

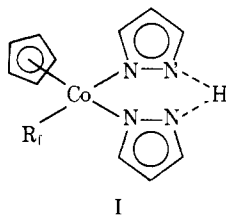
Metal Polypyrazolylborate Complexes. I. Reactions of Perfluoroalkylmetal Carbonyl Halides of Iron and Cobalt with Polypyrazolylborates¹

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Abstract: The cobalt derivatives $C_5H_5Co(CO)(R_f)I$ ($R_f = CF_3, C_2F_5, CF_3CF_2CF_2,$ and $(CF_3)_2CF$) react with the potassium polypyrazolylborates $K[(C_3H_3N_2)_nBH_{4-n}]$ ($n = 2, 3,$ and 4) in ethereal solvents at room temperature to give the red complexes $C_5H_5Co(R_f)(C_3H_3N_2)_nBH_{4-n}$ ($n = 2, R_f = CF_3, C_2F_5, CF_3CF_2CF_2,$ and $(CF_3)_2CF; n = 3, R_f = CF_3, C_2F_5,$ and $CF_3CF_2CF_2; n = 4, R_f = C_2F_5$ and $CF_3CF_2CF_2$) in which the polypyrazolylborates are bidentate ligands in all cases. The reactions between the cobalt derivatives $C_5H_5Co(CO)(R_f)I$ and potassium tetrakispyrazolylborate also give the brown-black boron-free derivatives $C_5H_5Co(R_f)(C_3H_3N_2)_2H$ ($R_f = C_2F_5, CF_3CF_2CF_2,$ and $(CF_3)_2CF$). Two stereoisomers of the compounds $C_5H_5Co(C_3F_7)(C_3H_3N_2)_2BH_2$ and $C_5H_5Co(C_2F_5)(C_3H_3N_2)_2B(C_3H_3N_2)_2$ have been separated in the pure state by column chromatography. The proton nmr spectrum indicates $C_5H_5Co(C_2F_5)(C_3H_3N_2)_3BH$ to be an inseparable mixture of stereoisomers in contrast to the corresponding trifluoromethyl and heptafluoro-*n*-propyl derivatives which each consist of a single stereoisomer. The heptafluoropropyliron derivative $C_3F_7Fe(CO)_4I$ reacts with potassium bispyrazolylborate at room temperature to give yellow $C_3F_7Fe(CO)_3(C_3H_3N_2)_2BH_2$ shown by its proton nmr spectrum to be a mixture of the facial and meridional isomers. A similar reaction of $C_3F_7Fe(CO)_4I$ with potassium trispyrazolylborate gives yellow $C_3F_7Fe(CO)_2(C_3H_3N_2)_3BH$.

During the last several years the polypyrazolylborates $[(C_3H_3N_2)_nBH_{4-n}]^-$ ($n = 2, 3,$ and 4) have been shown³ to form extensive series of stable complexes with transition metals, their carbonyls, and their cyclopentadienyls. An objective of the present work was an exploration of the consequences of introducing polypyrazolylborates as ligands in metal alkyls and perfluoroalkyls. This paper reports the reactions of various perfluoroalkylmetal halides of cobalt and iron with the polypyrazolylborates. The following features of this work were found to be particularly interesting. (1) The existence of geometrical isomers of several complexes which in some cases could be isolated in the pure state and which in other cases were detected by nmr spectroscopy. (2) Removal of the pyrazolyl ring from the tetrakispyrazolylborate anion by the complexes $C_5H_5Co(R_f)(CO)I$ to give the novel boron-free derivatives $C_5H_5Co(R_f)(C_3H_3N_2)_2H$ formulated as I.



I

Experimental Section

A nitrogen atmosphere was always 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.

Materials. The potassium polypyrazolylborates $K[(C_3H_3N_2)_nBH_{4-n}]$ were prepared from potassium borohydride and pyrazole

according to the published procedure.⁴ Commercial $Co_2(CO)_8$ was converted⁵ to $C_5H_5Co(CO)_2$ and then to $C_5H_5Co(CO)(R_f)I$ ($R_f = CF_3,$ ⁶ $C_2F_5,$ ⁶ *n*- $C_3F_7,$ ⁶ and $(CF_3)_2CF$) by the cited published procedures. The $C_3F_7Fe(CO)_4I$ was prepared from $Fe(CO)_5$ and 1-iodoheptafluoropropane.⁸ The potassium borohydride, pyrazole, and perfluoroalkyl iodides were all purchased from Columbia Organic Chemicals, Columbia, S. C.

