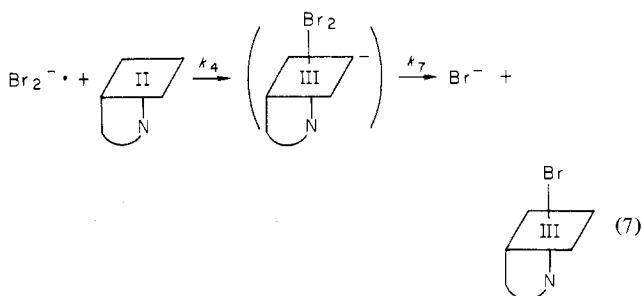


relatively small,  $K_5 = 1.8 \text{ M}^{-1}$ , its aquation is nearly complete at the bromide ion concentrations used in this work, 0.01–0.11 M  $\text{Br}^-$ . Correcting for the residual amount of  $\text{Br}^-[\text{Co(III)}]$ , only 20% at the highest  $[\text{Br}^-]$ , permits  $k_d$  to be calculated from the observed rate constant.

$$k_d = k_{\text{obsd}} / (1 + K_5[\text{Br}^-]) \quad (6)$$

The mean value is  $k_d = (6.4 \pm 0.7) \times 10^2 \text{ s}^{-1}$  ( $22 \pm 2 \text{ }^\circ\text{C}$ ,  $\mu = [\text{Br}^-] = 0.01\text{--}0.11 \text{ M}$ ). Thus reports  $k_d = 5.9 \times 10^2 \text{ s}^{-1}$  ( $26 \pm 1 \text{ }^\circ\text{C}$ ,  $\mu = 1.0 \text{ M}$ ). The absorbance decrease accompanying this reaction is consistent with that expected for reaction 5.

Between reactions 4 and 5 there can be seen a barely discernible spectral change, a slight rise in absorbance at 365 nm with  $k \sim (1 \pm 1) \times 10^4 \text{ s}^{-1}$ . The effect appears reproducible but it is sufficiently small in magnitude, only some 10% of the change for reaction 5 at 365 nm, that it remains of uncertain origin. One possibility is that it might arise from dissociation of  $\text{Br}^-$  from the dibromide adduct<sup>8</sup> of  $[\text{Co(III)}]$ , which one might envisage to be the primary product of reaction 4.



The conclusions from this study are the following: (a) the reaction of  $\text{Br}_2^-$  with  $\text{B}_{12r}$  proceeds by an inner-sphere mechanism, as has been established also by direct observation for some  $\text{M(II)}$  complexes including  $\text{Fe}^{2+}_{\text{aq}}$ ,<sup>10</sup>  $\text{Cr}^{2+}_{\text{aq}}$ ,<sup>10</sup>  $\text{Co}^{\text{II}}\text{NTA}$ ,<sup>11</sup>  $\text{Mn}^{\text{II}}\text{NTA}$ ,<sup>11</sup>  $\text{Ni}^{\text{II}}([\text{14}]\text{4,11-dieneN}_4)^{2+}_{\text{aq}}$ ,<sup>9</sup> and  $\text{Co}^{\text{II}}([\text{14}]\text{4,11-dieneN}_4)^{2+}$ <sup>12</sup> and inferred for others;<sup>2,3,13</sup> (b) the rate constants and concentrations are such that the reaction of  $\text{B}_{12r}$  with  $\text{Br}_2$  has as its second step reaction 4 rather than reaction 3 (at typical concentrations,  $\sim 99.7\%$  of the  $\text{Br}_2^-$  produced reacts by eq 4, 0.3% by eq 3); and (c) the aquation rate of bromocob(III)alamin can be verified by a completely independent method.

### Experimental Section

Solutions of vitamin  $\text{B}_{12r}$  were prepared by hydrogen reduction of  $\text{B}_{12a}$  over Adams' catalyst.<sup>14</sup> Solutions for pulse radiolysis contained the desired concentration of  $\text{B}_{12r}$  ( $15\text{--}60 \mu\text{mol dm}^{-3}$ ) and sodium bromide (0.01–0.11 M) in water and were saturated with nitrous oxide. The pulse duration was 4 ns. Data were collected and analyzed using equipment at Argonne National Laboratory, which has been described.<sup>15</sup>

**Acknowledgment.** The assistance of P. D. Walsh and R. M. Clarke in performing the experiments is gratefully acknowledged.

