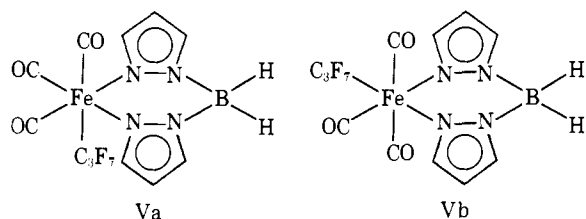


suggested<sup>12</sup> for the stable free acids  $H(C_3H_3N_2)_2BXY$  liberated upon acetic acid acidification of aqueous solutions of the polypyrazolylborates  $K[(C_3H_3N_2)_nBH_{4-n}]$  ( $n = 2, 3, \text{ and } 4$ ).

Reactions of the perfluoroalkyliron tetracarbonyl iodides  $R_fFe(CO)_4I$  with potassium polypyrazolylborates were less successful since most such reactions such as those of the pentafluoroethyl and heptafluoroisopropyl derivatives  $R_fFe(CO)_4I$  ( $R_f = C_2F_5$  or  $(CF_3)_2CF$ ) with potassium polypyrazolylborates, when carried out under the general conditions used in this work, led to complete decomposition without the isolation of any iron carbonyl complexes. However, the heptafluoropropyliron derivative  $C_3F_7Fe(CO)_4I$  reacted with potassium bispyrazolylborate and with potassium trispyrazolylborate to give the yellow tricarbonyl  $C_3F_7Fe(CO)_3(C_3H_3N_2)_2BH_2$  and the yellow dicarbonyl  $C_3F_7Fe(CO)_2(C_3H_3N_2)_3BH$ , respectively.

The yellow tricarbonyl  $C_3F_7Fe(CO)_3(C_3H_3N_2)_2BH_2$  can form a facial isomer Va and a meridional isomer Vb. The proton nmr spectrum of the  $C_3F_7Fe(CO)_3-$

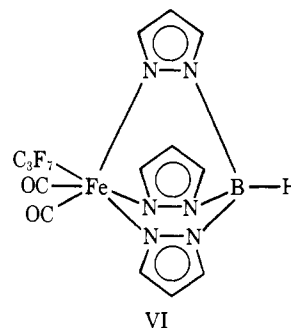


$(C_3H_3N_2)_2BH_2$  isolated from the reaction of  $C_3F_7Fe(CO)_4I$  with potassium bispyrazolylborate indicates this material to consist of about  $\sim 30\%$  of the facial isomer Va and about  $\sim 70\%$  of the meridional isomer Vb. The sets of pyrazolyl resonances to be assigned to each isomer Va and Vb can be deduced from the fact

(12) S. Trofimenko, *J. Amer. Chem. Soc.*, **89**, 3170 (1967).

that the two pyrazolyl rings are equivalent in the facial isomer Va since both rings are trans to carbonyl groups but nonequivalent in the meridional isomer Vb since one ring is trans to a carbonyl group and the other ring is trans to a heptafluoropropyl group. This nonequivalence of the two pyrazolyl rings in *mer*- $C_3F_7Fe(CO)_3-(C_3H_3N_2)_2BH_2$  is reflected in chemical shift differences of two of the three protons in the two pyrazolyl rings.

The yellow dicarbonyl  $C_3F_7Fe(CO)_2(C_3H_3N_2)_3BH$  exists as a single isomer VI, but the three pyrazolyl rings



are of two distinct types since one ring is trans to a  $C_3F_7$  group whereas the remaining two rings are trans to carbonyl groups. Again this difference is reflected in different nmr chemical shifts of the protons in these nonequivalent pyrazolyl rings. In the case of  $C_3F_7Fe(CO)_2(C_3H_3N_2)_3BH$  the assignment of the sets of nmr resonances to pyrazolyl rings trans to carbonyl or heptafluoropropyl is unambiguous since there are two pyrazolyl rings trans to carbonyl groups but only one pyrazolyl ring trans to a heptafluoropropyl group.

**Acknowledgment.** We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-71-2000.

## Metal Polypyrazolylborate Complexes. II. Reactions of Trimethylplatinum Derivatives with Polypyrazolylborates<sup>1</sup>

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Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30602. Received September 24, 1973

**Abstract:** Potassium trispyrazolylborate reacts with  $[(CH_3)_3PtI]_4$  or  $(CH_3)_3PtC_5H_5$  to give white  $(CH_3)_3Pt(C_3H_3N_2)_3BH$ . Similarly, potassium tetrakispyrazolylborate reacts with  $[(CH_3)_3PtI]_4$  to give white  $(CH_3)_3Pt(C_3H_3N_2)_4B$  in which the four pyrazolyl rings rapidly interchange at temperatures as low as  $-60^\circ$ . Potassium bispyrazolylborate reacts with  $[(CH_3)_3PtI]_4$  or with the solution obtained from stoichiometric quantities of  $[(CH_3)_3PtI]_4$  and  $AgPF_6$  to give white  $(CH_3)_3Pt(C_3H_3N_2)_2BH_2$  containing a novel boron-hydrogen-platinum bridge characterized by a relatively strong infrared band at  $2039\text{ cm}^{-1}$ . Reaction of  $(CH_3)_3Pt(C_3H_3N_2)_2BH_2$  with trimethyl phosphite results in rupture of this boron-hydrogen-platinum bridge to give the white complex  $(CH_3)_3Pt[(C_3H_3N_2)_2BH_2][P(OCH_3)_3]$ . Similar  $(CH_3)_3Pt[(C_3H_3N_2)_2BH_2]L$  complexes ( $L = (CH_3O)_3P, CO, \text{ pyrazole, and } 3,5\text{-dimethylpyrazole}$ ) can be prepared by reaction of  $[(CH_3)_3PtI]_4$  with potassium bispyrazolylborate in the presence of excess ligand L.

Platinum forms a series of trimethyl derivatives<sup>3</sup> of the general type  $(CH_3)_3PtXL_2$  ( $X = \text{halide or other}$

uninegative group;  $L = \text{electron pair donor ligand}$ ) containing six-coordinate octahedral platinum(IV). The tendency for these trimethylplatinum(IV) compounds to have a coordination number of six is so great that the ligand-free halides  $(CH_3)_3PtX$  (e.g.,  $X = I$ ) form cubane-type tetramers, I, in which the fifth and

(1) For part I of this series see R. B. King and A. Bond, *J. Amer. Chem. Soc.*, **96**, 1334 (1974).

(2) Postdoctoral research associate, 1971-1973.

(3) J. S. Thayer, *Organometal. Chem. Rev.*, **5**, 53 (1970).

