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Pyrazolyl carbon and proton NMR assignments for transition-metal poly(1-pyrazolyl)borates. Syntheses and NMR spectral studies of the (η^2-BR_2Pz_2) (Pz = 1-pyrazolyl) palladium and platinum complexes☆

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Abstract

The palladium(II) and platinum(II) complexes of $[MCl(\eta^2\text{-}BBu_2Pz_2)(PEt_3)]$ (Pz = 1-pyrazolyl) were prepared by treatment of $[MCl_2(PEt_3)]_2$ with $Na[BBu_2Pz_2]$ in CH_2Cl_2. Their ^{13}C and ^1H NMR spectroscopic properties were studied, and the pyrazolyl carbon and proton resonances were assigned. The resonating of pyrazolyl 3-C CH carbons at lower fields than 5-C was proposed as the criterion for ^{13}C NMR assignments of these pyrazolyl CH carbons in transition-metal poly(1-pyrazolyl)borate complexes. In addition, ^1H NMR assignment revisions of pyrazolyl 3-H and 5-H protons are also described for some (η^2-BPz_4) palladium(II) complexes reported previously.

Keywords: Platinum complexes; Palladium complexes; Pyrazolylborate

1. Introduction

The poly(1-pyrazolyl)borate ions $[BR_nPz_{4-n}]^-$ (Pz = 1-pyrazolyl group; R = H and non-coordinating substituents) have been widely used as chelating reagents with transition metals in coordination chemistry, and their complexes continue to attract much attention from various chemical points of view [1]. As a contribution to poly(1-pyrazolyl)borate chemistry, the present authors have studied the stereochemically non-rigid, i.e. fluxional motions [2] of their transition-metal complexes. For example, some mononuclear (η^2-BPz_4) palladium(II) complexes, such as $[PdCl(\eta^2\text{-}BPz_4)(PR_3)]$ and $[Pd(C\text{-}Y)(\eta^2\text{-}BPz_4)]$ (C-Y = cyclometallating chelates), which showed four stereochemically different pyrazolyl groups in NMR spectra at low temperatures, exhibited spectroscopic equivalence of all four pyrazolyl groups at high temperatures, due to fast mutual exchange of the groups [3].

In spite of numerous synthetic descriptions on transition-metal poly(1-pyrazolyl)borate complexes [1], to our knowledge, uncertainties still exist concerning the ^1H and ^{13}C NMR signal assignments corresponding to the positions 3 and 5 in the pyrazolyl rings [4,5]. Claramunt and co-workers [4a] gave a short summary account of the NMR assignment procedures in pyrazoles and alkali-metal poly(1-pyrazolyl)borate salts. However, for transition-metal poly(1-pyrazolyl)borate complexes, some additional studies are necessary. Two clear definite assignment procedures have been reported to date. The first procedure is based on their NMR couplings with non-zero-spin central-metal nuclei, such as ^{195}Pt [6]. The second one is based on stereochemical conformational analyses of the complexes by means of the ^1H NMR nuclear Overhauser effect (NOE), and a typical example is the case for pyrazolyl 5-H protons in $[RuCl_2(\eta^3\text{-}BPz_4)(NO)]$ [5]. However, for four-coordinated mononuclear palladium(II) complexes with η^2-BPz_4 ligands, attempts to observe similar ^1H NOE signals were not successful. As an alternative approach to the η^2-BPz_4 system, the present paper deals with the syntheses and comparative NMR spectral studies

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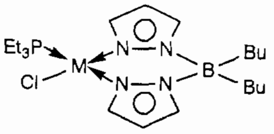
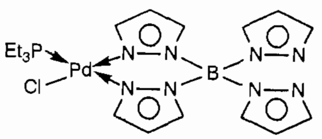
of palladium(II) and platinum(II) complexes, formulated as $[MCl(\eta^2\text{-}BBu_2Pz_2)(PEt_3)]$ (M = Pd (**1**), Pt (**2**)). In addition, ^1H NMR assignment revisions of pyrazolyl 3-H and 5-H protons are also described for some (η^2-BPz_4) palladium(II) complexes, reported previously from our laboratories [3].



