

Boron-Metal Compounds. IX¹

Dialkylamino Borine Iron Tetracarbonyls

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The reaction of $\text{Fe}_2(\text{CO})_9$ with boron bromide or boron iodide yields $\text{Fe}(\text{CO})_5$, $\text{Fe}(\text{CO})_4\text{X}_2$ and $[\text{Fe}(\text{CO})_4\text{BX}]_n$ ($\text{X}=\text{Br}, \text{I}$). The same type of products is formed if R_2NBBR_2 ($\text{R}=\text{CH}_3, \text{C}_2\text{H}_5$) is employed as the boron halide; the dialkylamino group remains attached to the boron. Besides nonvolatile $[\text{Fe}(\text{CO})_4\text{BNR}_2]_n$, volatile monomeric $(\text{CO})_4\text{FeBNR}_2$ is obtained in low yields, containing the unusual ligand R_2NB . Some spectroscopic properties of the novel coordination compounds are reported and some of their chemistry is discussed.

Introduction

Coordination compounds containing metal-boron bonds comprise a relatively young area of boron chemistry.² They can be discussed in terms of metal atoms containing boron radicals or groups as a ligand. A rather large group of compounds contain boron, carbon and metal atoms in a polyhedral framework;^{3,4,5} also sulfur,⁶ phosphorus,⁷ or arsenic⁸ may be part of the cage. The best known compounds of this type are the metal carbolllys,³ which have been correlated with the metallocenes due to the fact that the $\text{B}_5\text{C}_2\text{H}_{11}^{2-}$ ion contains a pentagonal face of three boron and two carbon atoms as well as 3 electron pairs, and this is reminiscent of C_5H_5^- . More recently smaller polyhedral metal boron compounds have been found such as $\text{CH}_3\text{GaC}_2\text{B}_5\text{H}_8$, in which the atoms Ga, B, and C are placed in the corners of an octahedron⁹ or $(2\text{-CH}_3\text{C}_3\text{B}_3\text{H}_5)\text{Mn}(\text{CO})_3$.¹⁰ Even smaller groups containing boron can act as a ligand. Thus the «borene» complexes are characterised by a BX_2 group, examples being *cis*-(C_6H_5)₂B-Mn(CO)₄P(C_6H_5)₃,¹¹ *trans*-[(C_2H_5)₃-

$\text{P}]_2\text{PtCl}(\text{B}(\text{C}_6\text{H}_5)_2)$,¹² *trans*-[TPE]₂Co(BBr₂)₂¹³ (TPE = (C_6H_5)₂P-CH₂-CH₂-P(C_6H_5)₂). Also borane BH_3 and its derivatives add to metal bases with formation of metal boron bonds as demonstrated by $(\text{CO})_5\text{MnBH}_3^-$.¹⁴

It is possible to visualize compounds with ligands of the type BX (B^1) or «borines».¹⁵ Boron monofluoride BF^{16} should somewhat resemble carbon monoxide; both compounds are isoelectronic and the high BF bond order in BF is ascertained spectroscopically. The free BF molecule, prepared by reaction of boron with BF_3 at high temperatures, has a sufficiently long existence to be trapped in a matrix.¹⁶ One may also speculate on the stability of monomeric BOR or BNR_2 and even BCR_2^- . Although these are expected to be unstable in the free state, they may well be stabilized by complex formation due to the fact that they may form a σ -bond via their lone electron pair attached to the boron atom which is also a possible acceptor for metal electrons in establishing back bonding. We report here results concerning the aminoborine group, R_2NB , as a ligand.

Experimental Section

The sensitivity of the compounds both to moisture and oxygen made it necessary to use Schlenk-tube techniques and high vacuum manipulations. Solvents were dried over LiAlH_4 or with A3 molecular sieves.

$\text{Fe}_2(\text{CO})_9$ was prepared by uv irradiation of $\text{Fe}(\text{CO})_5$,¹⁷ $\text{Br}_2\text{BN}(\text{CH}_3)_2$ and $\text{Br}_2\text{BN}(\text{C}_2\text{H}_5)_2$ were produced by mixing BBr_3 and $\text{B}(\text{NR}_2)_3$ in a 2:1 mole ratio followed by distillation.¹⁸ The method of Renner yielded BI_3 .¹⁹

The analytical procedure employed were as follows: a) boron was determined by alkalimetric titration as mannitol-boric acid after degradation of the compounds by $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ and separation as methylborate b) after alkaline decomposition of the samples and removal of iron hydroxide the halides were determined.

