

Figure 2.—Chemical shift of the OH proton resonance vs. temperature for a 1 mol % solution of dimethylboric acid in methylcyclohexane. Shifts relative to cyclohexane are calculated by subtracting 1.44 ppm from the chemical shift relative to tetramethylsilane (TMS).

purities, such as methylboric anhydride, than is dimethylboric acid from methylboric acid. The purification of dimethylboron chloride is also tedious.<sup>4</sup>

The broad OH stretching band in carbon tetrachloride and the concentration and temperature dependence of the hydroxyl proton chemical shift are typical for hydrogen-bonded protons. No attempt has been made to calculate the bond energy from the temperature dependence of the nmr spectrum, since the system involves several species in unknown concentrations. Further, extrapolation to obtain the maximum downfield shift of the hydrogen-bonded proton is somewhat uncertain (see Figure 2).

It is of interest to examine the present results in terms of a correlation proposed by Ferraro and Peppard;<sup>8</sup> these authors found a linear relation between the chemical shift of the hydroxyl proton in the region of "minor bond breaking" (*i.e.*, the relatively flat portion of Figure 1 at higher concentration) and the hydrogen-bond energy. A similar relation was noted between the bond energy and the difference in the infrared stretching frequencies of free and hydrogen-bonded OH groups.<sup>8</sup> Using this correlation, our value of *ca.* 7.3 ppm downfield from cyclohexane (8.7 ppm from tetramethylsilane) for the chemical shift of the hydroxyl proton in the region of minor bond breaking corresponds to a hydrogen-bond energy of 4.6 kcal. Furthermore, the value of 260  $\text{cm}^{-1}$  obtained by subtracting the frequency of the bonded OH from the frequency of the free OH corresponds to an energy of 4.8 kcal. The good agreement between

(8) J. R. Ferraro and D. F. Peppard, *J. Phys. Chem.*, **67**, 2639 (1963).

these two values leads us to place some confidence in the values obtained.

It is of interest to note that the shift of the hydroxyl proton of the monomer, *ca.* 4.3 ppm downfield from tetramethylsilane, occurs at a much lower field than that of the monomeric proton in ethanol, 0.76 ppm downfield.<sup>9</sup> This would indicate decreased shielding of the hydroxyl proton in dimethylboric acid, which is in keeping with the expected lowering of the electron density on the oxygen atom caused by the acceptor capability of the boron atom. Oxygen-boron back-donation would also account for the failure to observe any indication of intermolecular coordination; this is not unexpected, however, since methoxydimethylboron is not associated<sup>10</sup> despite the electron-releasing methyl group on oxygen.

Evidence for oxygen-boron  $\pi$  bonding, in terms of hindered rotation about the boron-oxygen bond, has recently been provided;<sup>11</sup> the splitting of the B-methyl resonance in methoxydimethylboron at  $-44^\circ$  was attributed to this effect. Splitting of the methylboron resonance in dimethylboric acid was not observed down to  $-100^\circ$ , presumably because very rapid hydrogen-bond breaking and forming averages out the environments of the B-methyl groups, irrespective of hindered rotation about the boron bond.

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(9) This value is derived from the work of E. D. Becker, U. Liddel, and J. N. Shoolery, *J. Mol. Spectry.*, **2**, 1 (1958), on the assumption that the central peak of the  $\text{CH}_3$  triplet is 8.83 ppm downfield from tetramethylsilane.

(10) G. E. Coates, *J. Chem. Soc.*, 3481 (1950); A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953).

(11) G. F. Lanthier and W. A. G. Graham, *Chem. Commun.*, 715 (1968).

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### Mössbauer Spectroscopy of Organometallic Compounds: $\text{Fe}(\text{C}_2\text{B}_9\text{H}_{11})_2^-$ and $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{C}_2\text{B}_9\text{H}_{11})$

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The recent publication of a detailed analysis of the nqr resonance in  $\text{Cs}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2\text{Co}$  and the comparison of the bonding in this carbollide with ferrocene and related molecules by Harris<sup>1</sup> prompt us to describe more fully the Mössbauer results referred to in that paper.