Reactions of Perfluoroalkylmetal Carbonyl Halides with Polypyrazolylborates (Table I). General Procedure. A mixture of the indicated quantities (Table I) of the solid perfluoroalkylmetal carbonyl halide and potassium polypyrazolylborate was treated at room temperature with 30–50 ml of diethyl ether (for some reactions mixed with tetrahydrofuran as specified in Table I). Upon introduction of the solvent, reaction with gas evolution was observed. After stirring for about 30 min at room temperature, solvent was removed at $\sim 25^\circ$ (35 mm). A concentrated diethyl ether solution of the residue was chromatographed on a 2×60 cm alumina column. The colored bands of product(s) were eluted with hexane containing increasing amounts of diethyl ether or with pure diethyl ether. Evaporation of the eluates at $\sim 25^\circ$ (35 mm) gave the products as crystalline solids which could be purified further by crystallization from mixtures of hexane and diethyl ether or by rechromatography in cases where two or more metal complexes were obtained. Analytical and melting point data on the new compounds so prepared are given in Tables II and III. Proton and fluorine nmr data are given in Table IV.

Reactions of the potassium poly(3,5-dimethylpyrazolyl)borates $K[(CH_3)_2C_3HN_2]_nBH_{4-n}$ ($n = 2$ and 3) with $C_5H_5Co(CO)(n-C_3F_7)I$ under similar conditions failed to give any analogous products but instead resulted in complete decomposition.

Discussion

Reactions of $C_5H_5Co(CO)(R_f)I$ with the potassium polypyrazolylborates $K[(C_3H_3N_2)_nBH_{4-n}]$ ($n = 2, 3,$ and 4) give compounds of the type $C_5H_5Co(R_f)(C_3H_3N_2)_nBXY$ ($X = Y = H; X = C_3H_3N_2; Y = H; X = Y = C_3H_3N_2$) in which the polypyrazolylborate ligand,

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(2) Postdoctoral research associate, 1971–1973.

(3) S. Trofimenko, *Accounts Chem. Res.*, **4**, 17 (1971); *Chem. Rev.*, **72**, 497 (1972).

Table I. Reactions of Perfluoroalkylmetal Halides with Potassium Polypyrazolylborates^a