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(1) VIII. Contribution: G. Schmid, *Chem. Ber.*, **103**, 528 (1970).

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(12) G. Schmid and H. Nöth, *Z. Naturforsch.*, **20b**, 1008 (1965).

(13) G. Schmid and H. Nöth, *Chem. Ber.*, **100**, 2899 (1967).

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(15) Note on the nomenclature of the compounds: In coordination compounds the group X_2B^- is called borene, the group XB borine; these and other groups as radicals are termed boryl for R_2B , borenyl for RB and borinyl for B .

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ed potentiometrically using a *Hillerkus* automatic potentiometer c) iron was determined using the standard oxidimetric procedures. IR-spectra were recorded with a Perkin-Elmer 117 of 225 model. ^{11}B -nmr spectra were obtained with a Varian HA 100 nmr spectrometer, $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ was used as an external standard and chemical shifts were evaluated by the side-band technique.

μ -Diethylaminoborenyl-tetracarbonyl-iron(II) and diethylaminoborine-tetracarbonyl-iron(O). A suspension was prepared from 7.20 g of $\text{Fe}_2(\text{CO})_9$ in 50 ml ether in a 100 ml flask. With vigorous stirring 4.8 g of $\text{Br}_2\text{BN}(\text{C}_2\text{H}_5)_2$ were added within 15 minutes. A dark brown solution and a precipitate formed during two days stirring at room temperature. The latter was removed by filtration using a G3 sintered disk funnel and washed twice with cold petrol ether. Qualitative analysis (only Fe and Br positive) and the ir spectrum (in nujol mull νCO : 2160, 2110 strong with shoulder and 2080 cm^{-1} ; lit.²⁰ for CHCl_3 solution: 2156, 2114, 2109, 2083 cm^{-1}) showed the product to be $(\text{CO})_4\text{FeBr}_2$.

The solvent was distilled from the filtrate *in vacuo* and condensed in a trap at -196° leaving behind a nonvolatile, brown, somewhat wet crystalline mass. After extraction with 10 ml of pentane, which removed an oily substance from the product assumed to be $[\text{BN}(\text{C}_2\text{H}_5)_2]_n$, the residue was treated with ether. Concentration of the ethereal solution *in vacuo* until crystallisation began resulted in the precipitation of 0.4 g (8%) of brown crystalline μ -diethylaminoborenyl-tetracarbonyl-iron(II).

Analysis: Found B, 4.3; Fe, 22.0; N, 5.56. Calcd for $\text{C}_8\text{H}_{10}\text{BFeNO}_4$ (250.8) B, 4.31; Fe, 22.25; N, 5.58.

The condensate was warmed to -78° , and again all volatiles removed at 10^{-5} mm pressure. This fraction collected at -196° consisted of ether and traces of $\text{Fe}(\text{CO})_5$. The material not volatile at -78° could not be separated further; it deposited a brown solid at room temperature, identical with the material obtained from the ether solution. The material was volatile at -20° ; its vapour pressure was somewhat lower as for $\text{Fe}(\text{CO})_5$. It is therefore assumed, that this material, which is a yellow liquid at -15° , consists of monomeric $(\text{C}_2\text{H}_5)_2\text{NBFe}(\text{CO})_4$ dissolved in $\text{Fe}(\text{CO})_5$.

Dimethylaminoborine-tetracarbonyl-iron(O). Similar to the procedure mentioned above 3.60 g of $\text{Fe}_2(\text{CO})_9$ were reacted with 2.20 g of $\text{Br}_2\text{BN}(\text{CH}_3)_2$ in diethyl ether. After two days the precipitate formed was removed from the brown solution. Removal of all volatile material from this solution yielded a residue of $[(\text{CH}_3)_2\text{NBFe}(\text{CO})_4]_n$.