#### Experimental Section

Samples of  $(\text{CH}_3)_4\text{N}[\text{Fe}(\text{C}_2\text{B}_9\text{H}_{11})_2]$  and  $(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_2\text{B}_9\text{H}_{11})$  were generously made available to us by Dr. P. Wegner and used

(1) C. B. Harris, *Inorg. Chem.*, **7**, 1517 (1968).

as received. Ferrocene was obtained commercially<sup>2</sup> and recrystallized from  $\text{CCl}_4$ . Ferricinium bromide was prepared in the usual manner,<sup>3</sup> washed copiously with  $\text{CCl}_4$ , and freed of excess solvent under vacuum. The sample of  $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)_2\text{CH}^+\text{BF}_4^-]$  was supplied by Dr. D. Dell of the Technion-Israel Institute of Technology and was used as received. The Mössbauer spectrometer—which was calibrated with high-purity Armo iron<sup>4</sup>—has been previously described.<sup>5</sup> All isomer shifts are reported with respect to the centroid of the sodium nitroprusside (SNP) Mössbauer spectrum<sup>6</sup> for which the room-temperature quadrupole splitting is  $1.7048 \pm 0.0025$  mm/sec.<sup>7</sup>

### Results and Discussion

The Mössbauer data on  $(\text{CH}_3)_4\text{N}[\text{Fe}(\text{C}_2\text{B}_9\text{H}_{11})_2]$  and related compounds are summarized in Table I and

TABLE I  
MÖSSBAUER PARAMETERS FOR  $\text{Fe}(\text{C}_2\text{B}_9\text{H}_{11})_2^-$   
AND RELATED COMPOUNDS

Absorber	Temp, °K	I.S. <sup>a</sup>	Q.S.
$(\pi\text{-C}_5\text{H}_5)_2\text{Fe}$ (I)	77	$0.773 \pm 0.020$	$2.417 \pm 0.020$
$(\pi\text{-C}_5\text{H}_5)_2\text{Fe}^+\text{Br}^-$ (II)	77	$0.655 \pm 0.040$	<i>b</i>
$(\text{CH}_3)_4\text{N}[\text{Fe}(\text{C}_2\text{B}_9\text{H}_{11})_2]$ (III)	140	$0.630 \pm 0.030$	...
$(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{C}_2\text{B}_9\text{H}_{11})$ (IV)	140	$0.608 \pm 0.030$	$0.520 \pm 0.030$
$[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)_2\text{CH}^+\text{BF}_4^-]$ (V)	100	$0.785 \pm 0.020$	$2.111 \pm 0.020$
$[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)_2\text{C}^+\text{ClO}_4^-]$	80	$0.75^c$	$2.05^c$
$[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)_2\text{CH}^+\text{ClO}_4^-]$	80	$0.67^c$	$2.05^c$

<sup>a</sup> With respect to SNP at 296°K. <sup>b</sup> Not resolved. The line width (full width at half-maximum) is  $0.556 \pm 0.040$  mm/sec. <sup>c</sup> Data taken from U. Zahn, P. Kienle, and H. Eicher, *Z. Physik*, **166**, 220 (1962).

in Figure 1. The data for ferrocene (I) and ferricinium bromide (II) provide a calibration of the effects on the Mössbauer parameters of removing one electron from ferrocene, which results in a decrease by  $-0.12$  mm sec<sup>-1</sup> in the isomer shift (relative to SNP) and, more dramatically, in a nearly complete collapse of the quadrupole splitting. This collapse is, of course, due to a decrease in the field gradient at the iron atom lattice point and may, in fact, involve a sign change as well. Quite similar effects have been reported<sup>8</sup> for related  $\pi$ -cyclopentadienyl compounds in which the parent [diamagnetic, nominally Fe(II)] compounds show quadrupole splittings in the range 2.2–2.5 mm/sec, while the ferricinium [nominally Fe(III)] analogs show unresolved (*i.e.*, less than  $\sim 0.3$  mm/sec) or small (*i.e.*,  $\sim 0.5$ – $0.7$  mm/sec) values of  $\frac{1}{2}e^2qQ$ . Moreover, the data for  $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)_2\text{CH}^+\text{BF}_4^-]$  (V) show<sup>9</sup> that when an electron is removed from the molecule while leaving the  $d^{10}$  configuration of the metal atom intact, the characteristically large quadrupole splitting in the <sup>57</sup>Fe resonance is maintained. The collapse of