1, M = Pd; 2, M = Pt.



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2. Experimental

2.1. General

Literature methods were used to prepare $[MCl_2(PEt_3)]_2$ [7], $Na[BBu_2Pz_2]$ [1d], $K[BH_2Pz_2]$ [1c], $Tl[B(3\text{-}t\text{-}BuPz)_4]$ (3-t-BuPz = 3-t-butylpyrazo-1-yl group) [5] and $[PdCl(\eta^2\text{-}BPz_4)(PEt_3)]$ (**3**) [3a]. An NMR spectrometer, JEOL model JNM GX-400, was used for observations of ^1H and ^{13}C NMR spectra, ^1H–^1H and ^1H–^{13}C correlation spectroscopy (COSY) and ^1H NOE. Reported R_f values were determined by standard thin-layer chromatographic (TLC) procedures, on 0.2 mm Merck silica gel 60 F-254 plates. Other general procedures were as described previously [5].

2.2. Preparations of $[MCl(\eta^2\text{-}BBu_2Pz_2)(PEt_3)]$

To 140 mg of crude $Na[BBu_2Pz_2]$ in 15 ml CH_2Cl_2 were added 106 mg of $[PdCl_2(PEt_3)]_2$ (0.18 mmol) in portions. After stirring for 3 h at room temperature, the solvent was removed in vacuo. Then, the residue was chromatographed on silica gel by elution with benzene to give a pale yellow wax-like material of $[PdCl(\eta^2\text{-}BBu_2Pz_2)(PEt_3)]$ (**1**) (21 mg, 0.04 mmol) in an 11% yield. M.p. 82 °C. R_f 0.47 (C_6H_6). *Anal.* Found: C, 46.51; H, 7.86; N, 10.54. Calc. for $C_{20}H_{39}N_4BClPPd$: C, 46.27; H, 7.57; N, 10.79%. The platinum(II) complex **2** was obtained as a similar colorless material in a 16% yield, by the analogous reaction of $[PtCl_2(PEt_3)]_2$ and succeeding chromatographic separations. M.p. 68 °C. R_f 0.63 (C_6H_6). *Anal.* Found: C, 39.80; H, 6.78; N, 8.95. Calc. for $C_{20}H_{39}N_4BClPPt$: C, 39.52; H, 6.47; N, 9.22%.

3. Results and discussion

Bidentate bis(1-pyrazolyl)borato complexes of palladium(II) and platinum(II), **1** and **2**, respectively, were prepared by treatment of chloro-bridged dinuclear complexes $[MCl_2(PEt_3)]_2$ [7] in dichloromethane with $Na[BBu_2Pz_2]$ [1d], followed by chromatographic separation on silica gel. In the case with $K[BH_2Pz_2]$ [1c], a similar treatment of $[PdCl_2(PEt_3)]_2$ gave only metallic palladium. FAB mass spectra of **1** and **2** showed the parent-ion signals centered at *m/z* 518 and 607, respectively, and confirmed their formulation as $[MCl(\eta^2\text{-}BBu_2Pz_2)(PEt_3)]$. In their ^1H and ^{13}C NMR spectra in CD_3CN, the two pyrazolyl groups were spectroscopically different, and with the help of ^1H–^1H and ^1H–^{13}C COSY observations, pyrazolyl NMR signals for each of the complexes were classified into two sets, as shown in Table 1. Fluxional motions via bond rupture between pyrazolyl 2-nitrogens and the metal, which lead to spectroscopic equivalence of the two coordinated pyrazolyl groups, did not occur for **1** and **2** even at 70 °C. As for the two n-butyl substituents on boron, they were equivalent spectroscopically, and indicated rapid inversion of the probably-boat-like six-membered $Pd\text{–}(N\text{-}N)_2\text{–}B$ ring in the complexes at room temperature. Cooling to −35 °C brought about appreciable changes in the ^1H NMR signal patterns of the two n-butyl substituents, through exerting some restriction on the ring inversion.

