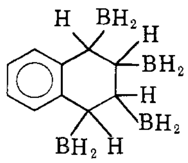
tributable to the bulky *t*-butyl groups, which rendered such secondary processes sterically unfavorable.

We now wish to describe another organoborane which contains the $-BH_2$ group and which also apparently exhibits no tendency to associate. The substance in question, 1,2,3,4-tetrakisdihydroboryl-1,2,3,4-tetrahydronaphthalene, probably has the structural formula



and represents also the first substantiated case of the isolation of an organoborane containing more than one $-BH_2$ group per molecule. The compound is prepared by adding to an ether solution of lithium borohydride the substance $C_{10}H_8(BCl_2)_4$, which, in turn, is produced by the procedure of Fox and Wartik.[2]

That the new polydihydroboryl compound is stable enough to be isolated and characterized at room temperature we attribute to high rotational barriers of the bonds between the carbons to which the $-BH_2$ groups are attached. This characteristic, because it would tend to discourage achievement of a favorable transition state, might be expected to render decomposition or association more difficult. Such evidence as is presently available[3] indicates that $BH_2C_2H_4BH_2$, in which the barrier to rotation about the carbon–carbon bond is low, is thermally quite unstable at room temperature. Efforts to confirm our views by examining the stabilities of a variety of appropriate polydihydroboryl compounds are now in progress.

$C_{10}H_8(BCl_2)_4$ was prepared, as described earlier,[2] by the interaction of B_2Cl_4 with naphthalene at room temperature. (By using refined molecular distillation techniques in the purification process, we have now shown that pure $C_{10}H_8(BCl_2)_4$ is not a liquid at room temperature, as originally reported, but exists as fine pale yellow needles which melt at 46.5–47.5°.) This substance (0.54 mmole) was then added to an excess of lithium borohydride dissolved in ether, and the mixture was stirred at room temperature for several hours. (Other similar reactions were allowed to proceed for periods up to 1.5 days with no substantial change in nature or quantity of products.) When the volatile materials resulting from this procedure were subjected to fractional condensation through a U-trap held at $-23°$, 26.8 mg. of a colorless liquid was retained. Passing through the U-trap, in addition to the solvent ether, were trimethoxyborane, ethyl chloride, diborane, and a trace of hydrogen.

When a sample of the colorless liquid was subjected to analysis (fuming nitric acid at 350° in a sealed tube) it was found to contain 24.6% B, 67.4% C, and a C/B ratio of 2.47. The calculated values for $C_{10}H_8(BH_2)_4$ are 24.1%, 66.9%, and 2.50, respectively. Treatment with excess water resulted in the release of 7.64 moles of hydrogen per mole of $C_{10}H_8(BH_2)_4$ (calculated value = 8.0). Based on the equation

$$C_{10}H_8(BCl_2)_4 + 8LiBH_4 \longrightarrow C_{10}H_8(BH_2)_4 + 8LiCl + 4B_2H_6$$

the yield of the polydihydroboryl compound was 28%. This low yield can be attributed, at least in part, to the loss of some of the $C_{10}H_8(BCl_2)_4$ through its interaction with the solvent ether, as shown by the formation of ethyl chloride and trimethoxyborane. $C_{10}H_8(BH_2)_4$ has a vapor pressure somewhat below 1 mm. at room temperature. It is rapidly destroyed upon exposure to air, a behavior which is characteristic of aliphatic substances containing boron–carbon bonds. On standing in the vacuum system it slowly liberates diborane and leaves behind a nonvolatile residue.

The infrared spectrum of $C_{10}H_8(BH_2)_4$ resembles that of the polydichloroboryl compound from which it was prepared except for the absence of the characteristic BCl_2 stretch band from 870 to 1000 cm.$^{-1}$,[4] and the presence of a new peak at 2490 cm.$^{-1}$ (assigned to BH_2 stetch) and a doublet at 1162, 1190 cm.$^{-1}$ (assigned to BH_2 deformation).[5] The absence of absorption in the 1700 cm.$^{-1}$ region would appear to rule out inter- or intramolecular hydrogen bridge bonding.