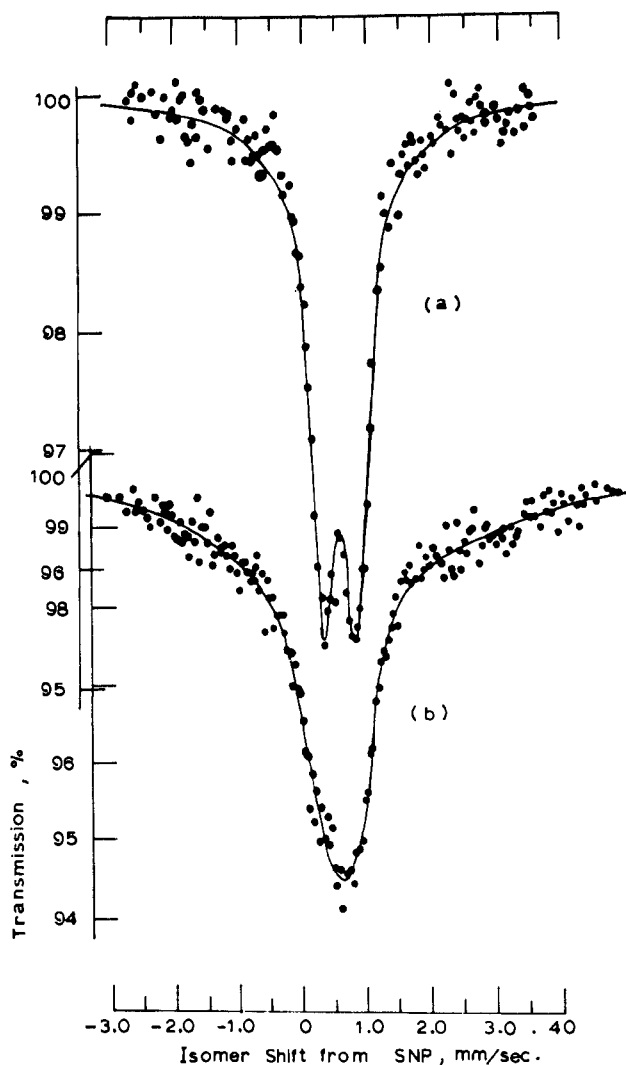


Figure 1.—Mössbauer spectra at 140°K: (a)  $(\pi\text{-C}_5\text{H}_5)_2\text{Fe}(\text{C}_2\text{B}_9\text{H}_{11})_2$ ; (b)  $(\text{CH}_3)_4\text{N}[\text{Fe}(\text{C}_2\text{B}_9\text{H}_{11})_2]$ . The source for both spectra is  $\text{Pd}^{67}\text{Co}$  at 296°K. The isomer shift scale is with respect to the centroid of sodium nitroprusside (SNP) at 296°K.

the quadrupole splitting which is observed<sup>8,10</sup> when ferrocene is oxidized to the ferricinium state has been examined in the elegant Mössbauer experiments by Collins,<sup>11</sup> who finds that  $V_{zz}$  is positive (*i.e.*, the electric field gradient is consistent with molecular orbital calculations<sup>12</sup>) and arises largely from the  $3d_0$  orbital of the metal atom.

From these data it is clear that the iron atom in both the biscarbonyl complex (III) and the cyclopentadienylcarbonyl complex (IV) is appropriately described as being nominally Fe(III) and that the electron vacancy (relative to a  $d^6$  configuration) is primarily localized on the metal atom rather than being delocalized on the ligands. The similarity in the isomer shift parameter for II, III, and IV supports the inference by Harris<sup>1</sup> that the electron-donating ability of the three boron atoms in the  $\text{C}_2\text{B}_3$  face of the car-

(2) Alfa Inorganics, Beverly, Mass.

(3) R. Riemschneider and D. Helm, *Ber.*, **89**, 155 (1956).

(4) H. Shechter, M. Ron, S. Niedzwiedz, and R. H. Herber, *Nucl. Instr. Methods*, **44**, 268 (1966).

(5) H. Braffmann, M. Greenspan, and R. H. Herber, *ibid.*, **42**, 245 (1966).

(6) National Bureau of Standards Miscellaneous Publication No. 260-13, U. S. Government Printing Office, Washington, D. C., July 28, 1967.

(7) U. Conser, private communication.