**Table I.** Proton Nmr Spectra of Trimethylplatinum Polypyrazolylborates and Related Compounds

Compound <sup>a</sup>	Solvent <sup>b</sup>	Proton nmr spectrum, $\tau$					$J(\text{CH}_3\text{Pt})$ , Hz	Other resonances
		Pyrazolyl ring			Me <sub>3</sub> Pt protons <sup>d</sup>			
		5 position	4 position	3 position				
Me <sub>3</sub> Pt(Pz <sub>4</sub> B)	CDCl <sub>3</sub>	2.40	3.69	2.40	9.00	70		
Me <sub>3</sub> Pt(Pz <sub>4</sub> B)	(CD <sub>3</sub> ) <sub>2</sub> CO	2.44 m (2.5)	3.71 t (2.5)	2.28 d (2.5)	9.01	70		
Me <sub>3</sub> Pt(Pz <sub>3</sub> BH)	CDCl <sub>3</sub>	2.48 d (2.5)	3.84 t (2.5)	2.37 d (2.5)	9.02	69		
Me <sub>3</sub> Pt(Pz <sub>2</sub> BH <sub>2</sub> )	CDCl <sub>3</sub> - CH <sub>2</sub> Cl <sub>2</sub>	2.72 d (2)	4.00 t (2)	2.53 d (2)	8.39 (Pz)	78		
Me <sub>3</sub> Pt(Pz <sub>2</sub> BH <sub>2</sub> )(CO)	CDCl <sub>3</sub> - CH <sub>2</sub> Cl <sub>2</sub>	2.67 d (2)	3.83 t (2)	2.47 d (2)	9.09 (BH)	64		
Me <sub>3</sub> Pt(Pz <sub>2</sub> BH <sub>2</sub> )[P(OMe) <sub>3</sub> ]	CDCl <sub>3</sub>	2.50 d	3.81 t	2.42 d	9.00 (Pz)	68	MeO: 6.73 d (II)	
Me <sub>3</sub> Pt(Pz <sub>2</sub> BH <sub>2</sub> )(PzH)	CDCl <sub>3</sub> - CH <sub>2</sub> Cl <sub>2</sub>	2.53 d (2)	~3.85 m	2.48 d (2)	8.94 d (9) (Pz)	68	Ring H from PzH: 2.71 (2H), ~3.85 m (1 H)	
Me <sub>3</sub> Pt(Pz <sub>2</sub> BH <sub>2</sub> )(3,5-Me <sub>2</sub> C <sub>3</sub> N <sub>2</sub> H <sub>2</sub> )	CDCl <sub>3</sub> - CH <sub>2</sub> Cl <sub>2</sub>	2.40 d (2)	3.71 t (2)	2.35 d (2)	9.43 d (12) (L)	56	CH <sub>3</sub> : 7.85 s, 8.39 s Ring H from Me <sub>2</sub> C <sub>3</sub> N <sub>2</sub> H <sub>2</sub> : 4.07 s	
Me <sub>3</sub> Pt[P(OCH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> I	CDCl <sub>3</sub>				8.81 dd (10, 8) (L)	57	CH <sub>3</sub> O: 6.21 d (10)	
Me <sub>3</sub> Pt(PMe <sub>2</sub> Ph) <sub>2</sub> I	CDCl <sub>3</sub> - CH <sub>2</sub> Cl <sub>2</sub>				8.86 t (8) (I)	71		
					8.92 dd (8, 6) (L)	56	CH <sub>3</sub> P: 8.26 t (8)	
					9.27 t (8) (I)	70	C <sub>6</sub> H <sub>5</sub> P: 2.53	

<sup>a</sup> Key: Me = methyl; Ph = phenyl; Pz = pyrazolyl. <sup>b</sup> The CH<sub>2</sub>Cl<sub>2</sub> ( $\tau$  4.83) was used as an internal standard in the indicated spectra. <sup>c</sup> Coupling constants in Hz are given in parentheses: s = singlet, d = doublet, t = triplet, dd = double doublet, m = multiplet. <sup>d</sup> In cases where the three methyl groups in the (CH<sub>3</sub>)<sub>3</sub>Pt unit are nonequivalent, the ligand trans to the methyl group is cited in parentheses after the chemical shift value of the methyl group.

sixth coordination positions of each platinum atom are filled by lone electron pairs of halogens bonded to other platinum atoms.

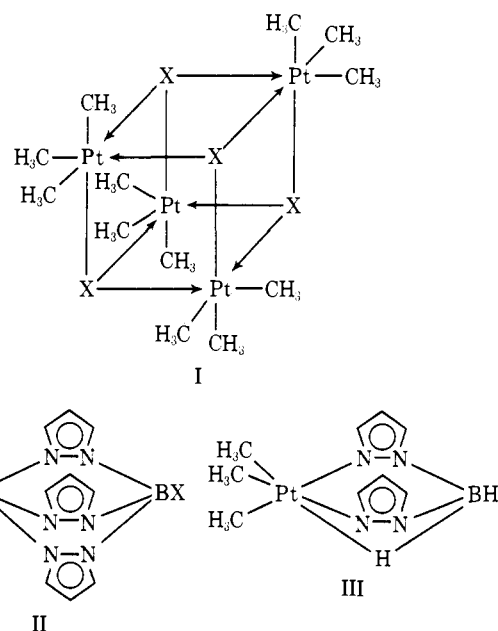
This paper describes the reactions of trimethylplatinum(IV) systems with the polypyrazolylborates<sup>4</sup> [(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>n</sub>BH<sub>4-n</sub>]<sup>-</sup>. In this work the uninegative tridentate trispyrazolylborate and tetrakispyrazolylborate ligands<sup>4</sup> were found to form the normal type of monometallic complexes (CH<sub>3</sub>)<sub>3</sub>Pt(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>BX (II, X = hydrogen or pyrazolyl) consistent with the need of a trimethylplatinum unit for a uninegative tridentate ligand to form an octahedral trimethylplatinum(IV) complex. However, the bispyrazolylborate ligand, which, unlike all previously studied ligands in the trimethylplatinum system, can normally act only as a nonbridging uninegative bidentate ligand, was found to form an unusual trimethylplatinum(IV) complex (III) with a novel platinum-hydrogen-boron bridge occupying the sixth coordination position of the platinum.

## Experimental Section

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and the microanalytical laboratory of the University of Georgia under the supervision of Mr. W. Swanson. Melting points were taken in capillaries and are uncorrected. Infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Each spectrum was calibrated against the 1601-cm<sup>-1</sup> band of polystyrene film. Proton nmr spectra (Table I) were taken either at 100 MHz on a Varian HA-100 spectrometer or at 60 MHz on a Varian T-60 spectrometer in the indicated solvents.

Unless otherwise specified a nitrogen atmosphere was provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of organometallic compounds, and (c) filling evacuated vessels containing organometallic compounds. In some cases specified below, argon rather than nitrogen was used for an inert atmosphere. Diethyl ether and tetrahydrofuran were purified by distillation under nitrogen over sodium benzophenone ketyl.

(4) S. Trofimenko, *Accounts Chem. Res.*, **4**, 17 (1971).



**Materials.** The potassium polypyrazolylborates K[(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>n</sub>BH<sub>4-n</sub>] ( $n = 2, 3$ , and 4) were prepared from potassium borohydride and pyrazole.<sup>5</sup> Reaction of potassium hexachloroplatinate(IV) with methylmagnesium iodide was used to prepare trimethylplatinum iodide tetramer<sup>6</sup> which was then treated with sodium cyclopentadienide to give the cyclopentadienyl<sup>7</sup> (CH<sub>3</sub>)<sub>3</sub>PtC<sub>5</sub>H<sub>5</sub>.