---

[2] W. B. Fox and T. Wartik, *J. Am. Chem Soc.*, **83**, 498 (1961).

[3] Efforts to prepare $BH_2C_2H_4BH_2$ by the reaction of $BCl_2C_2H_4BCl_2$ with lithium borohydride yielded an as yet uncharacterized liquid which, above $-45°$, decomposed with the liberation of diborane. In an earlier study G. Urry, J. Kerrigan, T. D. Parsons, and H. I. Schlesinger [*J. Am. Chem. Soc.*, **76**, 5299 (1954)] reported that their efforts to hydrogenate $BCl_2C_2H_4BCl_2$ resulted in products "unstable and difficult to purify."

[4] L. P. Lindemann and M. K. Wilson, *J. Chem. Phys.*, **24**, 242 (1956).

[5] L. J. Bellamy, W. Gerrard, M. F. Lappert, and R. L. Williams, *J. Chem. Soc.*, 2412 (1958).

Correspondence

The Probable Structure of $Fe_3(CO)_{12}$ as Obtained from the Structure of $HFe_3(CO)_{11}^-$

Sir:

The structure of triiron dodecacarbonyl has been the subject of much speculation and frustration, and no less than six widely differing molecular models have been proposed since its discovery.[1–6] An X-ray study of $Fe_3(CO)_{12}$ by Dahl and Rundle[7] *strongly* indicated that the iron atoms are located at the corners of a tri-

---

(1) W. Hieber and E. Becker, *Ber.*, **63**, 1405 (1930).

(2) R. Brill, *Z. Krist.*, **72**, 36 (1931).

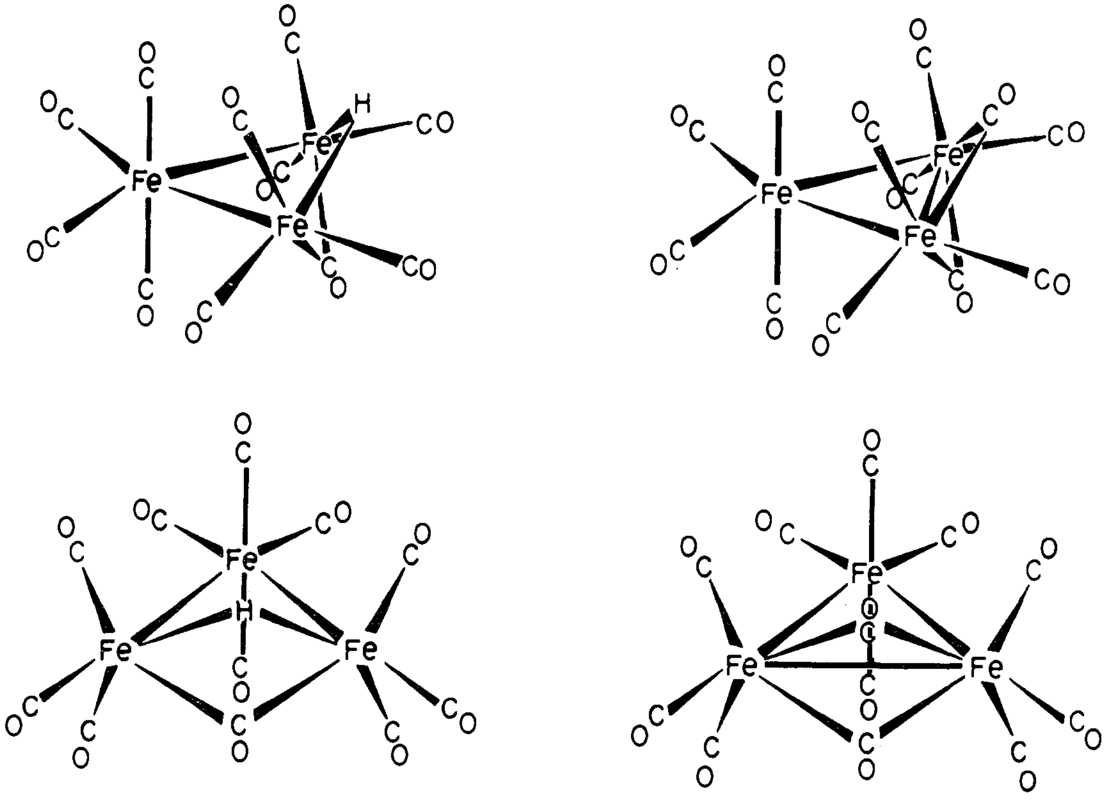
(3) W. Klemm, H. Jacobi, and W. Tilk, *Z. anorg. allgem. Chem.*, **201**, 1 (1931).