**Registry No.** Vitamin  $\text{B}_{12r}$ , 14463-33-3;  $\text{Br}_2^-$ , 12595-70-9.

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- (1) (a) Work at both Laboratories was supported through the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division. (b) Argonne National Laboratory. (c) Visiting scientist at Argonne National Laboratory from the Nuclear Research Centre Negev and the Ben-Gurion University of the Negev, Beer-Sheva, Israel. (d) Iowa State University.
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Contribution from the Department of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

### Synthesis of Two New Cobaltaborane Complexes: 1-( $\eta\text{-C}_5\text{H}_5$ ) $\text{CoB}_5\text{H}_9$ and 2-( $\eta\text{-C}_5\text{H}_5$ ) $\text{CoB}_9\text{H}_{13}$

Robert Wilczynski and Larry G. Sneddon\*

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Recent advances in metalborane chemistry continue to demonstrate the close electronic and structural relationships between traditional organometallic complexes and boron cage compounds. In this paper, we report that the direct reaction of pentaborane(9) and  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  using hot/cold reaction techniques results in the formation of two new cobaltaborane complexes, 1-( $\eta\text{-C}_5\text{H}_5$ ) $\text{CoB}_5\text{H}_9$  and 2-( $\eta\text{-C}_5\text{H}_5$ ) $\text{CoB}_9\text{H}_{13}$ . The new sandwich complex 1-( $\eta\text{-C}_5\text{H}_5$ ) $\text{CoB}_5\text{H}_9$  provides an additional bridge between the two areas of chemistry indicated above, since it is isoelectronic with ferrocene and is shown to exhibit a dynamic behavior which suggests that it is a close structural analogue of hexaborane(10).

### Experimental Section

**Materials.** Cyclopentadienylcobalt dicarbonyl,  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ , was obtained from Strem Chemicals and vacuum distilled before use. Pentaborane(9) was obtained from laboratory stock. All solvents were reagent grade and used without further purification. Preparative thin layer chromatography was conducted on 0.5 mm ( $20 \times 20 \text{ cm}$ ) silica gel F-254 plates (Merck). Column chromatography was performed on silica gel (Merck, 70–270 mesh).

**Physical Measurements.** Boron-11 NMR spectra at 32.1 MHz and proton NMR spectra at 100 MHz were obtained on a JEOL PS-100 pulse Fourier transform spectrometer equipped with the appropriate decoupling accessories. High- and low-resolution mass spectra were recorded on either an AEI MS-902 spectrometer located at the University of Virginia or a Perkin-Elmer Hitachi RMH-2 spectrometer. Infrared spectra were obtained on a Perkin-Elmer 521 spectrophotometer.

**General Procedure.** All reactions were run in a hot/cold reactor which consisted of an evacuated, cylindrical, quartz tube (30 mm diameter  $\times$  30 cm) equipped with a greaseless Teflon stopcock. During a reaction the tube was maintained in a vertical position and its central portion heated by a Variac-controlled heating tape, while the lower section was cooled with an appropriate bath.

In a typical reaction, 3 mmol of  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  and 5 mmol of  $\text{B}_5\text{H}_9$  were vacuum distilled into the reactor which was then maintained at  $225 \text{ }^\circ\text{C}/75 \text{ }^\circ\text{C}$  for 1 day with frequent interruptions for removal of the generated carbon monoxide. The reactor was then

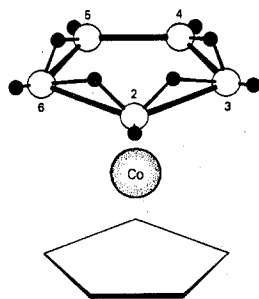


Figure 1. Proposed low-temperature structure of  $1-(\eta\text{-C}_5\text{H}_5)\text{CoB}_5\text{H}_9$ .