Perfluoroalkylmetal halide ^b	Potassium polypyrazolylborate ^c	Perfluoroalkylmetal compounds isolated as products ^{b-d}
CpCo(CF ₃)(CO)I (0.5 g, 1.42 mmol)	K[H ₂ BPz ₂] (0.5 g, 2.7 mmol)	CpCo(CF ₃)Pz ₂ BH ₂ (0.32 g, 0.94 mmol)
CpCo(C ₂ F ₅)(CO)I (2.0 g, 5 mmol)	K[H ₂ BPz ₂] (1.86 g, 10 mmol)	CpCo(C ₂ F ₅)Pz ₂ BH ₂ (0.98 g, 2.5 mmol)
CpCo(C ₃ F ₇)(CO)I (1.5 g, 3.3 mmol)	K[H ₂ BPz ₂] (1.2 g, 6.5 mmol)	CpCo(C ₃ F ₇)Pz ₂ BH ₂ (0.98 g, 2.2 mmol) (Isomer A)
		CpCo(C ₃ F ₇)Pz ₂ BH ₂ (0.12 g, 0.27 mmol) (Isomer B)
CpCo[CF(CF ₃) ₂](CO)I (0.5 g, 1.1 mmol)	K[H ₂ BPz ₂] (0.6 g, 3.2 mmol)	CpCo[CF(CF ₃) ₂]Pz ₂ BH ₂ (0.27 g, 0.61 mmol)
CpCo(CF ₃)(CO)I (0.5 g, 1.42 mmol)	K[HBPz ₃] (0.8 g, 3.1 mmol)	CpCo(CF ₃)Pz ₃ BH (0.37 g, 0.91 mmol)
CpCo(C ₂ F ₅)(CO)I (2.0 g, 5 mmol)	K[HBPz ₃] (2.5 g, 10 mmol)	CpCo(C ₂ F ₅)Pz ₃ BH (1.63 g, 3.6 mmol)
CpCo(C ₃ F ₇)(CO)I (2.2 g, 5 mmol)	K[HBPz ₃] (1.5 g, 6 mmol)	CpCo(C ₃ F ₇)Pz ₃ BH (1.8 g, 3.6 mmol)
CpCo[CF(CF ₃) ₂](CO)I (1.1 g, 2.5 mmol) ^e	K[HBPz ₃] (1.5 g, 6 mmol)	Product decomposed
CpCo(CF ₃)(CO)I	K[BPz ₄]	Product decomposed
CpCo(C ₂ F ₅)(CO)I (0.5 g, 1.25 mmol) ^e	K[BPz ₄] (1.0 g, 3.2 mmol)	CpCo(C ₂ F ₅)Pz ₄ H (0.16 g, 0.42 mmol)
		CpCo(C ₂ F ₅)Pz ₄ B (0.19 g, 0.36 mmol) (Isomer A)
		CpCo(C ₂ F ₅)Pz ₄ B (0.12 g, 0.23 mmol) (Isomer B)
CpCo(C ₂ F ₅)(CO)I (0.5 g, 1.25 mmol)	K[BPz ₄] (0.6 g, 1.9 mmol)	CpCo(C ₂ F ₅)Pz ₂ H (0.33 g, 0.88 mmol)
CpCo(C ₃ F ₇)(CO)I (1.0 g, 2.27 mmol) ^e	K[BPz ₄] (1.0 g, 3.2 mmol)	CpCo(C ₃ F ₇)Pz ₂ H (0.26 g, 0.61 mmol)
		CpCo(C ₃ F ₇)Pz ₄ B (0.19 g, 0.33 mmol)
CpCo[CF(CF ₃) ₂](CO)I (0.5 g, 1.1 mmol) ^e	K[BPz ₄] (0.6 g, 1.9 mmol)	CpCo[CF(CF ₃) ₂]Pz ₂ H (0.21 g, 0.49 mmol)
C ₃ F ₇ Fe(CO) ₄ I (1.2 g, 2.5 mmol)	K[H ₂ BPz ₂] (0.93 g, 5 mmol)	C ₃ F ₇ Fe(CO) ₃ Pz ₂ BH ₂ (0.72 g, 1.58 mmol)
C ₃ F ₇ Fe(CO) ₄ I (2.3 g, 5 mmol)	K[HBPz ₃] (2.5 g, 10 mmol)	C ₃ F ₇ Fe(CO) ₂ Pz ₃ BH (0.87 g, 1.76 mmol)

^a The reactions listed in this table were all run under the general conditions given in the Experimental Section. ^b Cp = π -cyclopentadienyl; C₃F₇ = *n*-heptafluoropropyl. ^c Pz = pyrazolyl. ^d The products are listed in the order eluted from the chromatography column. ^e These reactions were run in 1:1 tetrahydrofuran–diethyl ether rather than pure diethyl ether.

Table II. Some Properties of the New Compounds Containing Perfluoroalkyl and Polypyrazolylborate Groups

