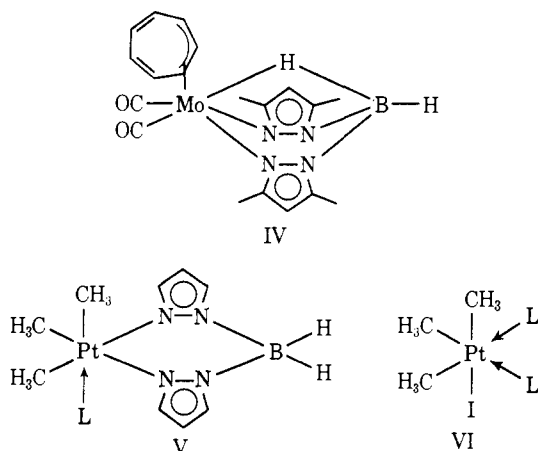


protons in the pyrazolyl rings of the polypyrazolylborate ligand and in the coordinated free pyrazole can be identified.

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  $(\text{CH}_3)_3\text{Pt}(\text{C}_3\text{H}_3\text{N}_2)_2\text{BH}_2 \cdot \text{L}$  (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, 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>

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

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

**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  $[\text{H}_2\text{B}(\text{C}_3\text{H}_3\text{N}_2)_2]_2\text{Fe}(\text{CO})_2$ . 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  $[\text{HB}(\text{C}_3\text{H}_3\text{N}_2)_3]_2\text{Fe}$ , (2) orange  $[\text{C}_3\text{H}_3\text{N}_2\text{Fe}(\text{CO})_2]_2$ , (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*- $\text{CH}_3\text{CH}=\text{CHFe}(\text{CO})_2(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$ , (5) yellow  $\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{Fe}(\text{CO})_2(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$ . The acyl derivative  $\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{Fe}(\text{CO})_2(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$  is decarbonylated quantitatively to the alkyl derivative *trans*- $\text{CH}_3\text{CH}=\text{CHFe}(\text{CO})_2(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$  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  $[\text{HB}(\text{CH}_3)_2\text{C}_3\text{HN}_2]_3\text{Fe}$  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  $\text{C}_3\text{F}_7\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_3\text{N}_2)_2\text{BH}_2$  and  $\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$ . 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).

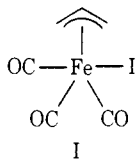
(3) A portion of this work was presented at the 24th Southeastern Regional Meeting of the American Chemical Society, Birmingham, Ala., Nov 1972; paper 180 in abstracts.

(4) Postdoctoral research associate 1971-1973.

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

reactions with various polypyrazolylborates.<sup>6</sup> Mixed allylmetal polypyrazolylborate complexes are known for metals other than iron such as molybdenum in compounds of the types (allylic)Mo(CO)<sub>2</sub>(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>BH<sup>7</sup> and (allylic)Mo(CO)<sub>2</sub>((CH<sub>3</sub>)<sub>2</sub>C<sub>3</sub>HN<sub>2</sub>)<sub>2</sub>BH<sub>2</sub><sup>8</sup> and palladium in the compound C<sub>3</sub>H<sub>5</sub>Pd(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>BH. The palladium compound is obtained from [C<sub>3</sub>H<sub>5</sub>PdCl]<sub>2</sub> and potassium trispyrazolylborate thereby providing a precedent for the reaction of an allylmetal halide with a polypyrazolylborate to give an allylmetal polypyrazolylborate.

This paper describes the details of our studies on reactions of allyliron tricarbonyl iodide (I) with various



polypyrazolylborates. Such reactions failed to give any iron complexes containing both allyl groups and polypyrazolylborate ligands. However, the following unusual features were observed in our study of reactions of allyliron tricarbonyl iodide with various polypyrazolylborates: (a) isomerization of the  $\pi$ -allyl group to a  $\sigma$ -propenyl group, (b) cleavage of a pyrazolyl ring from the polypyrazolylborate anion to give either a pyrazolylmetal carbonyl complex or an allylpyrazole metal carbonyl complex.

## Experimental Section

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, Atlantic Microanalytical Laboratory, Atlanta, Ga., Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., 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. In addition, the  $\nu$ (CO) regions of the infrared spectra were taken in a saturated hydrocarbon solvent such as hexane (unless otherwise specified). Each infrared spectrum was calibrated against the 1601-cm<sup>-1</sup> band of polystyrene film. Proton nmr spectra were taken at 100 MHz on a Varian HA-100 spectrometer in the indicated solvents.

A nitrogen atmosphere was routinely 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. Diethyl ether and tetrahydrofuran were purified by distillation under nitrogen over sodium benzophenone ketyl.

**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) and K[(3,5-(CH<sub>3</sub>)<sub>2</sub>C<sub>3</sub>HN<sub>2</sub>)<sub>3</sub>BH] were prepared by the published procedures<sup>9</sup> from potassium borohydride and pyrazole or 3,5-dimethylpyrazole, respectively. Allyliron tricarbonyl iodide (I) was prepared by reaction of Fe(CO)<sub>5</sub> with allyl iodide.<sup>10</sup>