opened to the vacuum line, and all volatile material was removed and subjected to vacuum line fractionation through 0,  $-78$ , and  $-196$  °C traps. The material passing the  $-78$  °C trap proved to be 3.8 mmol of unreacted  $\text{B}_5\text{H}_9$ , while a moderately air-sensitive, yellow, crystalline compound which was identified as  $1-(\eta\text{-C}_5\text{H}_5)\text{CoB}_5\text{H}_9$  (4 mg, 2% yield) was retained in the 0 °C trap. High-resolution mass measurement for  $^{12}\text{C}_5^{1}\text{H}_{14}^{11}\text{B}_5^{59}\text{Co}$  called for  $m/e$  188.0893; found 188.0888. IR ( $\text{CS}_2$  solution): 2535 (vs), 2515 (vs, sh), 1885 (w, sh), 1855 (m), 1835 (m, sh), 1760 (w), 1065 (m), 1050 (w), 1040 (w), 995 (s), 905 (w), 885 (m), 850 (m), 828 (s), 810 (m, sh), 783 (w), 755 (m, sh), 740 (s), 705 (m), 680 (m), 630 (w), 605 (w)  $\text{cm}^{-1}$ .

The residue remaining in the reactor was extracted with methylene chloride, filtered, and evaporated onto  $\sim 10$  g of silica gel which was added to a silica gel column and eluted with methylene chloride. This material was then separated by TLC using a 30% benzene in hexanes eluent to give two previously known compounds  $2-(\eta\text{-C}_5\text{H}_5)\text{CoB}_4\text{H}_8$  ( $R_f$  0.64, 0.8 mg) and  $1,2-(\eta\text{-C}_5\text{H}_5)_2\text{Co}_2\text{B}_4\text{H}_6$  ( $R_f$  0.25, 1.6 mg) and a new metalborane complex which was identified as  $2-(\eta\text{-C}_5\text{H}_5)\text{-CoB}_9\text{H}_{13}$  ( $R_f$  0.75, 2.5 mg, 0.9% yield, mp  $111\text{--}112$  °C). High-resolution mass measurement for  $^{12}\text{C}_5^{1}\text{H}_{18}^{11}\text{B}_9^{59}\text{Co}$  called for  $m/e$  236.1578; found 236.1590. IR ( $\text{CCl}_4$  solution vs.  $\text{CCl}_4$ ): 2580 (vs, sh), 2550 (vs), 2530 (vs, sh), 2505 (vs, sh), 1905 (w), 1865 (w), 1775 (w), 1600 (m, b), 1445 (w), 1420 (m), 985 (m), 928 (m), 915 (m), 885 (m), 820 (m, b), 665 (m), 595 (w), 588 (w), 500 (w), 400 (m)  $\text{cm}^{-1}$ .

In a separate experiment, the above reaction was repeated using identical conditions with the exception that 2 mmol of 2-butyne was also added to the reactor. This resulted in improved yields of both  $1-(\eta\text{-C}_5\text{H}_5)\text{CoB}_5\text{H}_9$  (3.9%) and  $2-(\eta\text{-C}_5\text{H}_5)\text{CoB}_9\text{H}_{13}$  (2.5%) as well as the formation of a number of new products which are still under investigation and will be reported separately.

## Results and Discussion

The two new cobaltaborane complexes were both formed in low yields from the reaction of pentaborane(9) with  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  using hot/cold reaction techniques. The sandwich complex  $1-(\eta\text{-C}_5\text{H}_5)\text{CoB}_5\text{H}_9$  is easily separated from the other products by vacuum-line fractionation to give a yellow, crystalline solid which is moderately air sensitive. Exact mass measurements support the proposed formula. The low-temperature  $^1\text{H}$  NMR and boron-11 NMR studies which are discussed below are consistent with the pyramidal structure of  $C_s$  symmetry, shown in Figure 1. The compound is seen to be a direct structural analogue of hexaborane(10) in which a cyclopentadienyl cobalt group has replaced an apex BH unit. Thus the cobalt is bonded to a  $\text{B}_5\text{H}_9^{2-}$  ring (isoelectronic with  $\text{C}_5\text{H}_5^-$ ) which contains four bridging hydrogens and one boron-boron bond. Four previous five-boron metalboranes,  $2-(\text{CO})_3\text{FeB}_5\text{H}_9$ ,<sup>1</sup>  $1-(\text{C}_5\text{H}_5)\text{FeB}_5\text{H}_{10}$ ,<sup>2</sup>  $2-(\text{C}_5\text{H}_5)\text{FeB}_5\text{H}_{10}$ ,<sup>2</sup> and  $2-(\text{CO})_3\text{MnB}_5\text{H}_{10}$ ,<sup>3</sup> have been reported, but this new cobaltaborane is unique since it exhibits the same fluxional behavior which has previously<sup>4</sup> been observed for hexaborane(10).