Fig. 1 shows the ^{13}C NMR spectra ranging from δ 133 to 144; the signals in this region were attributed to 3-C and 5-C CH carbons in the pyrazolyl groups. The platinum complex **2** showed ^{195}Pt satellites for some ^{13}C NMR signals, and in the respective signal sets (X_α and X_β in Table 1) for the two coordinated pyrazolyl groups, coupling constants of 3-C with ^{195}Pt nuclei were expected to be larger than those of 5-C. Accordingly, signals in the region at δ 139–144 of Fig. 1 were assigned to 3-C, and those at δ 133–136 to 5-C. Each of the coupling constants *J*(Pt–C) in the set X_β of **2** was smaller than the corresponding one in the set X_α, and the signal set X_β was associated with the pyrazolyl group, which locates at the position *trans* to PEt_3 with larger *trans*-influence [8].

^1H and ^{13}C NMR signal assignments have been performed in the tridentate BPz_4 complex of $[RuCl_2(\eta^3$-

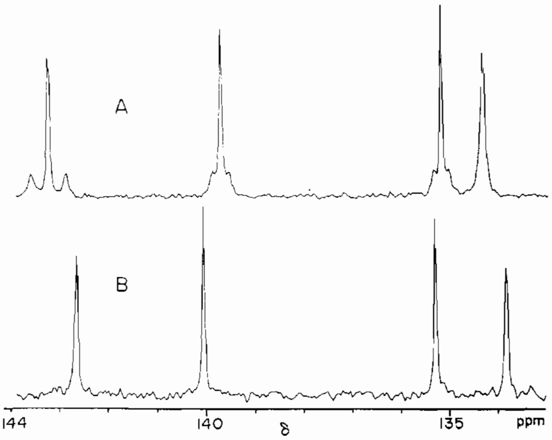

Fig. 1. Pyrazolyl 3-C and 5-C NMR signals of $[MCl(\eta^2\text{-}BBu_2Pz_2)(PEt_3)]$. In CD_3CN at 30 °C; A, Pt; B, Pd.

Table 1
NMR data of the pyrazolyl groups in transition-metal poly(1-pyrazolyl)borate complexes

	Group[e]	δ Values on ^{13}C NMR[g]			δ Values on ^{1}H NMR[j]		
	Pz	3-C	4-C	5-C	3-H	4-H	5-H
$[PdCl(\eta^2\text{-}BBu_2Pz_2)(PEt_3)]$[a]	X(1)	142.68	106.37	135.29	7.51	6.26	7.67
	X(1)	140.07	104.70	133.81	7.67	6.15	7.56
$[PdCl(\eta^2\text{-}BPz_4)(PEt_3)]$[a,b]	P(1)[f]	142.64	105.90[h]	135.33	7.76	6.28	6.58
	Q(1)[f]	141.98	105.67[h]	137.00	7.87	6.33	7.14
	R(1)+S(1)[f]	144.67	106.72	137.82	7.68(2)	6.38(2)	7.32
		142.10	106.60	134.00			7.07
$[PtCl(\eta^2\text{-}BBu_2Pz_2)(PEt_3)]$[a]	$X_\alpha(1)$	143.30	106.60	135.17	7.60	6.24	7.70
		(73.3)	(50.2)	(28.5)			
	$X_\beta(1)$	139.72	105.01	134.31	7.80	6.24	7.65
		(33.6)					
$[Pt(CH_3)(\eta^3\text{-}BHPz_3)\{CNC(CH_3)_3\}]$[c]	$X_{eq}(2)$	140.56	104.88	135.68			
		(32.4)	(20.6)	(11.8)			
	$X_{ax}(1)$	141.73	105.85	136.07			
		(38.2)	(20.6)				
$[RuCl_2(NO)(\eta^3\text{-}BPz_4)]$[d]	X(2)	144.26	108.06	137.21		[k]	
	X(1)	145.81	106.74	135.26[i]			
	Y(1)	142.78	108.16	135.61[i]			

[a] This work; in CD_3CN.