**Reaction of C<sub>3</sub>H<sub>5</sub>Fe(CO)<sub>3</sub>I with Potassium Bispyrazolylborate.** A mixture of 1.5 g (5.4 mmol) of C<sub>3</sub>H<sub>5</sub>Fe(CO)<sub>3</sub>I (I), 1.86 g (10 mmol) of potassium bispyrazolylborate, 40 ml of diethyl ether, and 40 ml of tetrahydrofuran was stirred for 3 hr at room temperature. Solvent was then removed at ~25° (35 mm). The residue was extracted with hexane. The filtered and concentrated hexane extracts were chromatographed on a 2 × 60 cm alumina column. A trace of unreacted C<sub>3</sub>H<sub>5</sub>Fe(CO)<sub>3</sub>I was first eluted with hexane. The major orange-yellow band of the product was eluted with 1:9 diethyl

ether-hexane. Evaporation of this eluate at ~25° (35 mm) followed by low temperature crystallization from hexane gave 0.94 g (44% yield) of yellow-orange [H<sub>2</sub>B(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>]<sub>2</sub>Fe(CO)<sub>2</sub>: mp 88°; infrared spectrum (cm<sup>-1</sup>)  $\nu$ (BH) frequencies at 2440 (m, br), 2365 (w), and 2298 (w);  $\nu$ (CO) frequencies at 2088 (s) and 2042 (s); other bands at 1507 (w), 1440 (w), 1414 (s), 1310 (m), 1221 (m), 1202 (m), 1198 (m), 1166 (m), 1153 (s), 1103 (w), 1076 (m), 1066 (s), 994 (w), 983 (vw), 902 (w), 888 (m), 776 (m), 761 (s), and 719 (m); proton nmr spectrum (CDCl<sub>3</sub> solution) unresolved resonances at  $\tau$  2.32, 2.70, 3.80, 4.04, and 4.50 of relative intensities 2:1:1:1:1, respectively.

*Anal.* Calcd for C<sub>14</sub>H<sub>16</sub>B<sub>2</sub>FeN<sub>4</sub>O<sub>2</sub>: C, 41.4; H, 3.9; N, 27.6. Found: C, 41.2; H, 4.0; N, 27.7.

**Reaction of C<sub>3</sub>H<sub>5</sub>Fe(CO)<sub>3</sub>I with Potassium Trispyrazolylborate.** A mixture of 8.0 g (26 mmol) of C<sub>3</sub>H<sub>5</sub>Fe(CO)<sub>3</sub>I, 8.0 g (32 mmol) of potassium trispyrazolylborate, 100 ml of tetrahydrofuran, and 100 ml of diethyl ether was stirred for 3 hr at room temperature. Solvent was then removed from the reaction mixture at ~25° (35 mm). The residue was extracted with 200 ml of diethyl ether in two portions. The diethyl ether extracts were chromatographed as described below. The residue from the diethyl ether extraction was extracted with 100 ml of dichloromethane in two portions. The dichloromethane extracts were treated with an equal volume of hexane and solvent slowly removed at ~35 mm. The light violet crystals were filtered and dried to give 4.2 g (56% yield) of the known<sup>11</sup> [HB(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>]<sub>2</sub>Fe identified by its infrared spectrum and elemental analysis.

*Anal.* Calcd for C<sub>18</sub>H<sub>16</sub>B<sub>2</sub>FeN<sub>6</sub>: C, 44.9; H, 4.1; N, 35.5. Found: C, 44.6; H, 4.2; N, 35.6.

The diethyl ether extracts were concentrated to 20 ml and then chromatographed on a 2 × 60 cm alumina column. The following compounds were eluted from this chromatogram in the order listed with the indicated solvents as eluents.

**A. Orange [C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>Fe(CO)<sub>3</sub>]<sub>2</sub>, Mp 103° (0.14 g, 2.6% yield).** This compound was eluted with hexane and purified by low temperature crystallization from hexane: infrared spectrum (cm<sup>-1</sup>)  $\nu$ (CH) frequency at 2923 (w);  $\nu$ (CO) frequencies at 2088 (s), 2049 (vs), 2014 (vs), and 1994 (w); other bands at 1480 (w), 1408 (w), 1400 (w), 1381 (m), 1300 (w), 1263 (vw), 1187 (w), 1060 (m), 1054 (m), 860 (vw), 748 (m), 741 (m), and 733 (m); proton nmr spectrum (CS<sub>2</sub> solution) unresolved resonances at  $\tau$  2.85 and 4.00 of approximate relative intensities 2:1, respectively.

*Anal.* Calcd for C<sub>12</sub>H<sub>6</sub>Fe<sub>2</sub>N<sub>4</sub>O<sub>6</sub>: C, 34.7; H, 1.4; N, 13.5; mol wt, 414. Found: C, 34.8; H, 1.4; N, 13.6; mol wt, 444 (benzene).

**B. Yellow (C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>C<sub>3</sub>H<sub>3</sub>)Fe(CO)<sub>3</sub>, Mp 61° (0.37 g, 4% yield).** This compound was eluted with hexane and purified by low temperature crystallization from hexane: infrared spectrum (cm<sup>-1</sup>)  $\nu$ (CH) frequencies at 3159 (m), 3146 (m), 3125 (w), 3058 (m), 3033 (w), 3000 (w), 2951 (w), and 2893 (w);  $\nu$ (CO) frequencies at 2036 (s), 1957 (s), and 1951 (s); other bands at 1512 (w), 1459 (m), 1453 (m), 1418 (w), 1406 (m), 1368 (w), 1308 (w), 1300 (w), 1263 (m), 1233 (w), 1199 (s), 1180 (w), 1094 (m), 1061 (m), 995 (vw), 969 (w), 932 (w), 904 (m), 876 (w), 858 (vw), 833 (w), 751 (s), and 742 (m); proton nmr spectrum (CS<sub>2</sub> solution) resonances at  $\tau$  2.53 (singlet), 2.86 (singlet), 3.88 (singlet), 5.42 (doublet, *J* = 12 Hz), 5.63 (doublet, *J*<sub>1</sub> = 12, *J*<sub>2</sub> = 3 Hz), 6.29 (triplet of doublets, *J*<sub>T</sub> = 8, *J*<sub>D</sub> = 3 Hz), 7.81 (double doublet, *J*<sub>1</sub> = 9, *J*<sub>2</sub> = 2 Hz), and 8.72 (double doublet, *J*<sub>1</sub> = 10, *J*<sub>2</sub> = 2 Hz) of approximate relative intensities 1:1:1:2:1:1:1, respectively.