The structure in Figure 1 indicates that the metalborane fragment has three types of terminal basal hydrogens and two types of bridging hydrogens, but the boron-11 spin-decoupled  $^1\text{H}$  NMR spectrum<sup>5</sup> at 25 °C (Figure 2A) shows, in addition to the resonance at 4.89 ppm due to the cyclopentadienyl hydrogens, only one resonance at 3.78 ppm for the five terminal hydrogens and only one resonance at  $-4.59$  ppm for the

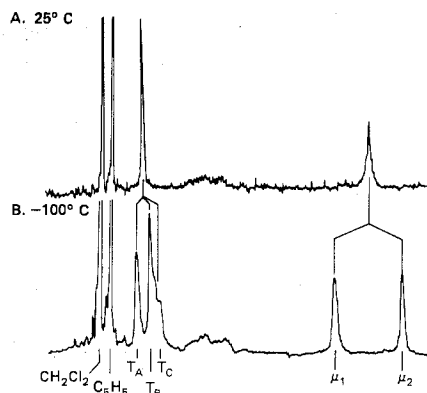


Figure 2. Boron-11 spin-decoupled 100-MHz  $^1\text{H}$  NMR spectra of  $1-(\eta\text{-C}_5\text{H}_5)\text{CoB}_5\text{H}_9$  in  $\text{CD}_2\text{Cl}_2$ ; T = terminal hydrogen,  $\mu$  = bridging hydrogen.

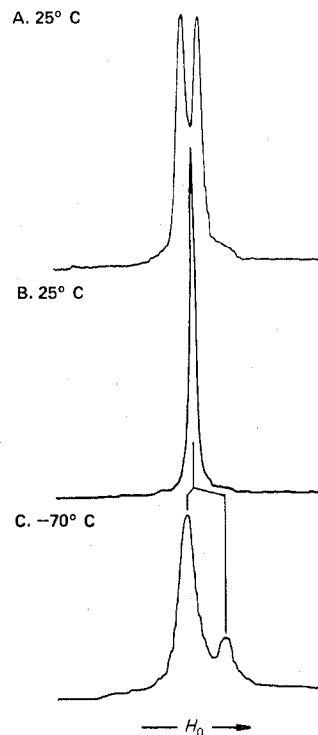


Figure 3. 32.1-MHz boron-11 NMR spectra of  $1-(\eta\text{-C}_5\text{H}_5)\text{CoB}_5\text{H}_9$  in  $\text{CD}_2\text{Cl}_2$ ; spectra B and C are proton spin decoupled.

four bridging hydrogens. Similarly the  $^{11}\text{B}$  NMR spectrum<sup>6</sup> at 25 °C (Figure 3A) consists of only one doublet at 12.8 ppm ( $J = 153$  Hz) which collapses to a sharp singlet (Figure 3B) upon proton decoupling. Thus both the  $^1\text{H}$  and  $^{11}\text{B}$  NMR data indicate a structure of  $C_{5v}$  rather than  $C_s$  symmetry at 25 °C. A similar behavior at ambient temperatures has previously been observed<sup>4</sup> for hexaborane(10) and has been found to arise from a rapid intramolecular migration of the bridging hydrogens about the basal boron ring. It was also found that this migration could be slowed at low temperatures, and spectra could be obtained which were consistent with a  $C_s$  structure. Similar results were obtained from the low-temperature NMR studies of  $1-(\eta\text{-C}_5\text{H}_5)\text{CoB}_5\text{H}_9$ .

