Syntheses and Spectral Properties of New Nitrosyl[poly(1-pyrazolyl)borato]ruthenium Complexes[†]

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Trichloro(nitrosyl)ruthenium(III) was treated with alkali-metal or thallium poly(1-pyrazolyl)borates M(BRPz$_3$) (Pz=1-pyrazolyl) to give new nitrosyl[poly(1-pyrazolyl)borato]ruthenium(III) complexes [RuCl$_2$(BRPz$_3$)(NO)] (**1**, R=Pz; **2**, R=H). A similar reaction with thallium tris(3,5-dimethyl-1-pyrazolyl)hydroborate TlBH(3,5-Me$_2$Pz)$_3$ (3,5-Me$_2$Pz=3,5-dimethyl-1-pyrazolyl) afforded the complex [RuCl$_2${BH(3,5-Me$_2$Pz)$_3$}(NO)] (**3**) as the minor product and the 3,5-dimethylpyrazole complex [RuCl$_3$(NO)(3,5-Me$_2$PzH)$_2$] as the major one. The observation of ν(NO) bands over the range 1870 to 1900 cm^{-1} determined the NO$^+$ linear coordination mode in these complexes, rather than NO$^-$ bent one. The ν(NO) values of **1**—**3** were larger than those of the corresponding known π-cyclopentadienyl analogues by ca. 90 cm^{-1}, indicating a smaller degree of π-back donation of metal–NO bonds in the former complexes. ^{1}H, ^{13}C, and ^{11}B NMR data of the new complexes are described. In ^{1}H NOE measurements of **1**, irradiation at a chemical shift of 5-H protons in the coordinated pyrazolyl groups induced a positive NOE on the 5-H proton in the uncoordinated group, and individual assignments of the pyrazolyl protons were carried out with the help of ^{1}H–^{1}H and ^{13}C–^{1}H COSY.

The utility of poly(1-pyrazolyl)borato ligands BH$_n$Pz$_{(4-n)}^-$ (Pz=1-pyrazolyl),[1—3] which were first discovered by Trofimenko,[2] has been demonstrated in synthesizing a variety of transition-metal complexes. The ligands, especially in the tripodal coordination mode, have been shown to confer considerable stability on organometallic complexes and novel fluxionality in NMR spectroscopy, and have been compared to π-cyclopentadienyl ligands from the standpoint that both types of ligands are uninegative and can occupy three facial coordination sites on a metal ion. Moreover, it has been generally accepted that substituent introduction on boron and pyrazolyl carbons can significantly change the chemical reactivities, as well as other properties of their transition-metal complexes.[1—3]

In addition to the early studies concerning first-row transition-metal and molybdenum complexes, many papers have been published concerning various second- and third-row complexes in recent years,[1] regarding ruthenium, however, only a handful of poly(1-pyrazolyl)borato complexes are known,[3] in spite of the well-known potentiality of ruthenium for affording highly efficient catalytic species in a variety of homogeneous catalytic reactions. As part of our objectives in developing their catalytic reaction systems, the present author has prepared some new nitrosyl[poly(1-pyrazolyl)borato]ruthenium(III) as catalyst precursors. The dual nature of the nitrosyl ligands as NO$^-$ and NO$^+$ coordination modes in transition-metal complexes is well-known, and the catalytic potential has been expected, which this duality provides.[4] For some nitrosyl complexes effective as catalysts in such reactions as olefin disproportionation and hydrogenation, their catalytic activities have been assumed to result from a facile redox process between metal and the nitrosyl ligand, which causes favorable stereochemical or structural changes about the metals.[4]

Concerning the NMR assignment of 3- and 5-H protons in the poly(1-pyrazolyl)borato ligands, there have been some arguments about uncertainty.[5] Therefore, ^{1}H NOE (Nuclear Overhauser Effect) measurements were carried out for the first time in order to prevent any obscurity in the assignment.