*Anal.* Calcd for C<sub>9</sub>H<sub>6</sub>FeN<sub>2</sub>O<sub>3</sub>: C, 43.6; H, 3.2; N, 11.3. Found: C, 43.7; H, 3.4; N, 11.7.

**C. Yellow CH<sub>3</sub>CH=CHFe(CO)<sub>2</sub>(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>BH, Mp 131° (0.07 g, ~1% yield).** This compound was eluted with a 1:1 mixture of diethyl ether and hexane and purified by low temperature crystallization from hexane. It was identified by comparison of its infrared and proton nmr spectra with those of authentic CH<sub>3</sub>CH=CHFe(CO)<sub>2</sub>(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>BH (see below) prepared by pyrolysis of the acyl derived CH<sub>3</sub>CH=CHC(O)Fe(CO)<sub>2</sub>(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>BH.

**D. Yellow CH<sub>3</sub>CH=CHC(O)Fe(CO)<sub>2</sub>(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>BH, Mp 126° (2.68 g, 28% yield).** This compound was eluted with a 1:1 mixture of diethyl ether and hexane and purified by low temperature crystallization from hexane: infrared spectrum (cm<sup>-1</sup>)  $\nu$ (CH) frequency at 3130 (w);  $\nu$ (BH) frequency at 2500 (m);  $\nu$ (CO) frequencies at 2051 (vs), 2038 (vs), 1988 (vs), 1972 (vs), and 1610 (vs); other bands at 1505 (m), 1412 (s), 1399 (s), 1316 (s), 1271 (w), 1219 (s), 1119 (s), 1101 (m), 1079 (m), 1050 (s), 1001 (m), 988 (m), 963

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(m), 931 (m), 896 (m), 880 (w), 847 (w), 823 (w), 798 (m), 782 (m), 767 (s), 759 (s), 732 (m), 719 (s), 715 (s), and 659 (s); proton nmr spectrum ( $C_6D_6$  solution) resonances at  $\tau$  2.47 (doublet,  $J = 2$  Hz), 2.70 (doublet,  $J = 2$  Hz), 2.74 (doublet,  $J = 2$  Hz), 3.91 (quartet,  $J = 6.0$  Hz), 4.06 (multiplet,  $J = 1.2$  Hz), 4.22 (triplet,  $J = 2$  Hz), and 8.80 (double doublet,  $J_1 = 6.0$ ,  $J_2 = 1.2$  Hz), of approximate relative intensities 2:3:1:1:1:3:3, respectively.

*Anal.* Calcd for  $C_{11}H_{12}FeN_2O_3$ : C, 45.7; H, 3.8; Fe, 14.0; N, 21.4; O, 12.2; mol wt, 394. Found: C, 46.7; H, 4.0, 4.2; Fe, 14.0; N, 21.9, 21.7; O, 12.1; mol wt, 367 (methyl ethyl ketone).

**Reaction of Allylpyrazole with  $Fe_2(CO)_9$ .** A mixture of 3.65 g (10 mmol) of  $Fe_2(CO)_9$ ,<sup>12</sup> 1.08 g (10 mmol) of *N*-allylpyrazole,<sup>13</sup> and 50 ml of hexane was stirred for 3 hr. Solvent was removed from the filtered reaction mixture at 25° (35 mm). The residue was dried for 3 hr at ~25° (0.1 mm). A solution of this residue in ~10 ml of 1:9 diethyl ether-hexane was chromatographed on a 2 × 60 cm alumina column. The yellow band was eluted with 1:9 diethyl ether-hexane and the eluate evaporated at ~25° (35 mm). The residue was purified by low temperature crystallization to give 0.39 g (15% yield) of yellow crystalline  $(C_3H_5N_2C_3H_3)Fe(CO)_3$ , mp 61°, with identical infrared spectra, proton nmr spectra, and elemental analyses (C, H, and N) with the product isolated from the reaction of  $C_3H_5Fe(CO)_3I$  with potassium trispyrazolylborate.

**Pyrolysis of  $CH_3CH=CHC(O)Fe(CO)_2(C_3H_3N_2)_3BH$ .** A solution of 0.5 g (1.27 mmol) of  $CH_3CH=CHC(O)Fe(CO)_2(C_3H_3N_2)_3BH$  in 100 ml of cyclohexane was boiled under reflux for 20 min. Solvent was then removed at ~25° (35 mm) and the residue chromatographed on a 2 × 60 cm alumina column in diethyl ether-hexane solution. The yellow band was eluted with 1:4 diethyl ether-hexane. Evaporation of the eluate at ~25° (35 mm) followed by low temperature crystallization from hexane gave 0.47 g (94% yield) of  $CH_3CH=CHFe(CO)_2(C_3H_3N_2)_3BH$ : mp 131°; infrared spectrum ( $cm^{-1}$ )  $\nu(CH)$  frequencies at 3146 (vw), 3132 (vw), 2980 (w), 2933 (w), 2912 (w), 2880 (vw), and 2856 (w);  $\nu(BH)$  frequency at 2490 (m);  $\nu(CO)$  frequencies at 2038 (s) and 1978 (s); other bands at 1500 (m), 1431 (m), 1411 (s), 1398 (s), 1313 (s), 1215 (s), 1185 (m), 1110 (s), 1073 (m), 1045 (s), 982 (m), 961 (m), 794 (m), 768 (m), 758 (s), 722 (m), and 712 (s); proton nmr spectrum ( $CS_2$  solution) resonances at  $\tau$  2.38 (doublet;  $J = 2$  Hz), 2.43 (doublet,  $J = 2$  Hz), 2.49 (doublet,  $J = 2$  Hz), 3.90 (triplet,  $J = 2$  Hz), 3.91 (doublet of quartets;  $J_D = 15.4$ ,  $J_Q = 1.3$  Hz), 4.45 (doublet of quartets;  $J_D = 15.4$ ,  $J_Q = 6.0$  Hz), and 8.16 (double doublet;  $J_1 = 6.0$ ,  $J_2 = 1.3$  Hz) of approximate relative intensities 2:1:3:3:1:1:3, respectively.