**Reaction of (CH<sub>3</sub>)<sub>3</sub>PtC<sub>5</sub>H<sub>5</sub> with Potassium Trispyrazolylborate.** A solution of 1.5 g (5 mmol) of (CH<sub>3</sub>)<sub>3</sub>PtC<sub>5</sub>H<sub>5</sub>, 2.52 g (10 mmol) of potassium trispyrazolylborate, and 50 ml of tetrahydrofuran was boiled under reflux for 45 min. Solvent was then removed. The residue was extracted with hexane and the filtered hexane extracts evaporated at ~25° (35 mm). The residue was purified by three low-temperature crystallizations from hexane followed by drying at 25° (0.1 mm) to give 1.2 g (54% yield) of white crystalline (CH<sub>3</sub>)<sub>3</sub>Pt(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>BH: mp 164° dec; infrared spectrum (cm<sup>-1</sup>)  $\nu(\text{CH})$  bands at 2940 (m), 2894 (m), and 2815 (m);  $\nu(\text{BH})$  band at 2508 (m);

(5) S. Trofimenko, *Inorg. Syn.*, **12**, 99 (1970).

(6) D. E. Clegg and J. R. Hall, *Inorg. Syn.*, **10**, 71 (1967).

(7) S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1529 (1965).

other bands at 1717 (w), 1512 (m), 1497 (m), 1423 (m), 1407 (s), 1397 (s), 1316 (s), 1262 (m), 1236 (m), 1221 (s), 1115 (s), 1076 (m), 1053 (s), 987 (s), 926 (w), 882 (m), 847 (w), 818 (m), 794 (s), 769 (s), 731 (m), 718 (s), and 666 (s).

*Anal.* Calcd for  $C_{12}H_{16}BN_6Pt$ : C, 31.9; H, 4.2; N, 18.6. Found: C, 32.3; H, 4.3; N, 19.0.

**Reaction of  $[(CH_3)_3PtI_4]$  with Potassium Trispyrazolylborate.** A mixture of 0.50 g (0.34 mmol) of  $[(CH_3)_3PtI_4]$ , 0.50 g (1.98 mmol) of potassium trispyrazolylborate, and 50 ml of diethyl ether was stirred at room temperature for 20 min. The yellow color of the  $[(CH_3)_3PtI_4]$  faded and a heavy white precipitate formed. The reaction mixture was filtered and solvent removed from the filtrate at  $\sim 25^\circ$  (35 mm). The residue was extracted with a 1:3 mixture of diethyl ether and hexane, and these extracts were filtered. Concentration of the filtrate and cooling to  $-78^\circ$  gave 0.26 g (44% yield) of white  $(CH_3)_3Pt(C_3H_3N_2)_2BH_2$ , mp  $166^\circ$  dec, identical by its infrared spectrum with an authentic sample of this compound prepared from  $(CH_3)_3PtC_2H_5$  and potassium trispyrazolylborate as described above.

**Reaction of  $[(CH_3)_3PtI_4]$  with Potassium Tetrakispyrazolylborate.** A solution of 0.5 g (0.34 mmol) of  $[(CH_3)_3PtI_4]$ , 0.5 g (1.58 mmol) of potassium tetrakispyrazolylborate, and 50 ml of tetrahydrofuran was boiled under reflux for 20 min. Solvent was then removed from the reaction mixture at  $\sim 25^\circ$  (35 mm). The residue was extracted with 100 ml of 1:1 diethyl ether-hexane in two portions. Solvent was removed from the filtered extracts at  $\sim 25^\circ$  (35 mm). Low-temperature crystallization of the residue from 1:1 diethyl ether-hexane gave 0.36 g (57% yield) of white crystalline  $(CH_3)_3Pt(C_3H_3N_2)_4B$ : mp  $183^\circ$  dec; infrared spectrum  $\nu(CH)$  bands at 2957 (w), 2905 (w), and 2827 (w); no  $\nu(BH)$  bands; other bands at 1538 (w), 1483 (s), 1407 (s), 1363 (s), 1271 (m), 1251 (w), 1242 (m), 1238 (m), 1166 (m), 1160 (m), 1142 (s), 1065 (s), 1056 (s), 1028 (s), 945 (m), 935 (m), 877 (m), 863 (w), 807 (m), 756 (s), 746 (s), and 680 (w).

*Anal.* Calcd for  $C_{15}H_{21}BN_8Pt$ : C, 34.7; H, 4.0; N, 21.6. Found: C, 34.6; H, 4.1; N, 21.7.

**Preparation of  $(CH_3)_3Pt(C_3H_3N_2)_2BH_2$ .** A solution of 0.367 g (0.25 mmol) of  $[(CH_3)_3PtI_4]$  in 50 ml of chloroform was treated with a solution of 0.253 g (1 mmol) of silver hexafluorophosphate in 50 ml of tetrahydrofuran. After standing for 5 min the yellow precipitate of silver iodide was removed by filtration and washed with chloroform. Solvent was removed from the combined filtrate and chloroform washings at  $\sim 25^\circ$  (35 mm).

The residue was dissolved in a mixture of 50 ml of diethyl ether and 50 ml of tetrahydrofuran. The solution was cooled to  $-78^\circ$  and treated at this temperature with a solution of 0.186 g (1 mmol) of potassium bispyrazolylborate in 20 ml of tetrahydrofuran. The resulting reaction mixture was allowed to warm to room temperature over 45 min. A light brown color developed. Solvent was then removed from the reaction mixture at  $\sim 25^\circ$  (35 mm). The residue was extracted with 125 ml of diethyl ether. Solvent was removed from the filtered diethyl ether extracts to give white crystals which were separated by filtration, washed with 10 ml of diethyl ether, and dried to give 0.193 g (51% yield) of  $(CH_3)_3Pt(C_3H_3N_2)_2BH_2$ , mp  $117^\circ$  dec.

The compound  $(CH_3)_3Pt(C_3H_3N_2)_2BH_2$  was also obtained from the reaction of  $[(CH_3)_3PtI_4]$  with potassium bispyrazolylborate without the intermediate  $AgPF_6$  treatment. However, the  $(CH_3)_3Pt(C_3H_3N_2)_2BH_2$  prepared by this more direct method was obtained in only 25–30% yield and was generally contaminated with unreacted  $[(CH_3)_3PtI_4]$ : infrared spectrum  $\nu(CH)$  bands at 2954 (m), 2886 (s), and 2806 (w);  $\nu(BH)$  and  $\nu(PtH)$  bands at 2485 (w), 2419 (s), 2388 (s), 2257 (w), and 2039 (s, br); other bands at 1497 (m), 1484 (s), 1402 (s), 1387 (s), 1375 (s), 1295 (m), 1281 (m), 1274 (m), 1247 (m), 1228 (m), 1220 (m), 1210 (s), 1191 (m), 1186 (m), 1178 (s), 1172 (m), 1140 (s), 1070 (m), 1060 (w), 1044 (s), 974 (w), 945 (m), 865 (m), 845 (w), 765 (s), 754 (s), 746 (s), 709 (s), 661 (w), 649 (w), 634 (s), 615 (m), and 607 (m).