The boron-11 spin-decoupled  $^1\text{H}$  NMR spectra were obtained over the range  $+25$  to  $-100$  °C. As the temperature is lowered, the bridge resonance broadens ( $-25$  °C) and then resolves below  $-45$  °C into two distinct peaks of equal area at  $-3.39$  and  $-5.87$  ppm, while the terminal resonance remains sharp and shifts slightly upfield to 3.65 ppm. As the solution is cooled further, the bridge proton peaks sharpen, and the terminal hydrogen peak first broadens and then splits into two

peaks, each of intensity 2, at 3.93 and 3.34 ppm, with the upfield peak showing a poorly defined shoulder of approximate intensity 1 near 3.10 ppm. The sums of the weighted averages of the chemical shifts of the terminal and bridge resonances observed at  $-100\text{ }^{\circ}\text{C}$  (Figure 2B) are each equal, within experimental error, to the chemical shifts of the single resonances observed for the terminal and bridge protons, respectively, at higher temperatures.

The proton-decoupled boron-11 spectra were also obtained in this temperature range. The single resonance observed at  $25\text{ }^{\circ}\text{C}$  broadens upon cooling of the solution and finally at  $-70\text{ }^{\circ}\text{C}$  resolves into two resonances (Figure 3C) at  $+15.2$  and  $+4.8$  ppm of relative areas 4:1. When the solution is cooled further, these resonances only broaden, and the expected resolution of the lower field resonance into two peaks was not observed. Again the sum of the weighted averages of the chemical shifts at  $-70\text{ }^{\circ}\text{C}$  is equal to the chemical shift of the single resonance at  $25\text{ }^{\circ}\text{C}$ .

It is clear from the above data that at low temperatures spectra can be obtained which are consistent with the structure shown in Figure 1 and that the  $C_{5v}$  structure apparent at room temperature arises, as in hexaborane(10), from the rapid migration of the bridging hydrogens about the five-boron ring.

Also obtained in this reaction was a second new cobaltaborane complex,  $2-(\eta\text{-C}_5\text{H}_5)\text{CoB}_9\text{H}_{13}$ , which is the third isomer of this cage system to be isolated. The compound was separated, along with the previously reported complexes  $2-(\eta\text{-C}_5\text{H}_5)\text{CoB}_4\text{H}_8$ <sup>7</sup> and  $1,2-(\eta\text{-C}_5\text{H}_5)_2\text{Co}_2\text{B}_4\text{H}_6$ <sup>7</sup> by TLC from the solids remaining in the reactor and was obtained as an air-stable, yellow, crystalline solid. Again, exact mass measurements are in agreement with the proposed formula. The boron-11 NMR spectrum<sup>6</sup> in  $\text{CD}_2\text{Cl}_2$  solution consists of five doublets at 17.0 ( $J = 133\text{ Hz}$ ), 14.6 (164), 9.0 (173), 1.7 (156), and  $-38.2$  ppm (155) with relative intensities 2:1:1:4:1. The boron-11 spin-decoupled  $^1\text{H}$  NMR spectrum<sup>5</sup> consists of eight resonances: a sharp peak of intensity 5 at 4.96 ppm due to the cyclopentadienyl hydrogens, five broad peaks of relative intensity 2:1:1:4:1 at 4.60, 4.01, 3.70, 3.03, and 0.26 ppm due to terminal B-H hydrogens, and two upfield peaks of relative intensity 2:2 at  $-2.00$  and  $-4.54$  ppm which may be assigned to nonequivalent boron bridging hydrogens.

Both of the previously discovered isomers,  $5-(\eta\text{-C}_5\text{H}_5)\text{CoB}_9\text{H}_{13}$ <sup>7,8</sup> and  $6-(\eta\text{-C}_5\text{H}_5)\text{CoB}_9\text{H}_{13}$ <sup>9</sup> are proposed to have structures based on a decaborane(14) framework in which a cobalt occupies one of the positions in the open face. Likewise, the NMR data presented above are also consistent with a decaborane(14)-like structure for the new isomer, but in this case the number and relative intensity of the resonances observed in both the  $^{11}\text{B}$  and  $^1\text{H}$  spectra clearly indicate that cobalt substitution occurs at the 2 position.

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**Registry No.**  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ , 12078-25-0;  $1-(\eta\text{-C}_5\text{H}_5)\text{CoB}_5\text{H}_9$ , 68457-41-0;  $2-(\eta\text{-C}_5\text{H}_5)\text{CoB}_9\text{H}_{13}$ , 68457-40-9.