*Anal.* Calcd for  $C_{11}H_{13}BF_2FeN_3O_2$ : C, 45.9; H, 4.1; Fe, 15.3; N, 22.9; O, 8.7; mol wt, 366. Found: C, 46.0, H, 4.2; Fe, 14.9; N, 22.8; O, 8.7; mol wt, 381 (methyl ethyl ketone).

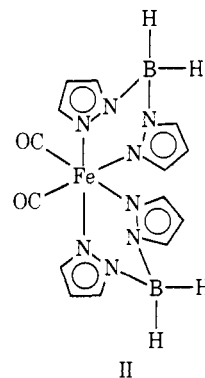
**Reaction of  $C_3H_5Fe(CO)_3I$  with Potassium Tris(3,5-dimethylpyrazolyl)borate.** A mixture of 6.0 g (19.5 mmol) of  $C_3H_5Fe(CO)_3I$ , 8.0 g (24 mmol) of potassium tris(3,5-dimethylpyrazolyl)borate, 100 ml of diethyl ether, and 100 ml of tetrahydrofuran was stirred for 2 hr at room temperature. The reaction mixture was filtered and solvent removed from the filtrate at ~25° (35 mm). The residue was extracted with 100 ml of diethyl ether in two portions. The purple insoluble solid residue from the diethyl ether extraction after crystallization from dichloromethane gave 4.93 g (63% yield) of  $[HB((CH_3)_2C_3HN_2)_3]_2Fe$ , identical by its infrared spectrum with authentic  $[HB((CH_3)_2C_3HN_2)_3]_2Fe$  obtained by mixing a solution of 0.5 g of ferrous sulfate in 50 ml of water with a solution of 0.5 g of potassium tris(3,5-dimethylpyrazolyl)borate in 20 ml of acetone.

The diethyl ether extract was concentrated to 10 ml and chromatographed on a 2 × 60 cm alumina column. Hexane first eluted an orange compound in insufficient quantity for identification. Further elution with 1:19 diethyl ether-hexane gave a yellow product. Evaporation of the eluate followed by low temperature crystallization of the residue from hexane gave 0.731 g (13.5% yield) of yellow  $[C_3H_3N_2C_3H(CH_3)_2]Fe(CO)_3$ : mp 58°; infrared spectrum ( $cm^{-1}$ )  $\nu(CH)$  bands too weak to be unequivocally observed;  $\nu(CO)$  bands at 2036 (s) and 1943 (vs); other bands at 1550 (w), 1543 (w), 1463 (m), 1444 (vw), 1418 (w), 1394 (w), 1266 (w), 1236 (m), 797 (m), and 666 (w) proton nmr spectrum ( $C_6D_6$  solution) resonances at  $\tau$  4.76 (singlet), 6.20 (doublet,  $J = 12$  Hz), ~6.4 (broad), 6.61 (doublet,  $J = 12$  Hz), 7.83 (doublet,  $J = 8$  Hz), 7.92 (singlet), 8.48 (singlet), and 8.72 (doublet,  $J = 9$  Hz) of approximate relative intensities 1:1:1:1:1:3:3:1, respectively.

*Anal.* Calcd for  $C_{11}H_{12}FeN_2O_3$ : C, 49.6; H, 4.5; N, 10.5. Found: C, 49.5; H, 4.6; N, 10.4.

## Discussion

The reaction between  $C_3H_5Fe(CO)_3I$  and potassium bispyrazolylborate at room temperature resulted not only in replacement of iodide but also in displacement of the allyl group and decarbonylation to give *cis*- $[H_2B(C_3H_3N_2)_2]_2Fe(CO)_2$  (II). The infrared spectrum



of this complex exhibited the two  $\nu(CO)$  frequencies expected for a *cis*- $L_4M(CO)_2$  derivative. The proton nmr spectrum confirmed the absence of an allyl group and the presence of two different types of pyrazolyl rings in equal quantities. This is consistent with the expected nonequivalence of the pair of pyrazolyl rings trans to carbonyl groups relative to the pair of pyrazolyl rings trans to each other.

The reaction between  $C_3H_5Fe(CO)_3I$  and potassium trispyrazolylborate gave the known<sup>11</sup> simple iron(II) derivative  $[HB(C_3H_3N_2)_3]_2Fe$  as the major product similar to the reported<sup>14</sup> reaction between  $C_3H_5Fe(CO)_2I$  and potassium trispyrazolylborate. However, the reaction of  $C_3H_5Fe(CO)_3I$  and potassium trispyrazolylborate besides giving  $[HB(C_3H_3N_2)_3]_2Fe$  as the major product also gave several novel minor products which could be separated by column chromatography. The formation of some of these products clearly involves cleavage of the boron-pyrazolyl bond similar to the formation<sup>5</sup> of the compounds  $C_3H_5Co(R_f)(C_3H_3N_2)_2H$  ( $R_f = C_2F_5$ ,  $C_3F_7$ , and  $(CF_3)_2CF$ ) from the corresponding  $C_3H_5Co(CO)(R_f)I$  derivatives and potassium tetrakispyrazolylborate.