(8) For a detailed summary of  $\pi$ -cyclopentadienyliron Mössbauer parameters see: E. Fluck in "Chemical Applications of Mössbauer Spectroscopy," V. I. Gol'danskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1968, Chapter 4; R. H. Herber, R. B. King, and G. K. Wertheim, *Inorg. Chem.*, **3**, 101 (1964).

(9) R. H. Herber in "Characterization of Organometallic Compounds," M. Tsutsui, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968.

(10) U. Zahn, P. Kienle, and H. Eicher, *Z. Physik*, **166**, 220 (1962).

(11) R. L. Collins, *J. Chem. Phys.*, **42**, 1072 (1965).

(12) J. P. Dahl and C. F. Ballhausen, *Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd.*, **33**, No. 5 (1961); E. M. Shustorovich and M. E. Dyatkina, *Dokl. Akad. Nauk SSSR*, **128**, 1234 (1959).

borane icosahedron is essentially identical with that of the carbon atoms.

Finally, it is worth noting that the quadrupole splitting in IV is nearly the same as that reported<sup>13</sup> for  $(\pi\text{-C}_5\text{H}_5)_2\text{Fe}^+\text{BF}_4^-$  (0.65 mm/sec at 80°K, 0.76 mm/sec at 298°K), while the unresolved splitting in III cannot be significantly different from that in II [a value <0.1 mm/sec was reported earlier<sup>14</sup>]. These data suggest very strongly that while the major contribution to  $1/2e^2qQ$  originates in the departure from cubic symmetry of the metal orbitals (primarily 3d), smaller contributions arising from distorting by steric effects of the bonding orbitals directed toward the ligands must be included in a quantitative consideration of the field gradient tensor at the iron atom lattice point. However, since the reported differences in the quadrupole splitting parameters of the  $\text{BF}_4^-$  and  $\text{ClO}_4^-$  ferrocene derivatives differ by only 2% of the splitting in the parent ferrocene molecule and are barely outside the reported errors of the individual measurements, such differences can be safely neglected in the qualitative considerations of the present discussion.

Unfortunately, the chemical aftereffects of the electron-capture decay in  $^{57}\text{Co}$  preclude an estimate of the similarity (or difference) between  $(\pi\text{-C}_5\text{H}_5)_2\text{Co}^+$  and the isoelectronic  $(\pi\text{-C}_5\text{H}_5)_2\text{Fe}$ , although experiments in which  $^{57}\text{Co}$ -labeled cobalticinium tetraphenylborate has been used as a source in conjunction with a narrow single-line absorber have been reported.<sup>14</sup>

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(13) R. A. Stukan, S. P. Gubin, A. N. Nesmejanov, V. I. Gol'danskii, and E. F. Makarov, *Teor. Eksperim. Khim. Akad. Nauk Ukr. SSR*, **2**, 805 (1966); U. Zahn, P. Kienle, and H. Eicher, "Proceedings of the International Conference on the Mössbauer Effect, Saclay, 1961," D. M. J. Compton and A. H. Schoen, Ed., John Wiley & Sons, Inc., New York, N. Y., 1962, p 271.

(14) G. K. Wertheim and R. H. Herber, *J. Chem. Phys.*, **38**, 2106 (1963); see also ref 8 of this paper.

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## Transition Metal Carbonyl Complexes of the (3)-1,2-Dicarbollide Ion

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Complexes of the (3)-1,2-dicarbollide ion,  $(3)\text{-1,2-B}_9\text{C}_2\text{H}_{11}^{2-}$ , with molybdenum, tungsten, manganese,

and rhenium carbonyls have recently been reported.<sup>1,2</sup>

It was reasonable to assume that chromium, iron, cobalt, and nickel carbonyls would also form stable complexes, analogs of the  $\pi$ -cyclopentadienylmetal carbonyls.

### Experimental Section

Chromium, iron, and cobalt carbonyls were obtained from Alfa Inorganics, Inc., Beverly, Mass. Chromatographic polyamide was obtained from Brinkmann Instrumens, Westbury, N. Y. Tetrahydrofuran was distilled from lithium aluminum hydride under nitrogen. All reactions and purification procedures were carried out under nitrogen. A Perkin-Elmer 621 grating infrared spectrophotometer was used for recording the infrared spectra of the complexes and the data given were compiled from spectra obtained using Nujol and Fluorolube mulls or suitable solutions. The  $^{11}\text{B}$  nmr spectra at 32 Mcps were obtained using a Varian HA-100 spectrometer. Analyses were carried out by Schwarzkopf Microanalytical Laboratories, Inc., Woodside, N. Y.