*Anal.* Calcd for  $C_9H_{17}BN_6Pt$ : C, 28.0; H, 4.6; N, 14.4; I, 0.0. Found: C, 27.9; H, 4.5; N, 14.1, 14.4; I, 0.0.

**Preparation of  $(CH_3)_3Pt(C_3H_3N_2)_2BD_2$ .** A mixture of 1.0 g (24 mmol) of sodium tetradeuterioborate (from Columbia Organic Chemicals) and 4.0 g (60 mmol) of pyrazole was heated to  $115^\circ$  for 1 hr with magnetic stirring. After cooling to  $80^\circ$  the mixture was treated with 60 ml of heptane. The white precipitate was filtered, washed with four portions of boiling heptane, and dried at  $50^\circ$  (0.1 mm) to give 3.86 g (92% yield) of very hygroscopic  $Na[(C_3H_3N_2)_2BD_2]$ . The infrared spectrum of this product exhibited  $\nu(BD)$  bands at 1789 (m), 1700 (m), and 1620 (m)  $cm^{-1}$ . The

proton nmr spectrum of this product ( $CDCl_3$  solution) exhibited resonances at  $\tau$  2.41 (doublet,  $J = 2$  Hz), 2.52 (doublet,  $J = 2$  Hz), and 3.98 (triplet,  $J = 2$  Hz).

A mixture of 0.48 g (2.7 mmol) of this  $Na[(C_3H_3N_2)_2BD_2]$ , 1.0 g (6.75 mmol) of  $[(CH_3)_3PtI_4]$ , and 50 ml of benzene was stirred under argon for 1 hr. The resulting solution was filtered under argon and the benzene removed at  $35^\circ$  (35 mm). The white solid was washed with two 10-ml portions of hexane and dried overnight at  $\sim 35^\circ$  (0.1 mm) to give 0.27 g (27% yield) of  $(CH_3)_3Pt(C_3H_3N_2)_2BD_2$ . The infrared spectrum of this solid was similar to that of  $(CH_3)_3Pt(C_3H_3N_2)_2BH_2$  except for the absence of the bands in the range 2500–2000  $cm^{-1}$  assigned to  $\nu(BH)$  and  $\nu(PtH)$  frequencies and the presence of additional bands at 1821 (m), 1795 (w), 1774 (w), 1719 (m), and 1470 (m)  $cm^{-1}$  assigned to the corresponding  $\nu(BD)$  and  $\nu(PtD)$  frequencies. Upon attempted purification the  $(CH_3)_3Pt(C_3H_3N_2)_2BD_2$  prepared by this sodium salt method decomposed thereby preventing reliable elemental analyses from being obtained.

An attempt to prepare a purer sample of  $(CH_3)_3Pt(C_3H_3N_2)_2BD_2$  by treating  $Na[(C_3H_3N_2)_2BD_2]$  with the solution obtained from  $[(CH_3)_3PtI_4]$  and silver hexafluorophosphate similar to the procedure described above for the preparation of  $(CH_3)_3Pt(C_3H_3N_2)_2BH_2$  led instead to decomposition.

**Reaction of  $(CH_3)_3Pt(C_3H_3N_2)_2BH_2$  with Trimethyl Phosphite.** A solution of 0.2 g (0.52 mmol) of  $(CH_3)_3Pt(C_3H_3N_2)_2BH_2$  in 20 ml of cyclohexane was treated with 0.5 g (4 mmol) of trimethyl phosphite. The resulting mixture was boiled under reflux for 10 min. Solvent was removed at  $\sim 25^\circ$  (35 mm) and the residue dried for 6 hr at  $25^\circ$  (0.1 mm) to remove excess trimethyl phosphite. The residue was then extracted with 20 ml of hexane. The filtered extracts were concentrated to  $\sim 2$  ml and cooled to  $-78^\circ$  to give 0.176 g (66% yield) of white crystalline  $(CH_3)_3Pt[(C_3H_3N_2)_2BH_2][P(OCH_3)_3]$  mp  $105^\circ$ ; infrared spectrum ( $cm^{-1}$ )  $\nu(CH)$  bands at 2952 (w), 2903 (w), and 2840 (w);  $\nu(BH)$  bands at 2419 (m), 2370 (vw, sh), and 2299 (w); other bands at 1500 (w), 1410 (m), 1308 (m), 1262 (m), 1249 (w), 1217 (m), 1190 (m), 1173 (w, sh), 1161 (m), 1080–1010 (s, br), 882 (m), 797 (s), 757 (s), 718 (w), 641 (m), 627 (w), and 613 (w).

*Anal.* Calcd for  $C_{12}H_{26}BN_4O_3P$ : C, 28.1; H, 5.1; N, 11.0. Found: C, 28.2, 28.1; H, 5.3, 5.1; N, 11.1, 10.9.

**Reactions of Mixtures of Trimethylplatinum Iodide Tetramer and Potassium Bispyrazolylborate with Various Ligands.** (a) **Pyrazole.** A mixture of 0.5 g (0.34 mmol) of  $[(CH_3)_3PtI_4]$  and 0.5 g (2.7 mmol) of potassium bispyrazolylborate in 30 ml of tetrahydrofuran was stirred for 10 min in an argon atmosphere. The mixture was then treated with a solution of 0.140 g (1.46 mmol) of pyrazole in 10 ml of tetrahydrofuran and boiled under reflux for 15 min. Solvent was then removed at  $\sim 25^\circ$  (35 mm). The residue was extracted with 100 ml of diethyl ether in two portions. The filtered diethyl ether extracts were evaporated at  $\sim 25^\circ$  (35 mm), and the residue was recrystallized from a mixture of diethyl ether and hexane at low temperatures to give 0.192 g (31% yield) of  $(CH_3)_3Pt[(C_3H_3N_2)_2BH_2]_2(C_3H_3N_2)H$ : mp  $119^\circ$ ; infrared spectrum ( $cm^{-1}$ )  $\nu(NH)$  band at 3368 (s);  $\nu(CH)$  bands at 3138 (m), 2960 (m), 2900 (s), and 2824 (m);  $\nu(BH)$  bands at 2432 (s), 2409 (s), 2358 (m), and 2288 (m); other bands at 1730 (w), 1613 (w), 1536 (w), 1521 (w), 1498 (m), 1470 (m), 1433 (w), 1408 (s), 1389 (m), 1368 (m), 1298 (m), 1270 (m), 1246 (m), 1201 (s), 1192 (m), 1188 (m), 1165 (m), 1153 (s), 1121 (m), 1094 (m), 1073 (m), 1057 (s), 1045 (m), 982 (w), 958 (m), 947 (w), 912 (w), 898 (w), 880 (m), 852 (m), 846 (w), 778 (s), 768 (s), 760 (s), 721 (w), 711 (m), 675 (m), 645 (w), 638 (m), 628 (w), and 613 (w).

*Anal.* Calcd for  $C_{12}H_{21}BN_6Pt$ : C, 31.7; H, 4.5; N, 18.4. Found: C, 31.7; H, 4.6; N, 18.3.