Compound ^a	Color	Mp, ^b °C	Analyses, % ^c			Infrared ^d ν (BH), cm ⁻¹
			C	H	N	
CpCo(CF ₃)Pz ₂ BH ₂	Red	147	Calcd 42.3 Found 42.2	3.9 3.8	16.5 16.5	2435 (m), 2390–2335 (br), 2286 (m)
CpCo(C ₂ F ₅)Pz ₂ BH ₂	Red	142	Calcd 40.0 Found 40.1	3.3 3.4	14.4 14.5	2431 (m), 2386 (w), 2347 (w), 2286 (w)
CpCo(C ₃ F ₇)Pz ₂ BH ₂ Isomer A	Red	151	Calcd 38.2 Found 38.4	2.9 3.0	12.7 12.8	2432 (m), 2420–2360 (br), 2302 (w)
CpCo(C ₃ F ₇)Pz ₂ BH ₂ Isomer B	Red	169	Calcd 38.2 Found 38.3	2.9 2.8	12.7 12.6	2450 (m), 2430 (m)
CpCo[CF(CF ₃) ₂]Pz ₂ BH ₂	Red	132	Calcd 38.2 Found 38.2	2.9 3.0	12.7 12.9	2412 (m), 2382 (m), 2350 (w), 2287 (w)
CpCo(CF ₃)Pz ₃ BH	Red	191	Calcd 44.3 Found 44.2	3.7 3.7	20.7 20.9	2435 (w), 2409 (m)
CpCo(C ₂ F ₅)Pz ₃ BH	Red	144	Calcd ^e 42.6 Found ^e 42.4	2.2 2.3	18.6 18.7	2450 (sh), 2435 (w), 2400 (sh), 2392 (m), 2374 (sh)
CpCo(C ₃ F ₇)Pz ₃ BH	Red	174	Calcd 40.2 Found 40.3	3.1 3.1	16.7 16.8	2453 (w), 2434 (m)
CpCo(C ₂ F ₅)Pz ₄ B Isomer A	Red	140	Calcd ^f 43.5 Found ^f 43.5	3.2 3.3	21.3 21.4	No ν (BH)
CpCo(C ₂ F ₅)Pz ₄ B Isomer B	Red	200	Calcd 43.5 Found 43.6	3.2 3.4	21.3 20.7	No ν (BH)
CpCo(C ₃ F ₇)Pz ₄ B	Red	194	Calcd 41.8 Found 41.5	3.0 3.1	19.6 19.2	No ν (BH)
C ₃ F ₇ Fe(CO) ₃ Pz ₂ BH ₂	Yellow	113	Calcd 31.0 Found 31.2	1.7 1.7	12.3 12.2	ν (BH) 2440 (m), 2385–2365 (br), 2297 (w) ν (CO) 2080 (s), 2033 (s), 2028 (s)
C ₃ F ₇ Fe(CO) ₂ Pz ₃ BH	Yellow	121	Calcd 34.0 Found 34.2	2.0 2.1	16.9 17.5	ν (BH) 2502 (s) ν (CO) 2074 (s), 2024 (s)

^a Cp = cyclopentadienyl, Pz = pyrazolyl, C₃F₇ = *n*-heptafluoropropyl. ^b Melting points reported in Tables II and III were taken in capillaries and are uncorrected. ^c Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany; Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.; Atlantic Microanalytical Laboratory, Atlanta, Ga.; and in the microanalytical laboratory of the University of Georgia under the direction of Mr. W. Swanson. ^d Infrared spectra in the ν (BH) region were taken in KBr pellets and those in the ν (CO) region were taken in cyclohexane solution. All reported spectra were recorded on a Perkin-Elmer Model 621 spectrometer with grating optics and calibrated against the 1601-cm⁻¹ band of polystyrene film. ^e Calcd: F, 20.8. Found: F, 20.7. ^f Calcd: F, 18.1. Found: F, 18.0.

regardless of the number of pyrazolyl rings, acts as a bidentate ligand with the nitrogen atoms of two of the pyrazolyl rings coordinated to the cobalt atom. These compounds are all red, relatively air-stable crystalline solids.

The possibilities for stereoisomers in compounds of the type C₅H₅Co(R_f)(C₃H₃N₂)₂BXY are of particular interest. X-Ray crystallographic studies on polypyrazolylborate complexes^{9,10} indicate that the chelate ring

consisting of the metal atom, the boron atom, and four nitrogen atoms from two pyrazolyl rings is nonplanar. Therefore in complexes of the type C₅H₅Co(R_f)(C₃H₃N₂)₂BXY where X and Y are equivalent (*i.e.*, hydrogen or pyrazolyl in the compounds under investiga-

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Table III. Some Properties of the Derivatives $C_5H_5Co(R_f)(C_3H_3N_2)_2H$

Compound	Color	Mp, °C		Analyses, %					Mol wt ^a
				C	H	N	F	B	
CpCo(C ₂ F ₅)Pz ₂ H	Black	110	Calcd	41.4	2.9	14.9	25.2	0.0	378
			Found	40.6	2.9	14.6	25.7	0.5	372
				40.7	3.0	14.6	24.9		403
CpCo(C ₃ F ₇)Pz ₂ H	Brown	98	Calcd	39.4	2.6	13.1	31.2	0.0	427
			Found	39.0	3.1	13.1	30.5	0.4	417
				39.2	2.6	13.1			406
CpCo[CF(CF ₃) ₂]Pz ₂ H	Black	106	Calcd	39.4	2.6	13.1		0.0	
			Found	39.2	2.6	13.1		0.5	
				39.2	2.6	13.1			

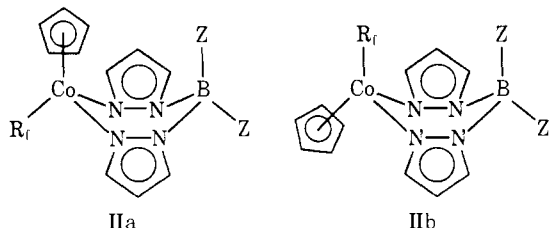
^a These molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., using a vapor pressure osmometer in chloroform solution.