$[(\text{CH}_3)_4\text{N}]_2[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_{11}]\text{Cr}(\text{CO})_3$ .—A solution of  $(\text{CH}_3)_3\text{NH}[(3)\text{-1,2-B}_9\text{C}_2\text{H}_{12}]$  (2.5 g, 13.0 mmol) dissolved in 100 ml of THF was dropped into a stirring suspension of NaH (2.0 g of a 56% dispersion in mineral oil, 46.7 mmol) in 50 ml of THF. The mixture was stirred at the reflux temperature for 3 hr. During the last 0.5 hr, a slow stream of nitrogen was passed over the solution to remove the trimethylamine generated. After cooling to room temperature, the solution was filtered, chromium hexacarbonyl (2.86 g, 13.0 mmol) was added, and the solution was irradiated in Pyrex with a Hanovia uv light for 72 hr under nitrogen.

The reaction mixture was filtered through Celite, the filtrate was evaporated, and the resulting residue was dissolved in 200 ml of water. The yellow solid obtained upon addition of aqueous tetramethylammonium chloride was collected under nitrogen, washed with water, dissolved in acetone, and chromatographed on polyamide. The bright yellow fraction obtained was recrystallized from acetone-ethanol to give bright yellow crystals of  $[(\text{CH}_3)_4\text{N}]_2[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_{11}]\text{Cr}(\text{CO})_3$  (2.48 g, 45.8%).

*Anal.* Calcd for  $\text{B}_9\text{C}_2\text{H}_{13}\text{CrN}_2\text{O}_3$ : B, 23.35; C, 37.47; H, 8.47; Cr, 12.48; N, 6.72. Found: B, 23.34; C, 37.23; H, 8.56; Cr, 12.20; N, 6.65.

The infrared spectrum of the complex shows carbonyl bands at 1875 (s), 1753 (s), and 1728 (s)  $\text{cm}^{-1}$  (Nujol mull). Other bands in the spectrum occur at 3034 (m), 2960 (w), 2545 (s), 2467 (s), 1482 (s), 1417 (m), 1287 (m), 1169 (w), 1151 (w), 1097 (m), 1068 (w), 1049 (w), 1033 (m), 1016 (m), 986 (m), 949 (s), 883 (w), 853 (w), 770 (w), 740 (w), 714 (w), and 696 (m)  $\text{cm}^{-1}$ .

The  $^{11}\text{B}$  nmr spectrum of the complex in acetonitrile shows resonances at +25.4 ppm (doublet) and +14.7 ppm (doublet) relative to  $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$  with relative intensities 1:2.

$[(\text{CH}_3)_4\text{N}]_2[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_{11}]\text{Fe}_2(\text{CO})_4$ .—Iron pentacarbonyl (6.9 g, 35.2 mmol) was added to the dicarbollide ion solution obtained from  $(\text{CH}_3)_3\text{NH}[(3)\text{-1,2-B}_9\text{C}_2\text{H}_{12}]$  (5.0 g, 26.0 mmol) and NaH (3.0 g of a 56% dispersion in mineral oil, 70.0 mmol) in 200 ml of THF following the procedure described above. The solution was stirred at the reflux temperature for 20 hr and filtered through Celite, and the solvent was removed *in vacuo* (condensation in a trap cooled with acetone-Dry Ice). The residue was dissolved in 200 ml of water and aqueous tetramethylammonium chloride was added. The pink precipitate was washed with water and ethanol and recrystallized from acetone-ethanol to give dark red microcrystalline  $[(\text{CH}_3)_4\text{N}]_2[(3)\text{-1,2-B}_9\text{C}_2\text{H}_{11}]\text{Fe}_2(\text{CO})_4$  (3.41 g, 41.2% yield based upon the boron compound used).

*Anal.* Calcd for  $\text{B}_{18}\text{C}_4\text{H}_{22}\text{Fe}_2\text{N}_2\text{O}_4$ : B, 30.56; C, 30.18; H,

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(2) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *ibid.*, **90**, 879 (1968).