(b) **3,5-Dimethylpyrazole.** A mixture of 0.5 g (0.34 mmol) of  $[(CH_3)_3PtI_4]$  and 0.5 g (2.7 mmol) of potassium bispyrazolylborate in 60 ml of tetrahydrofuran was stirred for 20 min in an argon atmosphere. A solution of 0.20 g (2.1 mmol) of 3,5-dimethylpyrazole in 10 ml of tetrahydrofuran was added and the resulting mixture boiled under reflux for 20 min. After cooling the reaction mixture was filtered and solvent removed from the filtrate at  $\sim 25^\circ$  (35 mm). The residue was extracted with diethyl ether and solvent removed from the filtered extracts at  $\sim 25^\circ$  (35 mm). The white crystalline residue was purified by low temperature crystallization from a mixture of diethyl ether and hexane to give 0.37 g (58% yield) of  $(CH_3)_3Pt[(C_3H_3N_2)_2BH_2]_2[(CH_3)_2C_3HN_2H]$ : mp  $129^\circ$ ; infrared spectrum ( $cm^{-1}$ )  $\nu(NH)$  band at 3433 (s);  $\nu(CH)$  bands at 3149 (m), 3115 (w), 2962 (s), 2902 (s), 2858 (w), and 2825 (s);  $\nu(BH)$  bands at 2428 (s), 2362 (s), 2304 (w), 2287 (m), and 2275 (w); other bands at 1735 (w), 1715 (w), 1631 (w), 1608 (w), 1578 (s), 1498 (s), 1466 (m), 1410 (s), 1390 (s), 1378 (m), 1299 (s), 1274 (s), 1243 (s), 1208 (s), 1190 (s), 1176 (m), 1162 (s), 1148 (s), 1098 (m), 1088 (m), 1060 (s), 1030 (s), 986 (s),

956 (m), 919 (w), 900 (m), 887 (s), 852 (w), 807 (s), 779 (m), 765 (s), 755 (s), 725 (m), 714 (m), 662 (w), 646 (s), 633 (m), 625 (w), and 615 (w).

*Anal.* Calcd for  $C_{14}H_{23}BN_6Pt$ : C, 34.7; H, 5.2; N, 17.4. Found: C, 34.9; H, 5.1; N, 17.7.

(c) **Carbon Monoxide.** A mixture of 0.5 g (0.34 mmol) of  $[(CH_3)_3PtI]_4$  and 0.5 g (2.7 mmol) of potassium bispyrazolylborate in 50 ml of tetrahydrofuran saturated with carbon monoxide was treated with carbon monoxide for 30 min at room temperature. Solvent was then removed at  $\sim 25^\circ$  (35 mm). The residue was extracted with 60 ml of diethyl ether saturated with carbon monoxide. Solvent was removed from the filtered extract at  $\sim 25^\circ$  (35 mm) and the residue dried at  $\sim 25^\circ$  (0.1 mm) to give 0.31 g of a white solid shown to contain the carbonyl  $(CH_3)_3Pt[(C_3H_3N_2)_2BH_2](CO)$  by the presence of a strong sharp  $\nu(CO)$  frequency of  $2125\text{ cm}^{-1}$  in hexane solution. This carbonyl rapidly lost carbon monoxide to give  $(CH_3)_3Pt(C_3H_3N_2)_2BH_2$  and therefore could not be purified for analyses.

(d) **Trimethyl Phosphite.** A mixture of 0.5 g (0.34 mmol) of  $[(CH_3)_3PtI]_4$  and 0.5 g (2.07 mmol) of potassium bis(3,5-dimethylpyrazolyl)borate in 50 ml of tetrahydrofuran was stirred for 10 min under argon at room temperature. After addition of 0.5 ml (0.53 g, 4.26 mmol) of trimethyl phosphite, the reaction mixture was boiled under reflux for 15 min. Solvent was then removed at  $\sim 25^\circ$  (35 mm) giving a yellow solid which was dried at  $\sim 25^\circ$  (0.1 mm) to remove excess trimethyl phosphite. The solid was extracted with 50 ml of hexane. The volume of the hexane extract was concentrated to 20 ml and the solution after filtration was cooled to  $-78^\circ$ . The white crystals were removed by filtration and purified by two low temperature crystallizations from hexane to give 0.36 g (43% yield) of  $(CH_3)_3Pt[P(OCH_3)_3]_2$ : mp  $128^\circ$ ; infrared spectrum ( $\text{cm}^{-1}$ )  $\nu(CH)$  bands at 2950 (m), 2926 (w), 2905 (m), and 2846 (w); no  $\nu(BH)$  bands; other bands at 1444 (m), 1249 (w), 1215 (m), 1183 (m), 1055 (s, sh), 1033 (s), 782 (m), 755 (m), and 733 (m).

*Anal.* Calcd for  $C_9H_{27}IO_3P_2Pt$ : C, 17.6; H, 4.4; P, 10.1; mol wt, 615. Found: C, 17.8; H, 4.5; P, 10.0; mol wt, 587 ( $CHCl_3$ ).

A similar reaction of 0.5 g (0.34 mmol) of  $[(CH_3)_3PtI]_4$ , 0.5 g (2.7 mmol) of potassium bispyrazolylborate, and 0.5 ml (0.53 g, 4.26 mmol) of trimethyl phosphite did not give  $(CH_3)_3Pt[P(OCH_3)_3]_2I$  but instead gave 0.41 g (59% yield) of  $(CH_3)_3Pt[(C_3H_3N_2)_2BH_2][P(OCH_3)_3]$ , mp  $105^\circ$ , identical with the product obtained from  $(CH_3)_3Pt(C_3H_3N_2)_2BH_2$  and trimethyl phosphite as described above.

(e) **Dimethylphenylphosphine.** A solution of 0.5 g (0.34 mmol) of  $[(CH_3)_3PtI]_4$  and 0.5 g (2.7 mmol) of potassium bispyrazolylborate in 60 ml of tetrahydrofuran in an argon atmosphere was treated with 0.5 ml (0.7 g, 5.1 mmol) of dimethylphenylphosphine.<sup>8</sup> The reaction mixture was boiled under reflux for 30 min. Solvent was then removed at  $\sim 25^\circ$  (35 mm) and the residue dried for 24 hr at  $\sim 25^\circ$  (0.1 mm) to remove excess dimethylphenylphosphine. The residue was extracted with 50 ml of dichloromethane in two portions. The filtered dichloromethane extracts were evaporated at  $\sim 25^\circ$  (35 mm). The residue was purified by three crystallizations from mixtures of dichloromethane and hexane to give 0.461 g (53% yield) of white crystalline  $(CH_3)_3Pt[P(CH_3)_2C_6H_5]_2I$ : mp  $168^\circ$ ; infrared spectrum ( $\text{cm}^{-1}$ )  $\nu(CH)$  bands at 2954 (s), 2894 (s), and 2812 (m); no  $\nu(BH)$  bands; other bands at 1570 (w), 1482 (m), 1434 (s), 1424 (s), 1414 (s), 1392 (s), 1326 (w), 1312 (w), 1302 (m), 1298 (m), 1283 (m), 1249 (m), 1213 (s), 1208 (s), 1161 (w), 1106 (m), 1073 (w), 1029 (w), 999 (w), 947 (s), 913 (s), 847 (m), 752 (s), 744 (s), 712 (s), 696 (s), and 678 (m).