[b] At −35 °C.

[c] Ref. [6a]; in $CDCl_3$.

[d] Ref. [5]; in $CDCl_3$.

[e] Signal sets of the pyrazolyl groups, X = coordinated, Y = uncoordinated; for subscripts, α and β, see text; the number of pyrazolyl groups shown in parentheses.

[f] Characterization of four Pz groups, P, Q, R and S, were not determined. However, two Pz groups showing 5-H signals at δ 6.58 and 7.07 are probably assignable to uncoordinated groups, in consideration of their coalescence at ~30 °C due to fast ring inversion of Pd–(N-N)$_2$–B. See Fig. 3.

[g] J(Pt–C) in parentheses; in Hz.

[h] Maybe interchangeable.

[i] Maybe interchangeable.

[j] Mutual coupling constants of pyrazolyl protons were significantly small. Moreover some proton signals showed additional weak couplings with ^{31}P and/or ^{195}Pt nuclei, and their signal-shapes were complex. Accordingly, coupling constants J in the ^{1}H NMR spectra are not listed here.

[k] Omitted. See Ref. [5].

BPz$_4$)(NO)] [5], and for both coordinated and uncoordinated pyrazolyl groups, 3-C CH carbon resonances have been described to be at δ 142–146, i.e. lower fields than those of 5-C at δ 135–138. Accordingly, ^{13}C NMR signals of the pyrazolyl 3-C and 5-C CH carbons in the (η^2-BBu$_2$Pz$_2$) complexes (**1** and **2**) were found to be at similar fields to those of the corresponding signals for the tridentate-type $[RuCl_2(\eta^3\text{-}BPz_4)(NO)]$. The present authors proposed the resonating of 3-C CH carbons at lower fields than 5-C as the appropriate criterion in ^{13}C NMR assignments of these pyrazolyl CH carbons[1]. The view that 3-C CH carbons resonate at lower fields than 5-C[2] was supported also by literature NMR data, such as those for many substituted pyrazoles [9] and for some tridentate poly(1-pyrazolyl)borato platinum(II) (Table 1) and tin(II) complexes [6,10]. Subsequent ^{1}H NMR assignments for pyrazolyl 3-H and 5-H protons of **1** and **2** became possible through ^{1}H–^{13}C and ^{1}H–^{1}H COSY observations (Fig. 2 and Table 1).

Thallium tetrakis(3-t-butylpyrazo-1-yl)borate Tl[B(3-t-BuPz)$_4$] was obtained by treatment of 3(5)-t-butylpyrazole (t-BuPz-H) with K[BH$_4$], followed by metal-ion exchange using thallium formate [5]. NMR spectroscopic equivalence of all four t-butylpyrazo-1-yl groups confirmed the exclusion of a conceivable blended introduction of some 5-t-butylpyrazo-1-yl groups (in place of 3-t-butylpyrazo-1-yl ones) on boron, due to

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[1] In contrast to ^{13}C NMR spectroscopy, which covers usually over ~210 ppm, ^{1}H NMR signal distribution is small generally (only less than ~15 ppm), and probably on that account, comparative NMR observations of pyrazolyl 3-H and 5-H protons of the complexes in the present study, without support from ^{13}C NMR and ^{1}H–^{13}C COSY observations, were not able to give a definite generalized criterion for their ^{1}H NMR assignment procedures.

[2] Claramunt and co-workers have also mentioned briefly the resonating of 3-C CH carbons at lower fields than 5-C, for N-substituted pyrazoles and alkali-metal poly(1-pyrazolyl)borate salts [4a].