Table IV. Proton and Fluorine Nmr Spectra of the New Compounds Reported in This Paper

Compound ^a	Pyrazole type	Proton nmr spectrum, ^{b,c}			C ₅ H ₅ protons	Fluorine nmr spectrum, ^{b,d}		
		Pyrazolyl ring				α-CF	β-CF	γ-CF
		5 position	4 position	3 position				
CpCo(CF ₃)Pz ₂ BH ₂	Coord	2.34 d (2)	3.73 t (2.5)	2.26 d (2.5)	4.71 s	11.9 s		
CpCo(C ₂ F ₅)Pz ₂ BH ₂	Coord	2.41	3.76 t (2.5)	2.31 d (3)	4.72 s	80	82	
CpCo(C ₃ F ₇)Pz ₂ BH ₂ (A)	Coord	2.27 d (2)	3.70 dd (2,3)	2.17 d (3)	4.76 s	79.4	115.8 t (7)	80.9 t (11.5)
CpCo(C ₃ F ₇)Pz ₂ BH ₂ (B)	Coord	2.19 d (2)	3.60 t (2)	2.02 d (2)	4.62 s	78.4	117.6	82.0 t (11)
CpCo[CF(CF ₃) ₂]Pz ₂ BH ₂	Coord	2.43	3.72 t (3)	2.25 d (3)	4.54 s	175.9	67.8 d (7.6)	
CpCo(CF ₃)Pz ₃ BH	Coord	2.28 d (2.5)	3.74 t (2.5)	2.14 d (2.5)	4.69 s	10.8		
	Uncoord	2.83 d (3)	3.59 t (3)	2.83 d (3)				
CpCo(C ₂ F ₅)Pz ₃ BH (A)	Coord	2.33 d (2.3)	3.77 t (2.3)	2.23 d (~2)	4.66 s	75.0	82.5	
	Uncoord	2.91 d (2.6)	3.65 t (2)	2.91 d (2.6)				
CpCo(C ₂ F ₅)Pz ₃ BH (B)	Coord	2.27 d (2.3)	3.55 t (2.5)	1.97 dd (2.5, 0.7)	5.13 s	75.4	82.2	
	Uncoord	3.34 d (2)	3.82 t (2.2)	2.43 d (~2)				
CpCo(C ₃ F ₇)Pz ₃ BH ^e	Coord	2.27	3.55 t (2.4)	1.97 dd (3,1)	5.09 s		119.8	
	Uncoord	3.41 d (2.4)	3.80 t (~2)	2.42 d (1.8)				
CpCo(C ₂ F ₅)Pz ₄ B (B) ^f	Coord	2.67 d (~2.8)	3.58 t (2.5)	2.25	5.10 s	80.6	80.5	
	Uncoord A	3.19 d (2.5)	3.66 t (~2)	2.25				
	Uncoord B	3.26 d (2.5)	3.78 t (~2)	2.25				
CpCo(C ₃ F ₇)Pz ₄ B ^f	Coord	2.56 d	3.49 t	2.12	5.06 s	78	117.5 t (5)	80.4 t (13)
	Uncoord A	3.07 d	3.56 t	2.12				
	Uncoord B	3.15 d	3.67 t	2.12				
CpCo(C ₂ F ₅)Pz ₂ H ^g	Coord	2.47	3.65 t (2)	2.25 d (2)	4.85 s	81	85	
CpCo(C ₃ F ₇)Pz ₂ H	Coord	2.30	3.56 t (2)	2.14 d (2)	4.76 s	82	117 (2)	80.1 t (13)
CpCo[CF(CF ₃) ₂]Pz ₂ H	Coord	2.40	3.63 t (~2.2)	2.23 d (2.1)	4.74 s	171	67.9 d (8.4)	
C ₃ F ₇ Fe(CO) ₃ Pz ₂ BH ₂	Coord							
Facial CO (30%)	Trans to CO	3.42 d (1.8)	4.51 t (~2.5)	2.64 d (2.3)				
C ₃ F ₇ Fe(CO) ₃ Pz ₂ BH ₂	Coord							
Meridional CO (70%)	Trans to CO	~2.97	4.01 t (2.3)	2.45 d (~2)		87.3 q (14)	117 s	80.4 t (14)
	Trans to C ₃ F ₇	~2.97	4.12 t (2.4)	2.47 d (~2)				
C ₃ F ₇ Fe(CO) ₂ Pz ₃ BH	Coord							
	Trans to CO	2.32 d (2.4)	3.76 t (~1.9)	1.93 d (~2)		87.8 q (14)	117.5 (s)	80.3 t (14)
	Trans to C ₃ F ₇	2.38 d (3.4)	3.82 t (~2.2)	1.93 d (~2)				