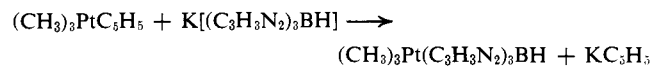
*Anal.* Calcd. for  $C_{19}H_{31}IP_2Pt$ : C, 35.5; H, 4.8; P, 9.6; mol. wt., 643. Found: C, 35.3; H, 4.9; P, 9.8; mol. wt., 592 ( $CHCl_3$ ).

## Discussion

The polypyrazolylborates  $[(C_3H_3N_2)_nBH_{4-n}]^-$  ( $n = 3$  and 4), which have at least three pyrazolyl rings, can function as tridentate ligands and hence can form complexes of the type  $(CH_3)_3Pt(C_3H_3N_2)_3BX$  (I; X = hydrogen or pyrazolyl) with the trimethylplatinum system. These complexes are white, air-stable crystalline solids. Their proton nmr spectra show that all three methyl groups of the trimethylplatinum system are equivalent which is consistent with structure II in which all three methyl groups are trans to equivalent

pyrazolyl rings. More surprisingly, the proton nmr spectrum of the tetrakispyrazolylborate complex  $(CH_3)_3Pt(C_3H_3N_2)_4B$  (II; X = pyrazolyl) shows only one set of resonances for all four pyrazolyl rings, although no more than three of the pyrazolyl rings can be coordinated with the metal atom for obvious steric reasons.<sup>4</sup> A fluxional process<sup>9</sup> making all four pyrazolyl rings equivalent on the nmr time scale therefore must occur in the tetrakispyrazolylborate complex  $(CH_3)_3Pt(C_3H_3N_2)_4B$ . This fluxional process is a relatively fast one since the nmr equivalence of all four pyrazolyl rings in  $(CH_3)_3Pt(C_3H_3N_2)_4B$  (II; X = pyrazolyl) persists at temperatures as low as  $-60^\circ$ . Related fluxional processes have been found<sup>10,11</sup> to occur in other tetrakispyrazolylborate complexes including the palladium derivative  $C_3H_3Pd(C_3H_3N_2)_4B$ .

The normal method for preparing trimethylplatinum polypyrazolylborate complexes is the reaction of trimethylplatinum iodide tetramer with the appropriate potassium polypyrazolylborate. However, the high tendency for formation of trimethylplatinum polypyrazolylborate complexes of the type II is demonstrated by the preparation of the trispyrazolylborate complex  $(CH_3)_3Pt(C_3H_3N_2)_3BH$  in fairly good yield by the displacement of the  $\pi$ -cyclopentadienyl ring with the trispyrazolylborate ligand according to the equation



A precedent for the displacement of a  $\pi$ -cyclopentadienyl ligand by the trispyrazolylborate anion is the reported<sup>12</sup> reaction of  $C_5H_5Fe(CO)_2I$  with  $K[(C_3H_3N_2)_3BH]$  to give  $[(C_3H_3N_2)_3BH]_2Fe$ .

The bispyrazolylborate anion can act only as a bidentate ligand and thus cannot form a complex of the type II upon reaction with trimethylplatinum derivatives. The reaction of potassium bispyrazolylborate with trimethylplatinum iodide tetramer gave a white solid exhibiting a strong but somewhat broad infrared band at  $2040\text{ cm}^{-1}$ . This infrared band was originally attributed to the  $\nu(NN)$  stretch of a dinitrogen complex  $(CH_3)_3Pt(N_2)(C_3H_3N_2)_3BH$  on the basis of analytical data for carbon, hydrogen, and nitrogen on a sample of this white solid.<sup>13</sup> However, a more detailed investigation of this white solid from potassium bispyrazolylborate and trimethylplatinum iodide tetramer revealed that this product frequently contained iodine apparently arising from unreacted trimethylplatinum iodide tetramer and furthermore decomposed over a variable period of days in a nitrogen filled container to a black solid.

These difficulties with the trimethylplatinum bispyrazolylborate complex were circumvented by preparing this complex by the following two-step procedure from trimethylplatinum iodide tetramer in which the iodine

(9) F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

(10) S. Trofimenko, *J. Amer. Chem. Soc.*, **91**, 3183 (1969).

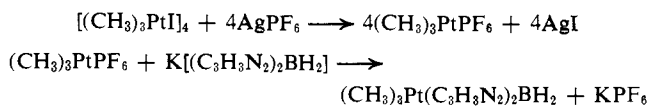
(11) P. Meakin, S. Trofimenko, and J. P. Jesson, *J. Amer. Chem. Soc.*, **94**, 5677 (1972).

(12) Footnote 23 of ref 4.

(13) Premature reports of this erroneous formula include the following: (a) *Chem. Eng. News*, Oct 23, 21 (1972); (b) Footnote 176 in S. Trofimenko, *Chem. Rev.*, **72**, 497 (1972); (c) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 385 (1973); (d) *Nachr. Chem. Techn.*, **20**, 453 (1972).

(8) K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

is removed completely in the first step by treatment with silver hexafluorophosphate



The white solid obtained from this sequence of reactions still exhibited the strong broad 2039-cm<sup>-1</sup> infrared band but analyzed for the nitrogen-free complex (CH<sub>3</sub>)<sub>3</sub>Pt(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub>. Therefore this 2039-cm<sup>-1</sup> infrared band cannot be a ν(NN) frequency.

The observations on the trimethylplatinum bispyrazolylborate complex (CH<sub>3</sub>)<sub>3</sub>Pt(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub> can be explained by structure III in which the sixth coordination position of the octahedral trimethylplatinum(IV) system is filled by bonding to one of the hydrogens of the BH<sub>2</sub> group of the bispyrazolylborate. Such bonding is not unprecedented having previously been demonstrated by X-ray crystallography<sup>14</sup> for the bis(3,5-dimethylpyrazolyl)borate molybdenum complex [H<sub>2</sub>B-(Me<sub>2</sub>C<sub>3</sub>HN<sub>2</sub>)<sub>2</sub>]<sub>2</sub>Mo(CO)<sub>2</sub>C<sub>7</sub>H<sub>7</sub> (IV). The strong 2039-cm<sup>-1</sup> infrared band in (CH<sub>3</sub>)<sub>3</sub>Pt(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub> can be assigned to the ν(PtH) (or possibly even the ν(BH)) involving the bridging hydrogen.