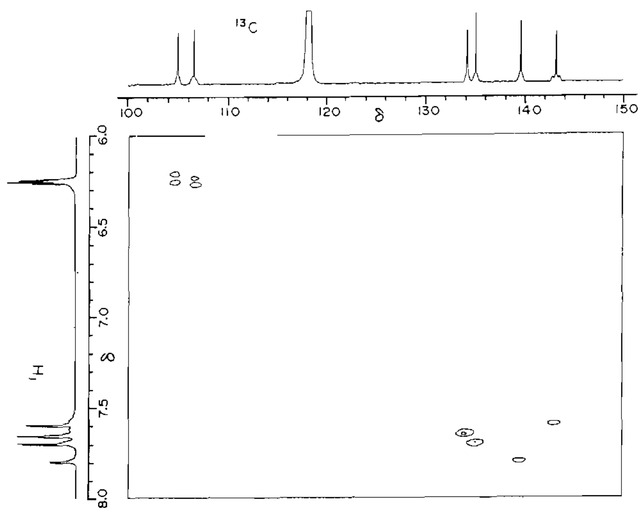

Fig. 2. ^{1}H–^{13}C COSY of [PtCl(η^2-BBu$_2$Pz$_2$)(PEt$_3$)] in CD$_3$CN.

steric bulkiness of the t-butyl substituents, and their ^{13}C NMR signals were assigned; δ 164.48 (3-C), 102.21 (4-C) and 135.76 (5-C) in CDCl$_3$. Furthermore, subsequent comparative NMR studies of the similar salt Tl[BPz$_4$] led us to determine its 3-C and 5-C assignments in CDCl$_3$ at δ 141.02 and 135.65, respectively[3]. (The 4-C signal was at δ 105.57.) Similar chemical-shift values have been described by Claramunt and co-workers [4a], for pyrazolyl CH carbons of alkali-metal salts M[BPz$_4$] in D$_2$O. Accordingly, as the criterion for the pyrazolyl 3-C and 5-C NMR assignments, the resonating of 3-C CH carbons at lower fields than 5-C was considered to be compatible with the case for these poly(1-pyrazolyl)borate salts also.

Fluxional motions of the BPz$_4$ ligands have already been studied by 100 MHz CW ^{1}H NMR by the present authors, for a few palladium(II) complexes. NMR assignments of pyrazolyl protons in these complexes seemed to be worthy of reexamination at this stage using high-resolution pulse FT-NMR spectroscopic techniques and two-dimensional spectral representation methods [11] developed in the last decade. Fig. 3 shows the temperature-dependent FT ^{1}H NMR spectra (400 MHz) for the pyrazolyl groups of [PdCl(η^2-BPz$_4$)(PEt$_3$)] (**3**) in CD$_3$CN, where there were three classes of NMR signals at δ 6.2–6.5, 6.6–7.4, and 7.6–8.0. At low temperatures (~ −35 °C), four signals, with some overlapping each other, were observed for each class, indicating a stereochemically rigid, 'frozen' η^2-coordinated structure of the BPz$_4$ ligand. Upon warming to high temperatures (~75 °C), one coalesced signal was observed for the respective classes. Spectroscopic equivalence of the four pyrazolyl groups was brought about by the fluxional motions of the BPz$_4$ ligand, via bond rupture between pyrazolyl 2-nitrogens and the metal. Fluxional motions of (η^2-BPz$_4$) palladium(II) complexes have been considered to involve the additional coordination of one uncoordinated pyrazolyl group near the palladium atom, dissociation of one pyrazolyl group