(4) N. V. Sidgwick and R. W. Bailey, *Proc. Roy. Soc.* (London), **A144**, 521 (1934).

(5) R. K. Sheline, *J. Am. Chem. Soc.*, **73**, 1615 (1951).

(6) L. F. Dahl and R. E. Rundle, *J. Chem. Phys.*, **27**, 323 (1957).

(7) L. F. Dahl and R. E. Rundle, *ibid.*, **26**, 1751 (1957).



$HFe_3(CO)_{11}^-$ $Fe_3(CO)_{12}$

Figure 1.—Molecular configuration of $HFe_3(CO)_{11}^-$ and probable configuration of $Fe_3(CO)_{12}$ derived by the substitution of a bridging carbonyl group for the presumed bridging hydrogen atom. It is suggested that the structure of $Fe_3(CO)_{11}^{2-}$ may be geometrically related to that of $HFe_3(CO)_{11}^-$ by deprotonation of the -1 anion without further degradation to give the dibasic anion which would be stabilized by an iron–iron bond in place of the Fe–H–Fe system. The resulting configuration differs somewhat from the one proposed for $Fe_3(CO)_{11}^{2-}$ on the basis of partial X-ray results [O. S. Mills, A. A. Hock, and G. Robinson, Abstract A, XVIIth International Congress of Pure and Applied Chemistry, Münich, Aug. 30–Sept. 6, 1959, p. 143].

angle, but a crystal disorder has prevented later attempts in this laboratory to obtain a solution of the complete structure. Mössbauer resonance experiments on $Fe_3(CO)_{12}$ carried out independently by several groups[8–10] have indicated two types of iron atoms in the trinuclear molecule—one iron having high localized point symmetry and two equivalent iron atoms having lower symmetry. These results have been interpreted[8–10] as being consistent only with a linear arrangement of iron atoms. Other spectral evidence including infrared data (which per se have been a source of much complexity and confusion) recently has been cited[11] as supporting a linear structure with bridging carbonyl groups.

We wish to report that a three-dimensional X-ray structural determination of the salt $[(C_2H_5)_3NH][HFe_3(CO)_{11}]$[12] has yielded a configuration for the mono-charged trinuclear anion, from which the probable configuration of $Fe_3(CO)_{12}$ can be obtained by the substitution of a bridging carbonyl group in the regular coordination site no doubt occupied by the bridging hydridic hydrogen atom (Figure 1). The resulting proposed structure for $Fe_3(CO)_{12}$ is in accord with the X-ray, Mössbauer, and *solid-state* infrared studies.

The dark crystals of $[(C_2H_5)_3NH][HFe_3(CO)_{11}]$ are triclinic with reduced cell parameters: a = 10.04 Å., b = 10.46 Å., c = 11.57 Å., α = 94° 19′, β = 90° 26′, γ = 104° 37′. The two formula species per unit cell occupy the general positions of the space group $P\bar{1}$. The nonhydrogen atomic coordinates were found from three-dimensional Fourier maps; an isotropic least-squares refinement of the structure yielded R_1 = 8.0% and R_2 = 9.2% for the 2013 observed reflections obtained photographically by an oscillation technique with Mo Kα radiation.

The $HFe_3(CO)_{11}^-$ anion possesses approximately C_s-m point symmetry with the mirror plane passing through one iron atom Fe(A), two of its attached carbonyl groups, the bridging carbonyl attached to the two iron atoms Fe(B), and presumably the hydrogen atom. The two equivalent Fe(A)–Fe(B) distances of 2.685 and

---

[8] M. Kalvius, U. Zahn, P. Kienle, and H. Eicher, *Z. Naturforsch.*, **17a**, 494 (1962).