^a Cp = cyclopentadienyl, Pz = pyrazolyl, C₃F₇ = *n*-heptafluoropropyl. ^b Key: s = singlet; d = doublet; t = triplet; q = quartet; dd = double doublet; other resonances were broad or had incompletely resolved fine structure; coupling constants in Hz are given in parentheses. ^c Proton nmr spectra were taken in CDCl₃ solutions and recorded on a Varian HA-100 spectrometer at 100 MHz. ^d Fluorine nmr spectra were taken in diethyl ether solutions and recorded on a Varian HA-100 spectrometer at 100 MHz. ^e This proton nmr spectrum remained essentially unchanged upon cooling to -60°. ^f The allocation of the resonances of the uncoordinated pyrazolyl rings to rings A and B is ambiguous and thus must be regarded as arbitrary. ^g This proton nmr spectrum remained essentially unchanged upon cooling to -40°.

tion) two isomers IIa and IIb (Z = X and Y) are possible. In isomer IIa the cyclopentadienyl ring is axial and the perfluoroalkyl group is equatorial whereas in isomer IIb the cyclopentadienyl ring is equatorial and



the perfluoroalkyl group is axial. We have isolated two isomers of $C_5H_5Co(C_3F_7)(C_3H_3N_2)_2BH_2$ (IIa and IIb; $R_f = n-C_3F_7$, Z = H) and of $C_5H_5Co(C_2F_5)(C_3H_3N_2)_2B(C_3H_3N_2)_2$ (IIa and IIb; $R_f = C_2F_5$, Z = pyrazolyl); this observation is consistent only with the nonplanarity of the chelate rings in these complexes.

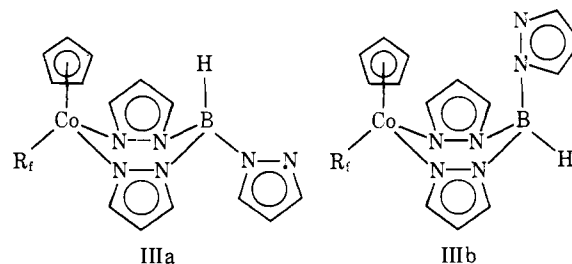
The proton nmr spectra of all of the products from reactions of $C_5H_5Co(CO)(R_f)I$ and potassium polypyrazolylborates (Table IV) except for the less strongly adsorbed isomer (isomer A) of $C_5H_5Co(C_2F_5)(C_3H_3N_2)_2B(C_3H_3N_2)_2$ (see below) are consistent with the proposed structures of type II particularly with regard to the pres-

ence of distinctly different sets of resonances for the coordinated and uncoordinated pyrazolyl rings. The usual uncertainties¹¹ about assignments of the resonances to the 3- or 5-protons of the pyrazolyl rings are present in the assignments given in Table IV. In the tetrakispyrazolylborate complexes $C_5H_5Co(R_f)(C_3H_3N_2)_2B(C_3H_3N_2)_2$ ($R_f = C_2F_5$ (isomer B) and C_3F_7) the four pyrazolyl rings exhibit sets of resonances (some overlapping) of relative intensities 2:1:1 arising from the two equivalent coordinated pyrazolyl rings and the two nonequivalent (see structures IIa and IIb) uncoordinated pyrazolyl rings, respectively. The proton nmr spectrum of isomer A of $C_5H_5Co(C_2F_5)(C_3H_3N_2)_2B(C_3H_3N_2)_2$ is reproducibly complex exhibiting in $CDCl_3$ solution besides a singlet cyclopentadienyl resonance at τ 4.96 pyrazolyl ring resonances at τ 1.76, 2.28, 2.61, 2.70 (triplet, $J \approx 2.5$ Hz), 3.28, 3.57 (triplet, $J = 2$ Hz), 3.70, and 3.78 of approximate intensities (relative to the C_5H_5 resonance as 5) of 1:3:1:2:2:2:1:3; in view of the correct elemental analyses on this isomer, the origin of this complex spectrum is unclear.