The first of these minor products to be eluted from the chromatogram of the  $C_3H_5Fe(CO)_3I-K[HB(C_3H_3N_2)_3]$  reaction mixture is an orange solid of the stoichiometry  $[C_3H_3N_2Fe(CO)_3]_2$ . The infrared spectrum of this compound exhibits no  $\nu(BH)$  frequencies and  $\nu(CO)$  frequencies at 2088, 2049, 2014, and 1994  $cm^{-1}$  which are similar to the  $\nu(CO)$  frequencies for other  $[LFe(CO)_3]_2$  compounds (e.g., reported<sup>15</sup>  $\nu(CO)$  for  $[C_6H_5SFe(CO)_3]_2$  in  $CS_2$ : 2073, 2036, 2003, and 1994  $cm^{-1}$ ). The proton nmr spectrum of  $[C_3H_3N_2Fe(CO)_3]_2$  exhibits singlet resonances at  $\tau$  2.85 and 4.00 of relative intensities 2:1 which may be assigned to the four protons on carbons adjacent to nitrogen atoms and the two protons on carbons not adjacent to nitrogen atoms in two equivalent pyrazolyl rings with two equivalent ends of each pyrazolyl ring. These data are in accord with structure III for the complex  $[C_3H_3N_2Fe(CO)_3]_2$ .

(12) E. H. Bray and W. Hübel, *Inorg. Syn.*, **8**, 178 (1966).

(13) I. L. Finar and K. Utting, *J. Chem. Soc.*, 5272 (1960).

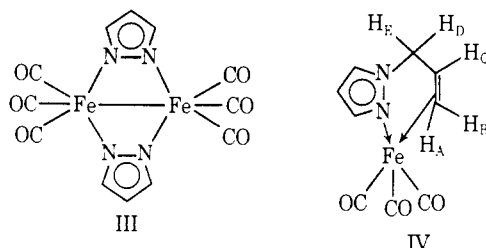
(14) Footnote 23 of ref 6.

(15) E. Kostiner, M. L. N. Reddy, D. S. Urch, and A. G. Massey, *J. Organometal. Chem.*, **15**, 383 (1968).

The presence of an iron-iron bond in III is necessary to give each iron atom the favored rare gas electronic configuration consistent with the diamagnetism indicated by the proton nmr spectrum.

A possibly similar  $[\text{C}_3\text{H}_3\text{N}_2\text{Fe}(\text{CO})_3]_2$  has been mentioned<sup>16</sup> as a reaction product of  $\text{Fe}_2(\text{CO})_9$  or  $\text{Fe}_3(\text{CO})_{12}$  with pyrazole but insufficient data are given for comparison of this reported compound with our  $[\text{C}_3\text{H}_3\text{N}_2\text{Fe}(\text{CO})_3]_2$ .

The second product to be eluted from the chromatogram of the  $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}-\text{K}[\text{HB}(\text{C}_3\text{H}_3\text{N}_2)_3]$  reaction mixture is a yellow solid  $(\text{C}_3\text{H}_3\text{N}_2\text{C}_3\text{H}_5)\text{Fe}(\text{CO})_3$ . The infrared spectrum of this compound exhibits  $\nu(\text{CO})$  frequencies at 2036, 1957, and 1951  $\text{cm}^{-1}$  similar to those found in (diene) $\text{Fe}(\text{CO})_3$  derivatives (e.g., reported<sup>17</sup>  $\nu(\text{CO})$  for the butadiene complex  $\text{C}_4\text{H}_6\text{Fe}(\text{CO})_3$ : 2051 and 1978  $\text{cm}^{-1}$ ). However, the splitting of the lower infrared  $\nu(\text{CO})$  frequency suggests that the two ends of the  $(\text{C}_3\text{H}_3\text{N}_2\text{C}_3\text{H}_5)$  donor unit are rather different. Structure IV for  $(\text{C}_3\text{H}_3\text{N}_2\text{C}_3\text{H}_5)\text{Fe}(\text{CO})_3$



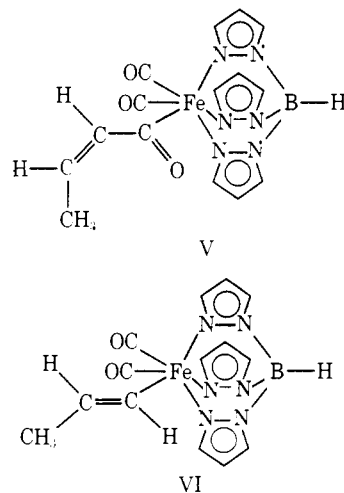
based on *N*-allylpyrazole is an obvious possibility; this proposal is strongly supported by the synthesis of the same  $(\text{C}_3\text{H}_3\text{N}_2\text{C}_3\text{H}_5)\text{Fe}(\text{CO})_3$  from *N*-allylpyrazole and  $\text{Fe}_2(\text{CO})_9$ .

The proton nmr spectrum of  $(\text{C}_3\text{H}_3\text{N}_2\text{C}_3\text{H}_5)\text{Fe}(\text{CO})_3$  also supports structure IV. The resonances at  $\tau$  2.53, 2.86, and 3.88 may be assigned to the three protons of the pyrazolyl rings. The pair of doublets at  $\tau$  5.42 and 5.63 may be assigned to the coupled ( $J = 12$  Hz) pair of geminal complexed olefinic protons ( $\text{H}_A$  and  $\text{H}_B$  in IV). The further splitting ( $J = 3$  Hz) of the  $\tau$  5.63 doublet can arise from the coupling of one of the geminal complexed olefinic protons of the allyl group with the remaining complexed olefinic proton; the resonance of the last complexed olefinic proton ( $\text{H}_C$  in III) appears at  $\tau$  6.29 as an incompletely resolved triplet of doublets. The double doublets at  $\tau$  7.81 and 8.72 can be assigned to the two coupled ( $J = 2$  Hz) saturated protons of the allyl group ( $\text{H}_D$  and  $\text{H}_E$  in IV) which each are split ( $J = 9-10$  Hz) by coupling with the center complexed olefinic proton ( $\text{H}_C$  in IV).