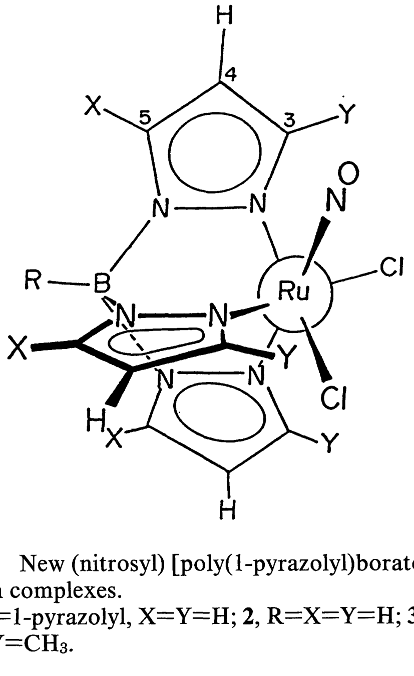

Fig. 1. New (nitrosyl) [poly(1-pyrazolyl)borato]ruthenium complexes.
1, R=1-pyrazolyl, X=Y=H; **2**, R=X=Y=H; **3**, R=H, X=Y=CH$_3$.

[†] Following the publication of "Nomenclature of Inorganic Chemistry" by IUPAC, the nitrosyl ligand is considered as being neutral in counting the formal oxidation number of ruthenium for the representation of its complexes in this paper. However, as described later, the nitrosyl ligand in the present new ruthenium(III) complexes was found to be in a NO$^+$ linear coordination mode, indicating an actual second-valent state of ruthenium.

Results and Discussion

Syntheses of New Ruthenium Complexes. Sodium tetrakis(1-pyrazolyl)borate $NaBPz_4$ was added to an ethanol solution of trichloro(nitrosyl)ruthenium(III). Recrystallization of the resulting precipitates from dichloromethane and benzene gave brown microcrystals of $[RuCl_2(BPz_4)(NO)]$ (**1**) in 26% yield. The microcrystals were soluble in dichloromethane, chloroform, and THF, but were sparingly soluble in benzene, diethyl ether, and ethanol.

In the case of hydrotris(1-pyrazolyl)borate anion $BHPz_3^-$, its potassium salt was treated with the trichloro(nitrosyl)ruthenium in THF to afford a mixture of some reaction products. Only brown microcrystals of $[RuCl_2(BHPz_3)(NO)]$ (**2**) were isolated after silica-gel column chromatographic separation. The yield was only 14%. The use of the thallium(I) salt of this anion increased the yield to 27%.

Thallium tris(3,5-dimethyl-1-pyrazolyl)hydroborate $TlBH(3,5\text{-}Me_2Pz)_3$ ($3,5\text{-}Me_2Pz$=3,5-dimethyl-1-pyrazolyl) gave the complex $[RuCl_2\{BH(3,5\text{-}Me_2Pz)_3\}(NO)]$ (**3**) as the minor product. The major one was found to be a 3,5-dimethylpyrazole complex of $[RuCl_3(NO)(3,5\text{-}Me_2PzH)_2]$ (**4**). Only the latter complex was isolated from a similar reaction of the potassium analogue. These findings indicated that bond cleavage between boron and pyrazolyl-nitrogen atoms in the tris(3,5-dimethyl-1-pyrazolyl)hydroborate anion occurred to a considerable extent in the course of the reaction with trichloro(nitrosyl)ruthenium, affording the boron-free pyrazole complex **4**. Fairly low yields of **1**—**3** were possibly due to the occurrence of the analogous cleavage of the respective poly(1-pyrazolyl)borate anions. King and Bond described similar cleavage of the poly(1-pyrazolyl)borato ligands in reactions with $[Fe(\pi\text{-}C_3H_5)I(CO)_3]$ and $[Co(\pi\text{-}C_5H_5)R_fI(CO)]$ (R_f=perfluoroalkyl).[6] From the analogous reaction of thallium tetrakis(3-*t*-butyl-1-pyrazolyl)borate, no distinguishable products were isolated.

Spectroscopic equivalence of the two 3,5-dimethylpyrazole ligands in **4** was observed in its ^1H and ^{13}C NMR spectra (vide infra, Tables 4 and 5). Figure 2 shows two probable configurations, i.e. *mer*, *trans*-configuration A and *facial*, *cis* one B. For a comparison, the complex $[RuCl_3(NO)(Pz_2CMe_2)]$ (**5**) {Pz_2CMe_2= 2,2-bis(1-pyrazolyl)propane} was prepared, where two neutral pyrazole-subunits form a *cis*-bidentate chelate to ruthenium. In contrast to **4**, this complex was insoluble in common organic solvents, and NMR observation was not possible. Although configuration determination of **4** should be deferred until X-ray analyses elucidate the molecular structure, it is tempting to suggest the *mer*, *trans*-configuration A for **4**. Among the known complexes $[RuCl_3(NO)L_2]$ (L=monodentate neutral ligands),[7] only the *mer*, *trans*-configurations of phosphine, sulfide, and selenide complexes have been determined by means of detailed spectroscopic and single crystal X-ray studies.