In order to obtain more direct evidence for the assignment of the 2039-cm<sup>-1</sup> band in (CH<sub>3</sub>)<sub>3</sub>Pt(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub> to a ν(PtH) or other frequency involving the BH<sub>2</sub> group, the deuterated derivative (CH<sub>3</sub>)<sub>3</sub>Pt(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BD<sub>2</sub> was prepared by converting commercial NaBD<sub>4</sub> to the very hygroscopic sodium salt Na[(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BD<sub>2</sub>] followed by reaction of this sodium salt with [(CH<sub>3</sub>)<sub>3</sub>PtI]<sub>4</sub>. In the resulting product the boron-hydrogen frequencies were shifted, as expected, from ~2400 to ~1800 cm<sup>-1</sup>. The 2039-cm<sup>-1</sup> band was absent in the deuterated product thus indicating its origin in (CH<sub>3</sub>)<sub>3</sub>Pt(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub> from a vibration involving the BH<sub>2</sub> protons such as a ν(PtH) frequency. Unfortunately, use of a sodium bispyrazolylborate for the preparation of deuterated (CH<sub>3</sub>)<sub>3</sub>Pt(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub> (which was necessary because we had no reasonable source of KBD<sub>4</sub>) did not give a completely pure product with [(CH<sub>3</sub>)<sub>3</sub>PtI]<sub>4</sub> even if the iodine was previously removed with silver hexafluorophosphate in contrast to the preparations using potassium bispyrazolylborate.

The proton nmr spectrum of (CH<sub>3</sub>)<sub>3</sub>Pt(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub> exhibited two resonances of relative intensities 2:1 from the trimethylplatinum unit. This is consistent with structure III in which two of the methyl groups are trans to pyrazolyl rings and the third methyl group is trans to the hydrogen atom bridging the platinum to the boron.

Reactions of (CH<sub>3</sub>)<sub>3</sub>Pt(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub> with an appropriate Lewis base might be expected to cleave the platinum-hydrogen-boron bridge to form an adduct of the type (CH<sub>3</sub>)<sub>3</sub>Pt(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub>·L (V) with retention of the six-coordinate platinum(IV) similar to the reported<sup>15</sup> cleavage of the molybdenum-hydrogen-boron bridge in IV and related compounds with Lewis bases. Reaction of (CH<sub>3</sub>)<sub>3</sub>Pt(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub> with excess trimethylphosphite gave such an adduct (CH<sub>3</sub>)<sub>3</sub>Pt[(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub>][P(OCH<sub>3</sub>)<sub>3</sub>] as a white crystalline solid. The infrared spectrum of this trimethyl phosphite adduct

did not exhibit the infrared band around 2040 cm<sup>-1</sup> attributed to the platinum-hydrogen-boron bridge in accord with structure V (L = (CH<sub>3</sub>O)<sub>3</sub>P) where this bridge has been cleaved. The proton nmr spectrum of the trimethyl phosphite adduct V (L = (CH<sub>3</sub>O)<sub>3</sub>P) exhibited two resonances of relative intensities 2:1 from the trimethylplatinum unit. This is in accord with the presence of two methyl groups trans to pyrazolyl rings and the third methyl group trans to the trimethyl phosphite ligand. The methyl resonances are split further into doublets by coupling with the spin 1/2 phosphorus atom of the trimethyl phosphite ligand. The <sup>3</sup>J(PH) coupling of the trimethyl phosphite phosphorus to the trans methyl group (12 Hz) is larger than the corresponding coupling to the cis methyl groups (9 Hz) in accord with observations on most other octahedral complexes.<sup>15</sup>

Another possible route to (CH<sub>3</sub>)<sub>3</sub>Pt(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub>·L derivatives (V) is the reaction between trimethylplatinum iodide tetramer and potassium bispyrazolylborate in the presence of the ligand under investigation without isolation of the intermediate (CH<sub>3</sub>)<sub>3</sub>Pt(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub>. The trimethyl phosphite derivative (CH<sub>3</sub>)<sub>3</sub>Pt[(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub>][P(OCH<sub>3</sub>)<sub>3</sub>] obtainable from (CH<sub>3</sub>)<sub>3</sub>Pt(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub> and trimethyl phosphite could also be prepared by a procedure of this type. Furthermore reaction between trimethylplatinum iodide tetramer and potassium bispyrazolylborate in a carbon monoxide atmosphere gave an unstable white solid which apparently is the monocarbonyl (CH<sub>3</sub>)<sub>3</sub>Pt[(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub>](CO) on the basis of a strong sharp infrared band at 2125 cm<sup>-1</sup> which appears to be a ν(CO) frequency. The proton nmr spectrum of the apparent monocarbonyl (CH<sub>3</sub>)<sub>3</sub>Pt[(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub>](CO) exhibits a set of pyrazolyl resonances and two methyl resonances in a 2:1 ratio from the nonequivalent methyl groups; these resonances have distinctly different chemical shifts from those of the carbonyl-free complex (CH<sub>3</sub>)<sub>3</sub>Pt(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub>. The apparent monocarbonyl (CH<sub>3</sub>)<sub>3</sub>Pt[(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub>](CO) readily loses its carbonyl group to form the carbonyl-free (CH<sub>3</sub>)<sub>3</sub>Pt(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub> (III); therefore a pure sample could not be obtained for elemental analyses. The instability of (CH<sub>3</sub>)<sub>3</sub>Pt[(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub>](CO) with respect to the loss of its carbonyl group is consistent with the formal +4 oxidation state of the platinum, the highest known oxidation state of a metal in a metal carbonyl derivative. Possibilities for retrodative bonding from the platinum atom to the carbonyl group in (CH<sub>3</sub>)<sub>3</sub>Pt[(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub>](CO) are limited because of the low electron density on the platinum atom arising from its high formal oxidation state; the limited amount of such retrodative bonding in (CH<sub>3</sub>)<sub>3</sub>Pt[(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub>](CO) is reflected in the relatively high ν(CO) frequency (2125 cm<sup>-1</sup>) of its carbonyl group.

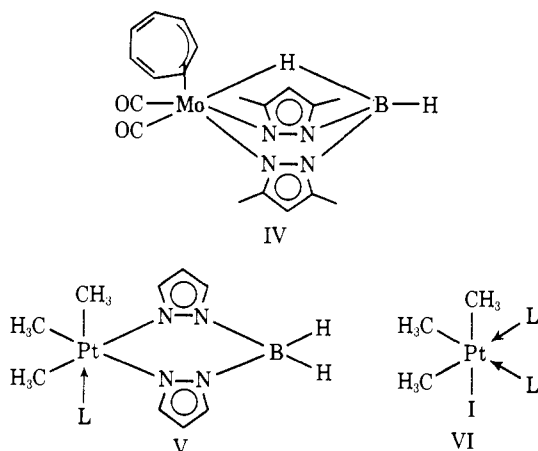
The reaction of a Lewis base ligand with a mixture of trimethylplatinum iodide tetramer and potassium bispyrazolylborate was used to prepare white crystalline complexes of the type (CH<sub>3</sub>)<sub>3</sub>Pt[(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>BH<sub>2</sub>]<sub>2</sub>·L containing the pyrazole and the 3,5-dimethylpyrazole ligands. These compounds contain pyrazolyl rings both in a polypyrazolylborate ligand and in a pyrazole ligand. They exhibit a strong infrared ν(NH) band in the range 3360–3440 cm<sup>-1</sup> from the nitrogen-hydrogen bond retained in the pyrazole or 3,5-dimethylpyrazole ligand. Distinct proton nmr resonances for the ring

(14) F. A. Cotton, J. L. Calderon, M. Jeremic, and A. Shaver, *J. Chem. Soc., Chem. Commun.*, 777 (1972).