The remaining two iron carbonyl derivatives obtained from the reaction between  $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}$  and potassium trispyrazolylborate are yellow compounds of the stoichiometries  $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$  and  $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_2(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$ . The dicarbonyl derivative exhibits the expected two strong metal carbonyl  $\nu(\text{CO})$  frequencies at 2038 and 1978  $\text{cm}^{-1}$ . The tricarbonyl exhibits two pairs of similar metal carbonyl  $\nu(\text{CO})$  frequencies at 2051 and 1988 and 2038 and 1972  $\text{cm}^{-1}$  apparently arising from conformational isomers

like those reported<sup>18</sup> for  $\text{CH}_3\text{SiCl}_2\text{Fe}(\text{CO})_2\text{C}_3\text{H}_5$  as well as a lower carbonyl  $\nu(\text{CO})$  frequency at 1610  $\text{cm}^{-1}$  assignable to an acyl carbonyl. This tricarbonyl is thus an acyl derivative of the type  $\text{C}_3\text{H}_5\text{COFe}(\text{CO})_2(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$  rather than a true iron tricarbonyl derivative  $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$ . The formulation of  $\text{C}_3\text{H}_5\text{COFe}(\text{CO})_2(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$  and  $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$  as a pair of acyl and alkyl derivatives related by decarbonylation is supported by the facile conversion of  $\text{C}_3\text{H}_5\text{COFe}(\text{CO})_2(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$  to  $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_2(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$  by heating in boiling cyclohexane. This decarbonylation of a  $\text{RCOFe}(\text{CO})_2(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$  derivative to the corresponding  $\text{RFe}(\text{CO})_2(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$  derivative proceeds under much milder conditions than the decarbonylations of similar  $\text{RCOFe}(\text{CO})_2\text{C}_3\text{H}_5$  derivatives to the corresponding  $\text{RFe}(\text{CO})_2\text{C}_3\text{H}_5$  derivatives which require ultraviolet irradiation,<sup>19</sup> mere heating being insufficient.

The proton nmr spectra of  $\text{C}_3\text{H}_5\text{COFe}(\text{CO})_2(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$  and  $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_2(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$  indicate that in both compounds the  $\text{C}_3\text{H}_5$  portions correspond to propenyl rather than allyl groups. In the acyl derivative  $\text{C}_3\text{H}_5\text{COFe}(\text{CO})_2(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$  the resonances at  $\tau$  2.47, 2.70, 2.74, and 4.22 may be assigned to the protons of the three pyrazolyl rings. These three pyrazolyl rings are of two distinct types since two of them are trans to carbonyl groups and the third ring is trans to the  $\text{C}_3\text{H}_5\text{CO}$  group; this nonequivalence is reflected in the observation of four rather than only three distinct pyrazolyl ring proton resonances. The remaining resonances in  $\text{C}_3\text{H}_5\text{COFe}(\text{CO})_2(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$  are a clean quartet at  $\tau$  3.91, a multiplet which could be another quartet at  $\tau$  4.06, and a double doublet at  $\tau$  8.80. This is consistent only with the formulation of the  $\text{C}_3\text{H}_5$  moiety in this complex as a propenyl group  $\text{CH}_3\text{CH}=\text{CH}$  where the double doublet at  $\tau$  8.80 is assigned to the three methyl protons split differently by the two nonequivalent olefinic protons and the multiplets at  $\tau$  3.91 and 4.06 to the olefinic protons which are each split into quartets by the three methyl protons. The complex  $\text{C}_3\text{H}_5\text{COFe}(\text{CO})_2(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$  is thus formulated as the propenylcarbonyl derivative  $\text{CH}_3\text{CH}=\text{CHCOFe}(\text{CO})_2(\text{C}_3\text{H}_3\text{N}_2)_3\text{BH}$  (V). The ob-



servations of the olefinic resonances of the propenyl

(16) V. N. Babin, L. A. Fedorov, N. S. Kochetkova, and Yu. A. Belousov, paper presented at the 5th International Conference on Organometallic Chemistry, Moscow, Aug 1971; paper 390 on p 429, Vol. II, of Abstracts.

(17) B. F. Hallam and P. J. Pauson, *J. Chem. Soc.*, 642 (1958).

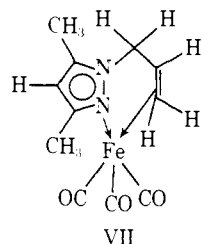
(18) W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **89**, 2773 (1967).

(19) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964).

group in V as simple quartets rather than double quartets suggests that the vicinal olefinic coupling constant is very small in accord with formulation of the propenylcarbonyl group as the indicated (V) isocrotonyl derivative (cis isomer) rather than the isomeric crotonyl derivative (trans isomer).<sup>20</sup>

Analysis of the proton nmr spectrum of  $C_3H_5Fe(CO)_2(C_3H_3N_2)_3BH$  is entirely analogous to the analysis of the proton nmr spectrum of  $C_3H_5COFe(CO)_2(C_3H_3N_2)_3BH$  (V) given above and shows that the  $C_3H_5$  moiety in  $C_3H_5Fe(CO)_2(C_3H_3N_2)_3BH$  again must be a propenyl rather than an allyl group indicating that this complex is  $CH_3CH=CHFe(CO)_2(C_3H_3N_2)_3BH$  (VI). However, the olefinic resonances of the propenyl group in VI are not simple quartets but double quartets with a vicinal coupling constant of 15.4 Hz in the range of trans vicinal olefinic coupling (12–19 Hz) rather than cis vicinal olefinic coupling (<12 Hz) in accord with formulation of  $CH_3CH=CHFe(CO)_2(C_3H_3N_2)_3BH$  as the indicated *trans*-propenyl derivative (VI) rather than the corresponding *cis*-propenyl derivative. Decarbonylation of  $CH_3CH=CHC(O)Fe(CO)_2(C_3H_3N_2)_3BH$  (IV) to  $CH_3CH=CHFe(CO)_2(C_3H_3N_2)_3BH$  (VI) thus appears to involve the essentially quantitative conversion of a *cis*-propenyl group to a *trans*-propenyl group.