Spectroscopic Studies of the New Ruthenium Complexes. As summarized in Table 2, these complexes showed IR $\nu(NO)$ bands in the range 1870 to 1900 cm^{-1}. The $\nu(NO)$ bands have been reported to be in 2000—1600 and 1725—1525 cm^{-1} for the NO^+ coordination mode with linear metal-N-O bonds and the NO^- mode with bent ones, respectively.[4a,4c,8] The $\nu(NO)$ values given in Table 2 determine the NO^+ linear coordination mode in these complexes.

Similarly to the case of $\nu(CO)$ bands in metal carbon-

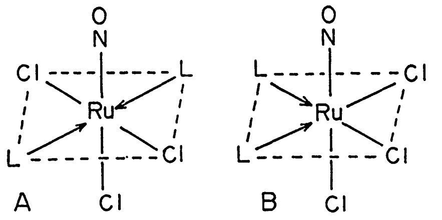

Fig. 2. Possible configurations for $[RuCl_3(NO)L_2]$ under the condition of two spectroscopically equivalent L ligands.
A, *mer, trans* configuration; B, *facial, cis* configuration.

Table 1. Syntheses of New Ruthenium Complexes

Complex		Analysis (%)[a]			Mp[b]
		C	H	N	θ_m/°C
(**1**)	$[RuCl_2(BPz_4)(NO)]$	30.37 (29.96)	2.60 (2.51)	26.05 (26.21)	>300[c]
(**2**)	$[RuCl_2(BHPz_3)(NO)]\cdot THF$	29.54 (29.29)	3.17 (3.13)	21.74 (21.74)	168—177
(**3**)	$[RuCl_2\{BH(3,5\text{-}Me_2Pz)_3\}(NO)]\cdot 0.25C_6H_6$	38.29 (38.21)	4.44 (4.57)	18.96 (18.90)	292
(**4**)	$[RuCl_3(NO)(3,5\text{-}Me_2PzH)_2]\cdot THF$	30.42 (30.95)	4.09 (4.33)	15.02 (15.04)	258—260
(**5**)	$[RuCl_3(NO)(Pz_2CMe_2)]\cdot 0.5H_2O$	25.59 (25.58)	3.05 (3.10)	16.30 (16.57)	264

a) Calculated values in parentheses. b) Measured on plate, unless noted otherwise. With decomposition. c) In evacuated sealed capillaries.

Table 2. IR Data of New Ruthenium Complexes[a]

Complex	ν(NO)	ν(BH)	ν(NH)
1	1894		
2	1893	2522	
3	1886	2560	
4	1874		3376
5[b]	1887		

a) In cm^{-1}. Measured in CH_2Cl_2, unless noted otherwise.
b) In KBr disk.

yls, the values ν(NO) have been correlated to the extent to which π-back donation from metals occurs in nitrosyl complexes.[4,8] The complexes [Ru(π-C_5R_5)Cl_2(NO)], i.e. π-cyclopentadienyl analogues to the poly(1-pyrazolyl)boratoruthenium **1**—**3**, have been described to show ν(NO) bands at 1809 and 1790 cm^{-1} for H and CH_3 as R, respectively.[9] The ν(NO) values of the present poly(1-pyrazolyl)borato complexes are larger than those of the π-cyclopentadienyl analogues by ca. 90 cm^{-1}, indicating a smaller degree of π-back donation of metal–NO bonds in **1**—**3**. Similar phenomena were noticed in the series of (carbonyl)ruthenium(II)[3b,3c] (Table 3) and (nitrosyl)molybdenum(III)[10] complexes reported previously.

On the contrary, it has also been described that Bruce's (carbonyl)[poly(1-pyrazolyl)borato]copper(I) complexes[11] show ν(CO) bands at lower wavenumbers than those of their π-cyclopentadienyl analogues, for example, 2083 cm^{-1} for [Cu($BHPz_3$)(CO)] vs. 2093 cm^{-1} for [Cu(π-C_5H_5)(CO)],[11a] and considerable stability of the Bruce's carbonyls has been recognized to result primarily from the strong σ-donor character of the poly(1-pyrazolyl)borato ligands. The copper complexes have an essentially sp^3-hybrid four-coordinate structure with a d^{10}-electron configuration, free of unoccupied d-orbitals, whereas the ruthenium complexes have an essentially d^2sp^3-hybrid six-coordinate structure with a d^6-electron configuration.

