for $C_{18}H_{27}B^{35}ClN_8O_3P^{106}Pd$: M, 586.1.

Reaction of $Na(BPz_4)$ with $[Pd_2Cl_4(SEt_2)_2]$

A mixture of $Na(BPz_4)$ (0.15 g, 0.50 mmol) and $[Pd_2Cl_4(SEt_2)_2]$ (0.13 g, 0.25 mmol) in THF was stirred overnight at room temperature. The solvent was removed *in vacuo* and the residue was recrystallized from dichloromethane and ethyl ether to afford pale-yellow powder of $[(BPz_4)Pd(BPz_4)PdCl_2]\cdot\frac{1}{2}CH_2Cl_2$ *III*, 0.12 g (0.14 mmol).

Preparations of III *and its bromo analogue* IV *using $Li_2[PdX_4]$ (X = Cl, Br)*

All equimolar quantity of $Na(BPz_4)$ was added to $Li_2[PdCl_4]$ in ethanol and the mixture was stirred overnight at room temperature. After removal of the solvent under vacuum without heating, recrystallization of the resulting solid from dichloromethane and ethyl ether gave *III*. A bromo analogue *IV* was prepared similarly, using $Li_2[PdBr_4]$.

Preparation of $[Pd(BPz_4)(en)]ClO_4$, V

Sodium tetrakis(1-pyrazolyl)borate $Na(BPz_4)$ (0.065 g, 2.2 mmol) was added in portions to $[PdCl_2(en)]$ (0.50 g, 2.1 mmol) in water/methanol (3/1), and the mixture was stirred for 4 h at room temperature. After filtration, an aqueous solution of $Na(ClO_4)$ (0.38 g, 3.1 mmol) was added to the filtrate with stirring. Upon concentration *in vacuo*, white microcrystals formed were collected and characterized as a complex *V*, 0.12 g (0.22 mmol).

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