(15) S. Trofimenko, *Inorg. Chem.*, 9, 2493 (1970).

protons in the pyrazolyl rings of the polypyrazolylborate ligand and in the coordinated free pyrazole can be identified.

Some reactions of Lewis base ligands with a mixture of trimethylplatinum iodide tetramer and potassium bispyrazolylborate or potassium bis(3,5-dimethylpyrazolyl)borate gave complexes of the type  $(\text{CH}_3)_3\text{PtL}_2\text{I}$  (VI) without incorporating the bispyrazolylborate



ligand rather than complexes of the type  $(\text{CH}_3)_3\text{Pt}-(\text{C}_3\text{H}_5\text{N}_2)_2\text{BH}_2 \cdot \text{L}$  (V) containing the bispyrazolylborate ligand. Dimethylphenylphosphine behaved in this manner to give  $(\text{CH}_3)_3\text{Pt}[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{I}$  completely analogous to other known compounds<sup>3</sup> of the type  $(\text{CH}_3)_3\text{PtL}_2\text{I}$  (VI). Trimethyl phosphite formed a complex  $(\text{CH}_3)_3\text{Pt}[\text{P}(\text{OCH}_3)_3]_2\text{I}$  with  $[(\text{CH}_3)_3\text{PtI}]_4$  in the presence of potassium bis(3,5-dimethylpyrazolyl)borate in contrast to the formation of  $(\text{CH}_3)_3\text{Pt}[(\text{C}_3-$

$\text{H}_3\text{N}_2)_2\text{BH}_2][\text{P}(\text{OCH}_3)_3]$  with  $[(\text{CH}_3)_3\text{PtI}]_4$  in the presence of potassium bispyrazolylborate.

The proton nmr spectra of the complexes  $(\text{CH}_3)_3\text{PtL}_2\text{I}$  (VI,  $\text{L} = (\text{CH}_3\text{O})_3\text{P}$  or  $(\text{CH}_3)_2\text{PC}_6\text{H}_5$ ) exhibit two platinum methyl resonances of 2:1 relative intensities arising from the two methyl groups trans to the trivalent phosphorus ligand and the single methyl group trans to the iodine atom, respectively. These are split by the  $^3J(\text{PH})$  coupling of the ligand phosphorus atoms to the methyl protons. In both compounds the resonance from the methyl group trans to the iodine is split into a 1:2:1 triplet arising from equivalent coupling with the two trivalent phosphorus ligands in cis positions relative to this unique methyl group. However, in both compounds the resonance from the two equivalent methyl groups trans to the trivalent phosphorus ligands is a double doublet with the outer lines barely above the noise level. This double doublet arises from nonequivalent  $^3J(\text{PH})$  coupling of the protons of these methyl groups to the phosphorus atoms of the ligands in cis and in trans positions relative to each of the two equivalent methyl groups. The methyl resonance of the coordinated dimethylphenylphosphine ligands in  $(\text{CH}_3)_3\text{Pt}[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{I}$  is a triplet arising from "virtual coupling" of the  $\text{PCH}_3$  protons with both ligand phosphorus atoms as a consequence of strong  $^2J(\text{PP})$  coupling between the phosphorus atoms of the two dimethylphenylphosphine ligands.<sup>16</sup>

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(16) F. B. Ogilvie, J. M. Jenkins, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 1916 (1970), and references cited therein.

## Metal Polypyrazolylborate Complexes. III. Reactions of Allyliron Tricarbonyl Iodide with Polypyrazolylborates<sup>1-3</sup>

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**Abstract:** Reaction of  $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}$  with potassium bispyrazolylborate in 1:1 diethyl ether-tetrahydrofuran at room temperature gives yellow-orange  $[\text{H}_2\text{B}(\text{C}_3\text{H}_5\text{N}_2)_2]_2\text{Fe}(\text{CO})_2$ . Reaction of  $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}$  with potassium trispyrazolylborate under similar conditions gives the following products: (1) violet  $[\text{HB}(\text{C}_3\text{H}_5\text{N}_2)_3]_2\text{Fe}$ , (2) orange  $[\text{C}_3\text{H}_5\text{N}_2\text{Fe}(\text{CO})_2]_2$ , (3) yellow  $(\text{C}_3\text{H}_5\text{N}_2\text{C}_3\text{H}_5)\text{Fe}(\text{CO})_3$ , (4) yellow *trans*- $\text{CH}_3\text{CH}=\text{CHFe}(\text{CO})_2(\text{C}_3\text{H}_5\text{N}_2)_3\text{BH}$ , (5) yellow  $\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{Fe}(\text{CO})_2(\text{C}_3\text{H}_5\text{N}_2)_3\text{BH}$ . The acyl derivative  $\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{Fe}(\text{CO})_2(\text{C}_3\text{H}_5\text{N}_2)_3\text{BH}$  is decarbonylated quantitatively to the alkyl derivative *trans*- $\text{CH}_3\text{CH}=\text{CHFe}(\text{CO})_2(\text{C}_3\text{H}_5\text{N}_2)_3\text{BH}$  in boiling hexane. The compound  $(\text{C}_3\text{H}_5\text{N}_2\text{C}_3\text{H}_5)\text{Fe}(\text{CO})_3$  listed above can also be prepared by reaction of *N*-allylpyrazole with  $\text{Fe}_2(\text{CO})_9$ . Reaction of  $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}$  with potassium tris(3,5-dimethylpyrazolyl)borate under similar conditions gives purple  $[\text{HB}(\text{CH}_3)_2\text{C}_3\text{HN}_2]_2\text{Fe}$  and yellow  $[\text{C}_3\text{H}_5\text{N}_2\text{C}_3\text{H}(\text{CH}_3)_2]_2\text{Fe}(\text{CO})_3$ . The infrared and proton nmr spectra of these new compounds are discussed.

The first paper of this series<sup>5</sup> reports the reactions of the perfluoroalkyliron tetracarbonyl halide  $\text{C}_3\text{F}_7\text{Fe}(\text{CO})_4\text{I}$  with the polypyrazolylborates to give the novel perfluoroalkyliron carbonyl polypyrazolylborates  $\text{C}_3\text{F}_7\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_5\text{N}_2)_2\text{BH}_2$  and  $\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2(\text{C}_3\text{H}_5\text{N}_2)_3\text{BH}$ . Another organoiron carbonyl halide of interest is allyliron tricarbonyl iodide,  $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}$  (I), which we believed might provide an entry to novel mixed allyliron carbonyl polypyrazolylborate complexes by

(1) For part II of this series see R. B. King and A. Bond, *J. Amer. Chem. Soc.*, **96**, 1338 (1974).

(2) For a preliminary communication of some of this work see R. B. King and A. Bond, *J. Organometal. Chem.*, **46**, C53 (1972).

(3) A portion of this work was presented at the 24th Southeastern Regional Meeting of the American Chemical Society, Birmingham, Ala., Nov 1972; paper 180 in abstracts.

(4) Postdoctoral research associate 1971-1973.

(5) R. B. King and A. Bond, *J. Amer. Chem. Soc.*, **96**, 1334 (1974).