Accordingly, delocalization of the π-electron system extended to the CO or NO ligand in the ruthenium complexes was expected to occur to a more significant extent than that in the copper complexes, and the π-donor ability of the poly(1-pyrazolyl)borato ligands was revealed to be not as large as that of the π-cyclopentadienyl ligands.[12,13]

Tables 4 and 5 summarize the NMR spectral data of the new complexes observed in $CDCl_3$.[14] Complexes **2** and **3** showed ^{13}C NMR resonances of three pyrazolyl groups,[14] which are classified into two groups in a 2 : 1 ratio. The classification was readily interpretable by

Table 3. ν(CO) Described for $BRPz_3$ and π-Cyclopentadienyl Ruthenium Complexes

Complex	ν(CO) (cm^{-1})
[Ru(azb)($BHPz_3$)$(CO)_2$][a]	2048 and 1988 (Nujol)
[Ru(π-C_5H_5)(azb)$(CO)_2$][a]	2033 and 1976 (C_6H_{12})
[RuCl($BHPz_3$)$(CO)_2$][b]	2071 and 2011
[RuCl(π-C_5H_5)$(CO)_2$][b]	2056 and 2008

a) azb=(phenylazo)phenyl. Ref. 3b. b) Ref. 3c.

Table 5. ^1H NMR Data of New Ruthenium Complexes[a]

Complex	Class[b]	3-H	4-H	5-H	CH_3	BH or NH
1	X[c]	8.00	6.45	7.87		
	Y[c]	8.28	6.33	7.87		
	Z[d]	7.98	6.68	7.95		
2	X[e]	7.91	6.44	7.80		ca. 4.6
	Y[f]	8.16	6.28	7.59		
3	X		5.92		2.65, 2.40	ca. 4.6
	Y		5.85		2.80, 2.34	
4	X		5.97		2.60, 2.33	10.77

a) δ Values from TMS. In $CDCl_3$. NMR data of solvent molecules of solvation, incorporated on crystallization, are omitted. b) Classes of pyrazolyl groups; X, two spectroscopically equivalent coordinated pyrazolyl groups; Y, unique coordinated pyrazolyl group; Z, uncoordinated pyrazolyl group. c) $J_{3,4}$=2.2 Hz, $J_{4,5}$=2.6 Hz, $J_{3,5}$=0.7 Hz. d) $J_{3,4}$=1.5 Hz, $J_{4,5}$=2.2 Hz, $J_{3,5}$=0.7 Hz. e) $J_{3,4}$=1.8 Hz, $J_{4,5}$=2.4 Hz. f) $J_{3,4}$=$J_{4,5}$=2.4 Hz.

Table 4. ^{13}C and ^{11}B NMR Data of New Ruthenium Complexes[a]

Compd.	^{13}C NMR[b]					^{11}B NMR[d]
	Class[c]	3-C	4-C	5-C	CH_3	
1	X	144.26	108.06	137.21		−18.4
	Y	145.81	106.74	135.26[e]		
	Z	142.78	ca. 108.16	135.61[e]		
2	X	143.24	107.86	136.86		−22.3 (117Hz)
	Y	144.53	106.58	135.15		
3	X	152.32	108.84	145.46	14.46 12.51	−27.7 (105Hz)
	Y	156.13	108.99	143.79	15.86 12.51	
4	X	153.70	107.85	142.88	14.56 11.13	

a) In $CDCl_3$. b) δ Values from TMS. NMR data of solvent molecules of solvation, incorporated on crystallization, are omitted. c) Classes of pyrazolyl groups; X, two spectroscopically equivalent coordinated pyrazolyl groups; Y, unique coordinated pyrazolyl group; Z, uncoordinated pyrazolyl group. d) δ Values from $B(OMe)_3$. Coupling constants J(BH) shown in parentheses. e) Maybe interchangeable.

an end-on view (i.e. Newman projection along the B–Ru axis) of the tridentate $BHPz_3$ and $BH(3,5\text{-}Me_2Pz)_3$ ligands with local C_{3v} symmetry (Fig. 1), since the normal disposition of two chlorine atoms and the nitrosyl group with regards to the ligands would make two of the three coordinated pyrazolyl groups identical and different from the third one. The complex **1** exhibited ^{13}C NMR resonances of the uncoordinated pyra-