[9] R. H. Herber, W. R. Kingston, and G. K. Wertheim, *Inorg. Chem.*, **2**, 153 (1963).

[10] E. Fluck, W. Kerler, and W. Neuwirth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 277 (1963).

[11] G. R. Dobson and R. K. Sheline, *Inorg. Chem.*, **2**, 1313 (1963), and references cited therein for earlier infrared work.

[12] *Cf.* J. R. Case and M. C. Whiting, *J. Chem. Soc.*, 4632 (1960).

2.696 Å. and the Fe(B)–Fe(B) distance of 2.577 Å. (individual e.s.d.'s of 0.003 Å.) for the isosceles triangle of iron atoms in $HFe_3(CO)_{11}^-$ compare favorably with the carefully measured distances (*i.e.*, 27-point interpolation of a 0.12 Å. grid with ellipsoidal Gaussian approximation) of 2.73, 2.75, and 2.64 Å. obtained for the triangular array of Fe–Fe vectors of $Fe_3(CO)_{12}$ from a three-dimensional Patterson function recomputed from the original X-ray data.[7] The presence of a symmetrically bridging hydrogen atom at its indicated coordination site[13] was not directly established for $HFe_3(CO)_{11}^-$ by the X-ray work but was inferred both from stereochemical and bonding considerations.[19] *The probable configuration for* $Fe_3(CO)_{12}$ *ideally possesses* C_{2v}*-2mm point symmetry and can be regarded as being formed by the insertion of a cis-*$Fe(CO)_4$ *group at one of the three bridging carbonyl positions of* $Fe_2(CO)_9$.

The Mössbauer spectrum of solid $Fe_3(CO)_{12}$[8-10] strongly supports the proposed configuration in that the isomeric shift for the quadrupole split peaks of the two iron atoms of lower symmetry is nearly identical with the isomeric shift found for the iron atoms in $Fe_2(CO)_9$. Also, the other iron atom is in an essentially octahedral environment, and consequently any quadrupole splitting would be expected to be small.

The proposed configuration for $Fe_3(CO)_{12}$ is consistent with *solid-state* spectra[6,22] from KBr pellets and from single crystals in that relatively strong bands in the bridging carbonyl region (compared to those in solution spectra) substantiate the existence of bridging carbonyl groups. The KBr pellet spectrum[6] shows two observed 1850 cm.$^{-1}$ bands in agreement with the predicted number for the proposed model containing two bridging carbonyl groups. The expected number of terminal carbonyl bands, however, is not resolved in the solid-state spectra.

We feel that this above evidence clearly provides a strong case for the heretofore elusive structure of $Fe_3(CO)_{12}$ in the solid state. Noteworthy is its nonconformity in configuration with that of the isomorphous compounds $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$.[23] Details of the X-ray results on $HFe_3(CO)_{11}^-$ will be reported in a later paper. X-Ray work on $Fe_3(CO)_{12}$ is being continued in an intensive effort to unravel the disorder and to verify the structure.

Acknowledgment.—Acknowledgment is made to the National Science Foundation for their generous financial support (G.P. 1523). We also acknowledge the partial support of NSF and WARF through the University Research Committee of Wisconsin for the use of the CDC 1604 computer.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSON 53706

LAWRENCE F. DAHL[24]
JOHN F. BLOUNT[25]

RECEIVED APRIL 5, 1965

---

[13] Recent structural work on a number of transition metal hydride compounds including K_2ReH_9,[14] $HMn(CO)_5$,[15] $HRh(CO)\{P(C_6H_5)_3\}_3$,[16] $HOsBr(CO)\{P(C_6H_5)_3\}_3$,[17] and $HPt\{P(C_2H_5)_3\}_2Br$[18] indicates that in such compounds a hydridic hydrogen atom invariably occupies a distinct coordination site in the coordination sphere of the metal to which it is bonded.

[14] S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, **3**, 558 (1964).

[15] S. J. La Placa, W. C. Hamilton, and J. A. Ibers, *ibid.*, **3**, 1491 (1964).

[16] S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, **85**, 3501 (1963); *Acta Cryst.*, **18**, 511 (1965).