The reaction between  $C_3H_5Fe(CO)_3I$  and the more sterically hindered potassium bis(3,5-dimethylpyrazolyl)borate was also investigated. As in the case of the corresponding reaction with the unsubstituted potassium trispyrazolylborate the major product is the simple iron(II) derivative of the type  $(HBPz_3)_2Fe$  with 3,5-dimethylpyrazolyl rings. The only other product obtained in identifiable quantities is a yellow solid  $[(CH_3)_2C_3HN_2C_3H_5]Fe(CO)_3$  apparently with structure VII completely analogous to the yellow complex  $(C_3H_3N_2C_3H_5)Fe(CO)_3$  (IV) discussed above. The resonances at  $\tau$  6.20,  $\sim$ 6.4, 6.61, 7.83, and 8.72 in the proton nmr spectrum of  $[(CH_3)_2C_3HN_2C_3H_5]Fe(CO)_3$  (VII) may be assigned to the five protons of the allyl



group and correspond to the resonances at  $\tau$  5.42, 6.29, 5.63, 7.81, and 8.72 in the proton nmr spectrum of  $(C_3H_3N_2C_3H_5)Fe(CO)_3$  (IV). The remaining resonances at  $\tau$  4.76, 7.92, and 8.48 (all singlets) may be assigned to the ring proton and the two methyl groups, respectively, of the dimethylpyrazolyl ring. No products corresponding to V and VI were isolated from the reaction of  $C_3H_5Fe(CO)_3I$  with potassium bis(3,5-dimethylpyrazolyl)borate. A very small orange band in the chromatogram of the mixture from this reaction may be an analog of III, but this was obtained in insufficient quantities for identification.

Figure 1 suggests a scheme for the reactions of

(20) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon, Oxford, 1966, pp 710–711.

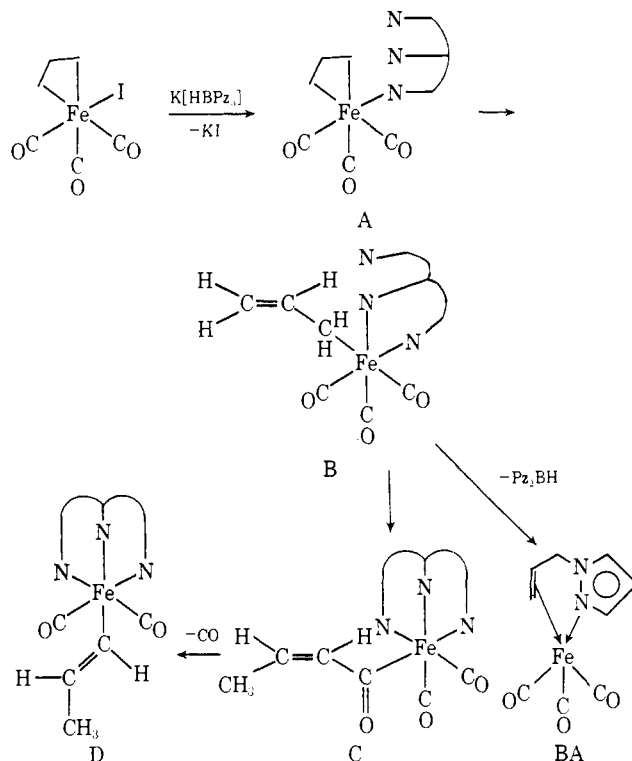


Figure 1. Proposed scheme for the reaction between allyliron tricarbonyl iodide and potassium trispyrazolylborate.

$C_3H_5Fe(CO)_3I$  with trispyrazolylborates which is consistent with experimental observations. In the first step the trispyrazolylborate anion replaces the iodide in  $C_3H_5Fe(CO)_3I$  to give the product A (not isolated) with a monodentate trispyrazolylborate ligand. A second nitrogen of the trispyrazolylborate ligand then partially displaces the allyl group converting the trihapto<sup>21</sup> allyl group into a monohapto<sup>21</sup> allyl group to give the product B (also not isolated) with a bidentate trispyrazolylborate ligand. The third nitrogen of the trispyrazolylborate ligand then displaces the monohapto allyl group in B. However, this allyl group is not lost completely but instead migrates to an adjacent carbonyl group to form an acyl derivative C. However, during this allyl migration a 1,3-hydrogen shift occurs thereby converting the allyl group to a propenyl group. The acyl derivative C corresponds to the first isolated compound  $CH_3CH=CHC(O)Fe(CO)_2(C_3H_3N_2)_3BH$  (V) of this sequence. This acyl derivative (C in Figure 1) can then undergo decarbonylation by the usual migration of an alkyl from a carbonyl group to the metal atom to give the propenyl derivative D corresponding to the isolated compound  $CH_3CH=CHFe(CO)_2(C_3H_3N_2)_3BH$  (VI).