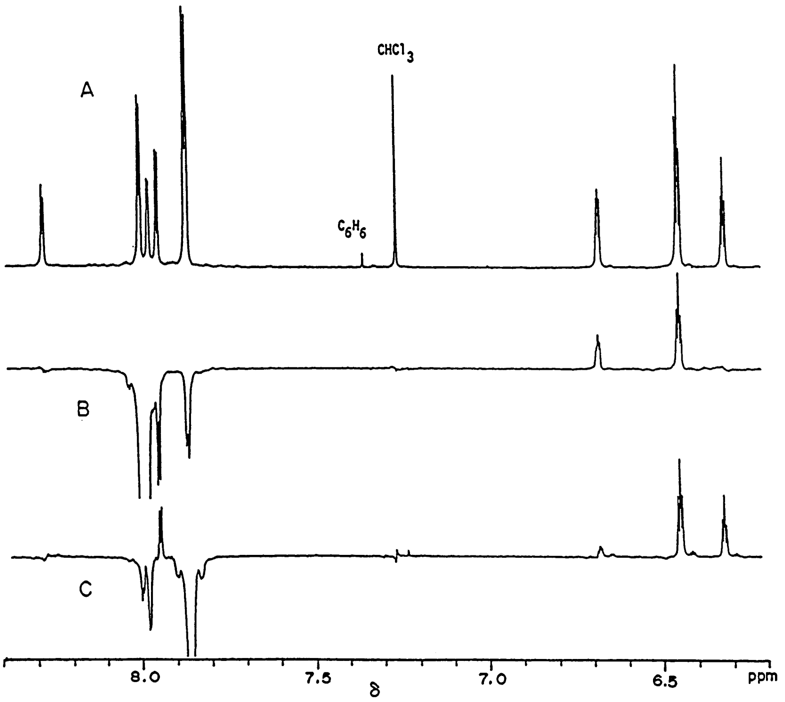

Fig. 3. ^1H NMR spectrum of the BPz_4 complex **1** and NOE observation.
A, ^1H NMR spectrum; B, NOE observation on irradiation at δ=8.00; C, NOE observation on irradiation at δ=7.87.

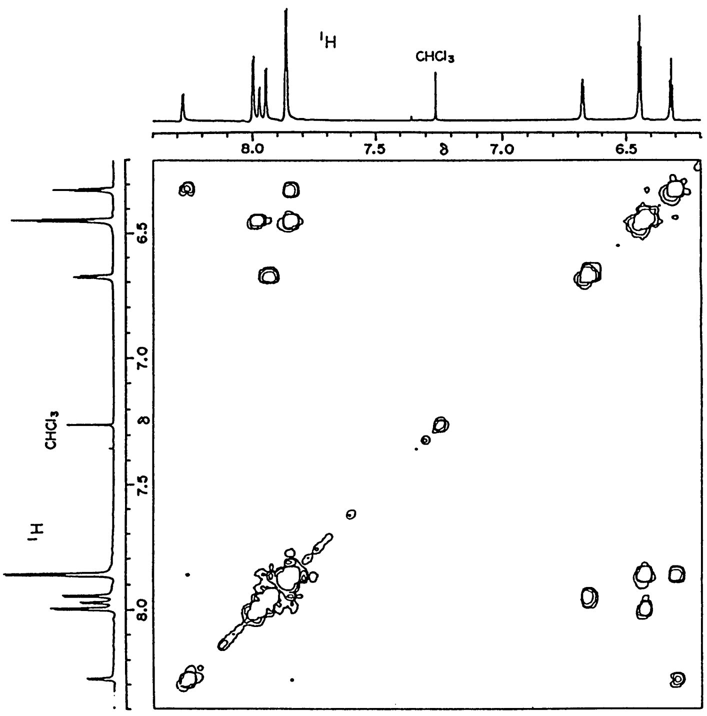

Fig. 4. The ^1H–^1H COSY spectrum of the BPz_4 complex **1**.