The stereoisomerism in the trispyrazolylborate complexes $C_5H_5Co(R_f)(C_3H_3N_2)_3BH$ is more complex since these compounds of the type $C_5H_5Co(R_f)(C_3H_3N_2)_2BXY$ where X and Y are nonequivalent have four stereoisomers if the chelate ring is nonplanar. The proton nmr spectrum of the pentafluoroethyl derivative $C_5H_5Co(C_2F_5)(C_3H_3N_2)_3BH$ indicates this compound to be a mixture of two stereoisomers in a 1:3 ratio which do not interconvert at temperatures up to 100°, where they begin to decompose. These two isomers of $C_5H_5Co(C_2F_5)(C_3H_3N_2)_3BH$, which were not separated on the chromatography column, exhibit not only distinctly different sets of resonances for both the coordinated and uncoordinated pyrazolyl ring protons but also distinctly different cyclopentadienyl resonances (chemical shift difference 0.47 ppm) for each isomer. The latter contrasts with the two isomers of $C_5H_5Co(C_3F_7)(C_3H_3N_2)_2BH_2$ which have a much smaller difference (0.14 ppm) in the chemical shifts of their cyclopentadienyl resonances. The proton nmr resonances from the more abundant isomer of $C_5H_5Co(C_2F_5)(C_3H_3N_2)_3BH$ (isomer A in Table IV) have essentially identical chemical shifts with the corresponding resonances found in the trifluoromethyl derivative $C_5H_5Co(CF_3)(C_3H_3N_2)_3BH$ whereas the resonances from the less abundant isomer of $C_5H_5Co(C_2F_5)(C_3H_3N_2)_3BH$ (isomer B in Table IV) have essentially identical chemical shifts with the corresponding resonances found in the heptafluoropropyl derivative $C_5H_5Co(C_3F_7)(C_3H_3N_2)_3BH$. Furthermore, the cyclopentadienyl resonances in the more abundant isomer of $C_5H_5Co(C_2F_5)(C_3H_3N_2)_3BH$ (isomer A) and in $C_5H_5Co(CF_3)(C_3H_3N_2)_3BH$ have essentially identical chemical shifts (within 0.1 ppm) with the cyclopentadienyl resonances in the bispyrazolylborate complexes $C_5H_5Co(R_f)(C_3H_3N_2)_2BH_2$ ($R_f = CF_3$, C_2F_5 , and $n-C_3F_7$) whereas the cyclopentadienyl resonances in the less abundant isomer of $C_5H_5Co(C_2F_5)(C_3H_3N_2)_3BH$ (isomer B) and $C_5H_5Co(C_3F_7)(C_3H_3N_2)_3BH$ have essentially identical chemical shifts (all within 0.07 ppm) with the cyclopentadienyl resonances in the tetrakispyrazolylborate complexes $C_5H_5Co(R_f)(C_3H_3N_2)_2B(C_3H_3N_2)_2$ ($R_f = C_2F_5$ and $n-C_3F_7$).

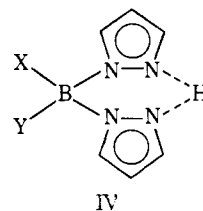
The large cyclopentadienyl chemical shift difference