The boron-free products of the type  $(PzCH_2CH=CH_2)_2Fe(CO)_3$  (*i.e.*, IV and VII; Pz = pyrazolyl ring) can arise from a branching of the scheme indicated in Figure 1 to give the product BA. In the case of the reaction of  $C_3H_5Fe(CO)_3I$  with potassium tris(3,5-dimethylpyrazolyl)borate, the reaction appears to proceed exclusively along this branch of the scheme in Figure 1 with exclusion of the other branch leading to products C and D. Whether this difference in the course of the reactions of  $C_3H_5Fe(CO)_3I$  with potassium

(21) For a summary of the "hapto" system of nomenclature see F. A. Cotton, *J. Amer. Chem. Soc.*, **90**, 6230 (1968).

trispirazolyborate or with potassium tris(3,5-dimethylpyrazolyl)borate arises from weaker acidity of bis(3,5-dimethylpyrazolyl)borane because of the electron-releasing effect of the methyl substituents on the pyrazolyl rings or from the increased steric demands of three 3,5-dimethylpyrazolyl rings relative to three pyrazolyl rings is presently unclear.

The major products from reactions between  $C_3H_5Fe(CO)_3I$  and potassium trispirazolyborates are the iron(II) complexes  $(HBPz_3)_2Fe$  where all of the ligands originally bonded to the iron atom (*i.e.*, allyl, carbonyl, and iodine) have been displaced by trispirazolyborate ligands. These products are not listed in the scheme in Figure 1, since their origin is ambiguous. The  $(HBPz_3)_2Fe$  compounds may arise from displacement of the propenyl and two carbonyl groups in an intermediate of type D with a second trispirazolyborate anion or by displacement of the allyl group in an inter-

mediate of type A with a second trispirazolyborate anion followed by attack of the uncomplexed nitrogen atoms of both trispirazolyborate ligands on the metal atom with loss of all of the carbonyl groups. The latter pathway is made more probable by the observed reaction of  $C_3H_5Fe(CO)_3I$  with potassium bispyrazolyborate to give the dicarbonyl *cis*- $[H_2B(C_3H_3N_2)_2]_2Fe(CO)_2$  (II). In the bispyrazolyborate system there are insufficient nitrogens on the bispyrazolyborate ligands after displacement of both the allyl and iodine in  $C_3H_5Fe(CO)_3I$  to replace all of the carbonyl groups then remaining on the iron. In this system two carbonyl groups must remain on the iron atom after all available nitrogen atoms for coordination from the bispyrazolyborate ligands are used.

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

## Structure of the $10\pi$ Electron Cyclooctatetraene Dianion in Potassium Diglyme 1,3,5,7-Tetramethylcyclooctatetraene Dianion, $[K((CH_3OCH_2CH_2)_2O)]_2[C_8H_4(CH_3)_4]$

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**Abstract:** The structure of the potassium salt of a cyclooctatetraene dianion has been determined. As predicted by the Hückel theory this  $10\pi$  electron system is aromatic with eightfold molecular symmetry and average C-C bond lengths of 1.407 (6) Å. Yellow air-sensitive crystals of potassium diglyme bis(1,3,5,7-tetramethylcyclooctatetraene) dianion,  $[K((CH_3OCH_2CH_2)_2O)]_2[C_8H_4(CH_3)_4]$ , crystallize in space group  $P\bar{1}$  ( $C_i$ ) with  $a = 9.757$  (3),  $b = 10.026$  (4),  $c = 8.793$  (3) Å,  $\alpha = 97.15$  (1)°,  $\beta = 112.35$  (1)°, and  $\gamma = 109.95$  (1)° with  $\rho_{\text{calc}} = 1.16$  g cm<sup>-3</sup> for  $Z = 1$ . All atoms, including hydrogen atoms, have been located and their positions and thermal parameters refined by full-matrix least-squares procedures to a conventional  $R$  factor of 5.5% for 855 reflections with  $F^2 > 3\sigma(F^2)$  collected with an automated X-ray diffractometer. The structure consists of an ion trimer which lies on an inversion center. The two potassium ions are related by inversion and lie on either side of the cyclooctatetraene ring such that all the K-C bond lengths are equal and average 3.003 (8) Å. The opposite side of each potassium ion is coordinated by the three ether oxygens at an average distance of 2.835 (14) Å. All atoms in the carbocyclic ring lie in the plane to within experimental error and the ring is not significantly puckered; the two independent methyl groups are bent out of the plane of the ring by only 0.5 and 2.6°.

One of the first successes of quantum chemistry in its application to organic compounds was the explanation of the unusual stability of "aromatic" compounds. The Hückel  $4n + 2$  rule for single carbocyclic rings is the most generally used result.<sup>2</sup> Probably the two most important predictions of this rule were the instability of uncomplexed cyclobutadiene and the conversion of the alternating double bond tub geometry of the  $8\pi$  electron cyclooctatetraene molecule to a symmetrical planar  $10\pi$  electron dianion.<sup>3</sup> Although

many physical studies have been carried out on the dianion, much speculation has been made regarding its planar geometry, and structures have been determined for some of its complexes;<sup>4-11</sup> no definitive structural data have been available for cyclooctatetraene dianion itself. We report here the results of such a

(1) (a) National Institutes of Health Predoctoral Fellow, 1969-1972. (b) Alfred P. Sloan Fellow, 1971-1973.

(2) E. Hückel, *Z. Phys.*, **70**, 203 (1931); **76**, 628 (1932); "International Conference on Physics, London, 1934," Vol. II, The Physical Society, London, 1935, p 9; *Z. Elektrochem.*, **43**, 752 (1937).

(3) The first preparation of the cyclooctatetraene dianion and the prediction of its structure were reported by T. J. Katz, *J. Amer. Chem. Soc.*, **82**, 3784, 3785 (1960). Other references in this area can be found in A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

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(5) A. Avdeef, K. N. Raymond, K. O. Hodgson, and A. Zalkin, *Inorg. Chem.*, **11**, 1083 (1972).

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(7) K. O. Hodgson and K. N. Raymond, *Inorg. Chem.*, **12**, 458 (1973).

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