[17] P. L. Orioli and L. Vaska, *Proc. Chem. Soc.*, 333 (1962).

[18] P. C. Owston, J. M. Partridge, and J. M. Rowe, *Acta Cryst.*, **13**, 246 (1960).

[19] The existence of a symmetrical, delocalized metal–hydrogen–metal bridging system involving two transition metals was ascertained from a three-dimensional X-ray study of $HMn_3(CO)_{10}(BH_3)_2$.[20] Previous X-ray evidence for a similar symmetrical bent three-center metal–hydrogen–metal bond was acquired from a three-dimensional structural investigation of $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$, for which the probable position of the hydrogen at a regular coordination site was obtained.[21]

Examination of the molecular parameters of $HFe_3(CO)_{11}^-$ shows the five nonhydrogen ligands (*viz.*, the one bridging and three terminal carbonyl groups and the unique iron, Fe(A)) to be octahedrally disposed about the two similarly coordinated Fe(B) atoms. The essentially identical localized environments of these two iron atoms strongly imply that the hydrogen is symmetrically placed on the noncrystallographic mirror plane between the two Fe(B) atoms. If the hydrogen were associated with only one Fe(B), the two Fe(B) atoms then would possess different coordination numbers and presumably considerably different arrangements of their nonhydrogen ligands. A symmetrically bridging hydrogen atom occupies the sixth octahedral coordination site about each Fe(B) atom and thereby enables the geometry of $HFe_3(CO)_{11}^-$ to be considered as similar to that of $Fe_2(CO)_9$ by the replacement of two bridging carbonyl groups with a *cis*-$Fe(CO)_4$ group and a bridging hydrogen.

Both kinds of iron atoms in $HFe_3(CO)_{11}^-$ obey the "inert gas rule" (*i.e.*, only the bonding MO's are utilized) in agreement with the anion's diamagnetism. A symmetrical bridging hydrogen enables each of the Fe(B) atoms to obtain a closed-shell configuration without the need for an iron–iron bond between the two Fe(B) atoms. Since the one bridging and three terminal carbonyl groups together with the Fe(A)–Fe(B) bond can be considered as "effectively" donating eight electrons to each of the zerovalent Fe(B) atoms (at. no. 26), the binuclear hydrido Fe(B)–H–Fe(B) interaction may be described in terms of three-center MO's (with each of the three resulting MO's made up of linear combinations of a σ-type orbital for each Fe(B) and the central 1s hydrogen orbital), of which only the bonding one is occupied with one electron contributed by the hydrogen atom and the other electron formally supplied from the -1 charge of the anion. The use of such a delocalized three-center bond by which the two electrons are distributed over both Fe(B) atoms (as well as the hydrogen atom) results in a closed-shell configuration for each Fe(B) atom.

The similarity of the corresponding Fe–Fe distances in $HFe_3(CO)_{11}^-$ with those of $Fe_3(CO)_{12}$ indicates that the bent Fe(B)–H–Fe(B) system in the monocharged anion may be considered as arising from the protonation of an Fe–Fe single bond in $Fe_3(CO)_{11}^{2-}$. A similar conclusion that a symmetrical metal–hydrogen–metal system can be regarded as the protonation of a metal–metal bond without considerable change in metal–metal distance was reached for $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$.[21]

[20] H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2753 (1965).

[21] R. J. Doedens and L. F. Dahl, *ibid.*, **87**, 2576 (1965).

[22] Although the solution spectra of $Fe_3(CO)_{12}$ reveal two weak bands in the bridging carbonyl region in agreement with the proposed model, the paucity of observed bands, two or possibly three,[11] in the terminal carbonyl region (as contrasted with the minimum number of at least seven predicted bands) together with the intensities of the bridging carbonyl bands being an order of magnitude weaker in intensity compared to the terminal carbonyl bands indicates possible dissociation and/or conformational change in solution. In any event, the arguments outlined in this communication are based on the probable structure of $Fe_3(CO)_{12}$ in the solid state.

[23] E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962).

[24] Alfred P. Sloan Research Fellow, 1963–1965.

[25] National Science Predoctoral Fellow, 1962–1964.