between the two isomers of the trispyrazolylborate complex $C_5H_5Co(C_2F_5)(C_3H_3N_2)_3BH$ suggests that in at least one isomer the cyclopentadienyl ring must be in an axial position where it can be shielded by the uncomplexed pyrazolyl ring. The similarities in the cyclopentadienyl chemical shifts between those of $C_5H_5Co(CF_3)(C_3H_3N_2)_3BH$ and isomer A of $C_5H_5Co(C_2F_5)(C_3H_3N_2)_3BH$ and those of the bispyrazolylborate complexes $C_5H_5Co(R_f)(C_3H_3N_2)_2BH_2$ suggest that these trispyrazolylborate complexes must have the configuration IIIa with the cyclopentadienyl rings and hydrogen atoms in the axial positions. Furthermore the similarities in the cyclopentadienyl chemical shifts between those of $C_5H_5Co(C_3F_7)(C_3H_3N_2)_3BH$ and isomer B of $C_5H_5Co(C_2F_5)(C_3H_3N_2)_3BH$ and those of the tetrakispyrazolylborate complexes $C_5H_5Co(R_f)(C_3H_3N_2)_2B(C_3H_3N_2)_2$ suggest that these trispyrazolylborate complexes must have the configuration IIIb with the cyclopenta-



dienyl and uncomplexed pyrazolylborate rings in the axial positions. Our observations suggest that an isomer pair of the type IIa and IIb where the positions of a cyclopentadienyl ring and a perfluoroalkyl group bonded to a metal are interchanged can be separated readily by chromatography whereas an isomer pair of the type IIIa and IIIb where the positions of a pyrazolyl ring and a hydrogen atom bonded to a boron atom are interchanged cannot be separated readily by chromatography under normal conditions.

The major products from the reactions of the perfluoroalkylcobalt halides $C_5H_5Co(R_f)(CO)I$ with potassium tetrakispyrazolylborate are not the red complexes of the type $C_5H_5Co(R_f)(C_3H_3N_2)_2B(C_3H_3N_2)_2$ discussed above but brown-black boron-free complexes apparently of the stoichiometry $C_5H_5Co(R_f)(C_3H_3N_2)_2H$ (Table III). These complexes are diamagnetic (Faraday balance) and monomeric (molecular weight determinations in CH_2Cl_2) thereby making necessary the "extra" hydrogen atom. The proton nmr spectra of the $C_5H_5Co(R_f)(C_3H_3N_2)_2H$ complexes ($R = C_2F_5$, C_3F_7 and $(CF_3)_2CF$) indicate both pyrazolyl rings to be equivalent. The complexes $C_5H_5Co(R_f)(C_3H_3N_2)_2H$ are nonelectrolytes in nitromethane. All of these data taken together strongly suggest structure I for the $C_5H_5Co(R_f)(C_3H_3N_2)_2H$ derivatives. The bonding of the unique hydrogen atom in the cobalt complexes $C_5H_5Co(R_f)(C_3H_3N_2)_2H$ (I) to the two pyrazolyl rings may be similar to the "chelated proton" structure (*i.e.*, IV; X = Y = H or pyrazolyl or X = H, Y = pyrazolyl)

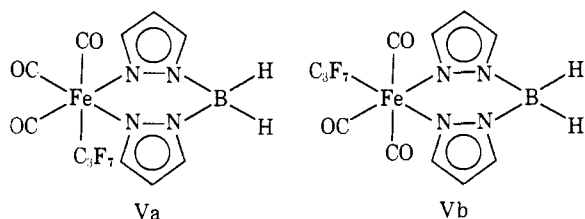


(11) S. Trofimenko, *J. Amer. Chem. Soc.*, **91**, 588 (1969).

suggested¹² 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 $C_3F_7Fe(CO)_3-$

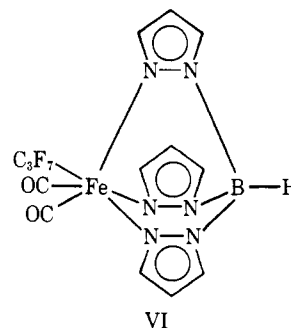


$(C_3H_3N_2)_2BH_2$ isolated from the reaction of $C_3F_7Fe(CO)_4I$ with potassium bispyrazolylborate indicates this material to consist of about $\sim 30\%$ of the facial isomer Va and about $\sim 70\%$ of the meridional isomer Vb. The sets of pyrazolyl resonances to be assigned to each isomer Va and 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 Polypyrazolylborates¹

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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° . 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 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 $(CH_3)_3Pt[(C_3H_3N_2)_2BH_2]_2[P(OCH_3)_3]$. Similar $(CH_3)_3Pt[(C_3H_3N_2)_2BH_2]_2L$ 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 derivatives³ 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).