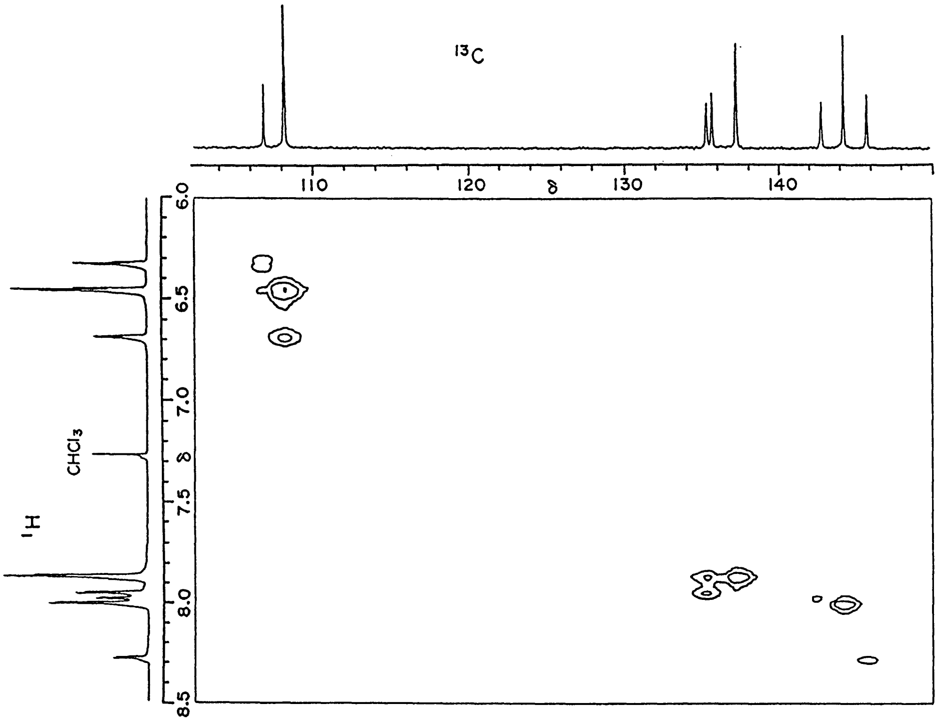

Fig. 5. The ^{13}C–^{1}H COSY spectrum of the BPz_4 complex **1**.

zolyl group, in addition to those of the three coordinated ones.

The ^{1}H NMR spectrum of the BPz_4 complex **1** is shown in Fig. 3-A. Four pyrazolyl groups were classified into three by a 2 : 1 : 1 ratio, similar to the ^{13}C NMR data, with the help of ^{1}H–^{1}H COSY (Correlation Spectroscopy) (Fig. 4) and a ^{1}H–^{1}H selective decoupling technique. Two stereochemically equivalent coordinated pyrazolyl groups (Fig. 1) gave the signal set X at δ=6.45 (2H), 7.87 (2H, overlapping), and 8.00 (2H). The remaining two unique groups were associated with a set Y of the signals at δ=6.33 (1H), 7.87 (1H, overlapping), and 8.28 (1H), and the other set Z at δ=6.68 (1H), 7.95 (1H), and 7.98 (1H).

Signals in the range δ=5.8 to 6.8 were obviously 4-H protons in the respective sets of the pyrazolyl groups. In order to prevent any obscurity in the NMR assignment of the 3- and 5-H protons, NOE measurements of **1** were carried out in this study. No similar work has so far been described concerning known poly(1-pyrazolyl)borato complexes. The NOE difference-spectra (B and C in Fig. 3) were obtained by saturating signals at δ=8.00 and 7.87, respectively. The irradiation at δ=8.00 (set X) accompanied unavoidably some simultaneous partial irradiation of the signal at δ=7.98 (set Z) owing to their close chemical shifts, and did not give any positive NOE signals except for the neighboring 4-H protons attached to the same pyrazolyl rings.[15] On the contrary, irradiation at δ=7.87 in the set(s) of X (and Y)[16] brought about a positive NOE signal at δ=7.95, belonging to the set Z. NOE value is defined as the percent variation of the intensity of a signal when another signal is saturated, and the value obtained at δ=7.95 was +5.4%. This finding clearly revealed the stereochemically close positions of the protons for the signals at δ=7.87 and 7.95. These protons were assigned to 5-H, and the set Z, which includes the signal at δ=7.95, was determined for the uncoordinated pyrazolyl group (Fig. 1).[16] The remaining set Y was attributed to the coordinated but also unique group. The signal at δ=8.00 was associated with the 3-H protons in the set X. Other NMR signals of **1** were assigned readily,[17] and the results are listed in Table 5. The ^{1}H NMR assignment was consistent with the above-described ^{13}C NMR data, as can be seen from ^{13}C–^{1}H COSY in Fig. 5. Thus, the present work demonstrated for the first time the utility of ^{1}H NOE measurements with the help of ^{1}H–^{1}H and ^{13}C–^{1}H COSY, in the assignment of 3- and 5-H protons of the poly(1-pyrazolyl)borato complexes. NMR data of **1** were helpful in analogous assignments of the other complexes, **2**—**4**.