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Contribution from the Department of Chemistry,  
University of Pittsburgh, Pittsburgh, Pennsylvania 15260

## Mössbauer Spectra of Substituted Pyridinehemes

William M. Connor and Darel K. Straub\*

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The interaction of bases with hemes (porphyrinatoiron(II) complexes) has been studied extensively because of the similarity of the resulting hemochromes to several hemoprotein systems. Particularly, the affinity of pyridine and various substituted pyridines for hemes with several differently substituted porphyrins has been measured spectrophotometrically,<sup>1</sup> and, more recently, thermodynamic functions have been reported for the reactions of six substituted pyridines with four different hemes.<sup>2</sup> The strength of the iron-pyridine bonds has been found to depend upon the substituents on both the pyridine and porphyrin rings; differences have been rationalized in terms of  $\sigma$  and  $\pi$  bonding characteristics of the substituted pyridine ligands.

We felt it worthwhile to determine whether Mössbauer spectroscopy would be sensitive enough to reflect the differences in the strengths of  $\sigma + \pi$  interactions between tetraarylporphyrinehemes and substituted pyridines. The few Mössbauer data reported so far include only the bis(pyridine)hemes of a few different porphyrins and the bis(3-picoline)- and bis(4-picoline)hemes of octaethylporphyrin.<sup>3</sup>

## Experimental Section

$\alpha,\beta,\gamma,\delta$ -Tetra(*p*-anisidyl)porphyrin,  $\text{PMXPPH}_2$ , was prepared by the standard procedure from anisaldehyde and pyrrole in refluxing propionic acid.<sup>4</sup> The iron complex  $[\text{PMXPPFeCl}]$  was prepared in dimethylformamide,<sup>5</sup> isolated, treated with gaseous hydrogen chloride in methylene chloride solution to remove traces of the binuclear  $\mu\text{-oxo}$  complex,  $[(\text{PMXPPFe})_2\text{O}]$ , and recrystallized several times by diethyl ether precipitation from methylene chloride solution.

The bis(pyrrrolidine)hemochrome  $[\text{PMXPPFe}\cdot 2\text{Pyr}]$ <sup>3d</sup> was prepared by gently refluxing a solution of about 1 g of  $[\text{PMXPPFeCl}]$  in about 60 mL of pyrrolidine for 15 min, filtering to remove insoluble  $[(\text{PMXPPFe})_2\text{O}]$ , and reducing to small volume by vacuum distillation of excess amine. The crystals which resulted upon cooling of the solution to room temperature were collected and recrystallized from hot pyrrolidine. Finally the product was washed with ether and dried under vacuum at room temperature for 24 h.

**Bis(4-methylpyridine)tetra(*p*-anisidyl)porphyrinatoiron(II),  $[\text{PMXPPFe}\cdot 2(4\text{-MePy})]$ .** A 0.65-g sample of the bis(pyrrrolidine)hemochrome was placed in a test tube with approximately 3 mL of 4-methylpyridine and heated with stirring to  $105\text{ }^{\circ}\text{C}$ . The heterogeneous solution was kept at  $105\text{--}110\text{ }^{\circ}\text{C}$  for 10 min, placed under vacuum, and held at the same temperature for an additional 30 min to remove free pyrrolidine. After the solution was cooled to room temperature, the crystalline product was collected on a glass frit and washed with ether.

This general method was used to prepare the pyridine (Py), 3- and 4-acetylpyridine (3/4-AcPy), and 3,5-dimethylpyridine (3,5-Me<sub>2</sub>Py) hemochromes. For the 3- and 4-cyanopyridine (3/4-CNPy) and 4-dimethylaminopyridine (4-DMApy) hemochromes, about 3 g of the solid pyridines was used in the reactions.

Purity of the pyridinehemochromes was established by Mössbauer spectroscopy and from the complete disappearance of the infrared NH deformation mode which occurs at  $895\text{ cm}^{-1}$  in the pyrrolidinehemochrome. The 3- and 4-acetylpyridinehemochromes contained the expected carbonyl stretching frequency at  $1700\text{ cm}^{-1}$ , and the 3-