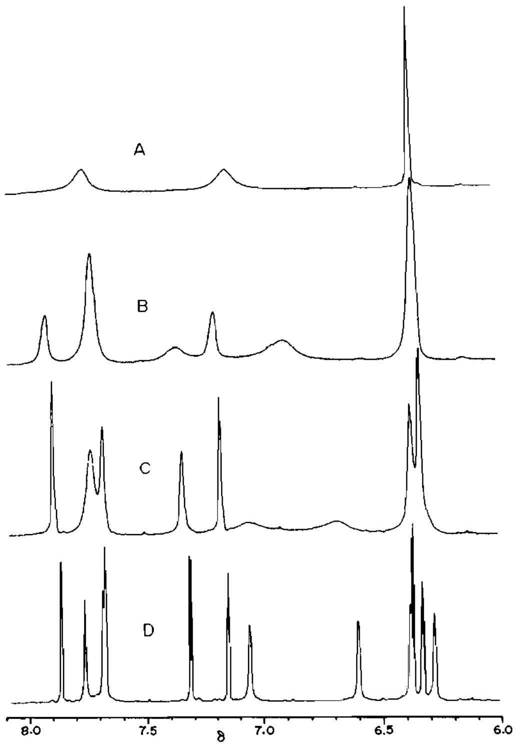

Fig. 3. Temperature-dependent ^{1}H NMR (400 MHz) of pyrazolyl protons in [PdCl(η^2-BPz$_4$)(PEt$_3$)] in CD$_3$CN. A, 75; B, 30; C, 0; D, −35 °C.

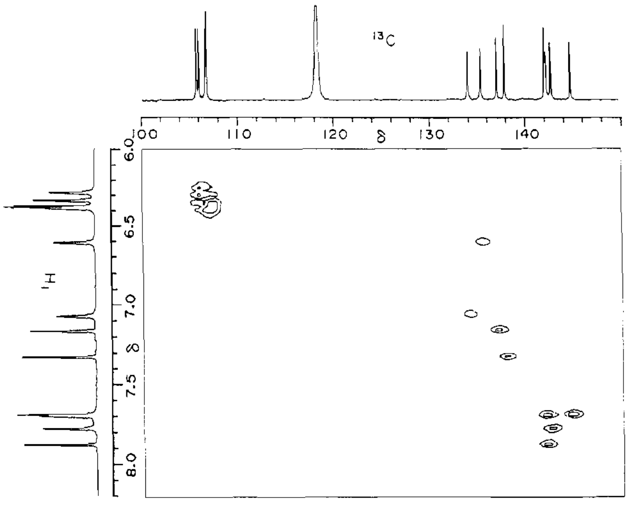

Fig. 4. ^{1}H–^{13}C COSY of [PdCl(η^2-BPz$_4$)(PEt$_3$)] in CD$_3$CN at −35 °C.

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[3] ^{13}C NMR chemical shift difference between the t-butyl-substituted 3-C carbon (δ 164.48) and unsubstituted one (δ 141.02) of the two kinds of thallium salts were compatible with the difference between the quaternary pyrazolyl-ring carbon, i.e. 3-C (δ 161.99; D$_2$O) in a 3-t-butylpyrazolate anion and the 3(5)-C (δ 140.04; D$_2$O) in a pyrazolate anion and also the difference between the quaternary *ipso*-carbon (δ 150.5) in t-butylbenzene and benzene carbons (δ 128.5).

coordinated previously, and inversion of the boat-like six-membered Pd–(N-N)$_2$–B ring [3].

The ^{1}H signals (nearly apparent triplets) at δ 6.2–6.5 were readily assigned to 4-H protons of the BPz$_4$ ligand. As for the remaining two classes, the signals at δ 6.6–7.4, distributed over a wider field, had been attributed previously [3a] to 3-H protons and the last one at δ 7.6–8.0 had been attributed to 5-H, by considering that chemical environment differences among the four 5-H protons, located near the sp^3-hybrid boron atom, would be comparatively smaller than those among the four 3-H protons. However, consideration of the above-described ^{13}C NMR chemical-shift values (3-C and 5-C) and of ^{1}H–^{13}C COSY (Fig. 4) has led to an alteration of the 3-H and 5-H assignments previously given. That is, the signals at δ 6.6–7.4 of **3** were associated with 5-H, and those at δ 7.6–8.0 with 3-H.

Similar NMR assignment revisions should also be performed for the [Pd(C-E)(η^2-BPz$_4$)] complexes, studied previously by the present authors [3b,c], but the discussion described there, such as that on *trans*-effects of the coexisting ligands, is still valid. Revisions have only been made to the 3-H and 5-H NMR signal assignments in the BPz$_4$ ligands.

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