As for the NMR fluxionality of the poly(1-pyrazolyl)borato ligands,[1c,2b,2e] the ^{1}H NMR spectra of **1** and **2** did not show any significant temperature-dependent change from −60 to 55 °C. The lack of fluxionality was in sharp contrast to the case of Trofimenko's complexes of $[Mo(\pi\text{-allyl})(BRPz_3)(CO)_2]$ with temperature-dependent trigonal-twist-rotation around the B–Mo axis.[2b,2e]

Further studies are currently in progress to apply these poly(1-pyrazolyl)boratoruthenium complexes as catalyst precursors to some homogeneous catalytic reactions, and results will be published elsewhere.

Experimental

General Procedures. Alkali-metal poly(1-pyrazolyl)borates[2a,2c,2f] and 2,2-bis(1-pyrazolyl)propane[18] were prepared according to methods described in the literature. Trichloro(nitrosyl)ruthenium monohydrate is commercially available or its pentahydrate was obtained by reported methods.[19] Wakogel C-200 was used for silica-gel column chromatography. Preparative operations were performed under nitrogen.

IR spectra were obtained by a JASCO A-100 spectrometer. ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on a JEOL model JNM GX-400 spectrometer operating at 399.7, 100.4, and 128.2 MHz, respectively, by use of tetramethylsilane as an internal standard for the former two nuclei and trimethyl borate as an external standard for the third. The chemical shifts δ are reported in parts per million from these standards, and downfield shifts are noted as positive in all cases. Melting points were determined on a Yanagimoto MP-S3 microstage apparatus and are uncorrected.

Conversion of Potassium Poly(1-pyrazolyl)borates to Thallium Analogues. The conversion of the $BHPz_3$ salt has been performed using thallium formate and water as a solvent,[3b] and this procedure was also applicable to the BPz_4 salt. On the other hand, the solubility properties of the $BH(3,5\text{-}Me_2Pz)_3$ and $B(3\text{-}t\text{-}BuPz)_4$ ($3\text{-}t\text{-}BuPz$=3-*t*-butyl-1-pyrazolyl) salts are slightly different, and it thus seems to be noteworthy to describe their conversion procedures in more detail.[2c,2f]

Potassium tris(3,5-dimethyl-1-pyrazolyl)hydroborate (520 mg, 1.55 mmol), washed well with hexane to remove any free 3,5-dimethylpyrazole impurity, was dissolved in methanol and mixed with thallium formate (390 mg, 1.55 mmol) in methanol. After stirring for 2 h, the solvent was evaporated under reduced pressure, and the dichloromethane extract of the residue was washed with methanol to give white microcrystals of thallium tris(3,5-dimethyl-1-pyrazolyl)hydroborate (410 mg, 0.82 mmol) in 53% yield. Mp 273 °C (melt with sublimation).

The reaction of potassium tetrakis(3-*t*-butyl-1-pyrazolyl)borate was performed in methanol in a manner similar to that of the $BH(3,5\text{-}Me_2Pz)_3$ salt. At the working-up stage, hexane extract was collected to afford a white powder of thallium tetrakis(3-*t*-butyl-1-pyrazolyl)borate in 56% yield. Mp 174—175 °C.

Reaction of the BPz_4 Anion with $RuCl_3(NO)$. Sodium tetrakis(1-pyrazolyl)borate (150 mg, 0.50 mmol) was added to an ethanol solution (10 ml) of trichloro(nitrosyl)ruthenium (120 mg, 0.50 mmol). After stirring overnight at room temperature, the resulting precipitates were recrystallized from dichloromethane and benzene to give brown microcrystals (63 mg, 0.13 mmol) of $[RuCl_2(BPz_4)(NO)]$ in 26% yield. For further purification, silica-gel column chromatographic separation was effective by elution with dichloromethane. The reaction of the potassium salt showed similar results.

Reaction of the $BHPz_3$ Anion with $RuCl_3(NO)$. Thallium hydrotris(1-pyrazolyl)borate (190 mg, 0.46 mmol) was mixed with trichloro(nitrosyl)ruthenium (104 mg, 0.44 mmol) in THF (20 ml). The mixture was stirred for 4 h. After removing the solvent under reduced pressure, a dichloromethane extract of the residue was chromatographed on a silica-gel column, eluting with dichloromethane to give a brown solid upon evaporation. Recrystallization from THF and diethyl ether afforded brown microcrystals (60 mg, 0.12 mmol) of $[RuCl_2(BHPz_3)(NO)]\cdot THF$ in 27% yield. A similar reaction of the potassium salt gave the same product in 14% yield.

Reaction of the $BH(3,5\text{-}Me_2Pz)_3$ Anion with $RuCl_3(NO)$. Trichloro(nitrosyl)ruthenium (130 mg, 0.55 mmol) in THF (15 ml) was treated with thallium tris(3,5-dimethyl-1-pyrazolyl)hydroborate (280 mg, 0.56 mmol) and the mixture was stirred for 3 h at ambient temperature. Silica-gel column chromatographic separation was performed for the dichloromethane extract from the reaction mixture. A brown band upon elution with benzene and dichloromethane (1/1) gave green-tinged brown microcrystals (26 mg, 0.050 mmol) of $[RuCl_2\{BH(3,5\text{-}Me_2Pz)_3\}(NO)]\cdot 0.25C_6H_6$ in 9% yield. The dichloromethane eluate of the ensuing reddish-pink band was evaporated, and recrystallization of the residue from THF and hexane afforded reddish-brown microcrystals (39 mg, 0.078 mmol), which were characterized as $[RuCl_3(NO)(3,5\text{-}Me_2PzH)_2]\cdot THF$ (14% yield).

Reaction of 2,2-Bis(1-pyrazolyl)propane. Trichloro(nitrosyl)ruthenium (74 mg, 0.31 mmol) was allowed to react with 2,2-bis(1-pyrazolyl)propane (70 mg, 0.40 mmol) in ethanol (15 ml). The mixture was stirred overnight and the resulting precipitates were collected and washed with diethyl ether. Pale-yellow microcrystals (81 mg, 0.19 mmol) were obtained and assigned to the complex $[RuCl_3(NO)(Pz_2CMe_2)]\cdot 0.5H_2O$ (62% yield).

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13) The complexes [$RuCl_2(BHPz_3)(NO)$] and [$RuCl(BHPz_3)(CO)_2$][3c] in C_6D_6 showed ^{11}B NMR resonances at $\delta=-22.6$ {$J(BH)=111$ Hz} and $\delta=-22.3$ {$J(BH)=113$ Hz}, respectively, which were a little higher fields than that of [$Cu(BHPz_3)(CO)$][11a] at $\delta=-20.3$ {$J(BH)=103$ Hz]. The present author suggests some negative charge was retained on boron in **1**—**3**, at the expense of the electron delocalization to the nitrosylruthenium moiety, and was associable with the above-mentioned easy cleavage of the poly(1-pyrazolyl)borate anions in the reactions with trichloro(nitrosyl)ruthenium. Alkali-metal salts of poly(alkyl-substituted 1-pyrazolyl)borate, where alkyl substituents increase electron density on boron, were hydrolyzed gradually upon exposure to moist air with release of some alkyl-substituted pyrazoles.

14) For ruthenium and some other transition-metal complexes with tridentate poly(1-pyrazolyl)borates, ^{13}C NMR signals of 3-C were observed usually at lower fields than those of 5-C. A subsequent paper is in preparation concerning a reinvestigation of the ^1H and ^{13}C NMR assignment of known poly(1-pyrazolyl)borato complexes. A similar short description has appeared concerning alkali-metal poly(1-pyrazolyl)borates.[5b]

15) Negative NOE signals were observed for some interrelations between the 3- and 5-H protons on the same pyrazolyl rings.

16) In the case where the uncoordinated pyrazolyl group does not rotate around the axis through the 1-nitrogen atom of the group and the boron atom, two 5-H protons in the coordinated pyrazolyl groups are conceivably located at the close positions to the 5-H proton in the uncoordinated group under consideration (Fig. 1), and are thought to be responsible for the positive NOE signal of the latter proton. However, the present author presumed the other case, in which the uncoordinated pyrazolyl group rotates freely around the axis, since the ^1H NMR spectra of **1** did not show any significant temperature-dependent change from −60 to 55 °C. In this case, all three 5-H protons in the coordinated pyrazolyl groups are responsible on the average, for the positive NOE observed. Similar free rotation of the terminal uncoordinated pyrazolyl group was described for some BPz_4 complexes.[2e]

17) By considering ^{13}C–^1H COSY in Fig. 5, the present author distinguished between 3- and 5-H proton signals in the set Y.

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