Analysis: Found B, 4.6; Fe, 24.89; Calcd for $\text{C}_6\text{H}_6\text{BFeNO}_4$ (222.8): B, 4.86; Fe, 25.07.

The yellow condensate obtained was separated into two main fractions at 10^{-5} mm $\text{Fe}(\text{CO})_5$ —characterised by its mp. (-20°) and ir spectrum—condensing in a trap held at -78° , while ether and $(\text{CH}_3)_2\text{NBFe}(\text{CO})_4$ collected at -196° . Under dynamic vacuum ether was pumped off at -100° into a trap held at -196° , leaving behind ~ 0.1 g ($\sim 4\%$) of colourless crystals of $(\text{CH}_3)_2\text{NBFe}(\text{CO})_4$, mp. -25° .

Analysis: Found B, 4.5; Fe, 24.8; N, 5.9; Calcd for $\text{C}_6\text{H}_6\text{BFeNO}_4$ (222.8): B, 4.86; Fe, 25.07; N, 6.29.

The product decomposed readily at room temperature forming a dark brown material.

μ -Bromoborenyl-tetracarbonyl-iron(II). A suspension of 7.20 g of $\text{Fe}_2(\text{CO})_9$ in 50 ml ether was treated with 5.00 g of BBr_3 dissolved in 20 ml ether. After stirring the mixture for 24 hours at room temperature the precipitate formed was removed and all volatile material distilled from the filtrate. The yellow condensate could be separated into ether and $\text{Fe}(\text{CO})_5$, but no other volatile component was detected. Extraction of the brown residue and concentration of the extract yielded 0.7 g (13.5%) of $[\text{BrBFe}(\text{CO})_4]_n$ which separated from the solution on standing at -25° .

Analysis: Found B, 4.1; Br, 33.50; Fe, 21.80; Calcd for C_4BBFeO_4 (258.6): B, 4.18; Br, 30.90; Fe, 21.59.

μ -Iodoborenyl-tetracarbonyl-iron(II). Similar to the procedure for the preparation of $[\text{BrBFe}(\text{CO})_4]_n$ the corresponding iodo compound was obtained by treating 7.20 g of $\text{Fe}_2(\text{CO})_9$ and 7.80 g of BI_3 in 80 ml ether at room temperature. After 12 hours the mixture was worked up yielding 1.2 g of $[\text{IBFe}(\text{CO})_4]_n$ (16.9%) as a dark-brown, microcrystalline material.

Analysis: Found B, 3.06; Fe, 17.81; I, 41.2; Calcd for C_4BFeIO_4 (305.6): B, 3.54; Fe, 18.27; I, 41.53.

Reactions of μ -diethylaminoborenyl-tetracarbonyl-iron(II) a) Reaction with bromine (1:1): 0.39 g of $[(\text{C}_2\text{H}_5)_2\text{NBFe}(\text{CO})_4]_n$ suspended in 50 ml CCl_4 were treated with 0.25 g of Br_2 , dissolved in 40 ml CCl_4 . After stirring the mixture for 1 hour, the precipitate formed was isolated and washed with some cold pentane and finally dried *in vacuo*. Yield: 0.5 g of $(\text{C}_2\text{H}_5)_2\text{NB}(\text{Br})\text{Fe}(\text{CO})_4$.

Analysis: Found B, 2.7; Br, 36.2; Fe, 13.05; Calcd for $\text{C}_8\text{H}_{10}\text{BBBr}_2\text{FeNO}_4$ (410.7): B, 2.63; Br, 38.92; Fe, 13.60.

The product, when treated with bromine in CCl_4 (0.40 g $(\text{C}_2\text{H}_5)_2\text{NBBr}(\text{Br})\text{Fe}(\text{CO})_4$ and 0.16 g Br_2) produced a reddish precipitate of $(\text{CO})_4\text{FeBr}_2$, identified by its ir spectrum. After concentration the filtrate showed a ^{11}B -nmr signal at 25.5 ppm (lit.²¹ -26.7 ppm for neat liquid) demonstrating the presence of $(\text{C}_2\text{H}_5)_2\text{NBBr}_2$ in solution.

b) Reaction with CO. A 100 ml magnetically stirred autoclave was charged with 0.30 g of $[(\text{C}_2\text{H}_5)_2\text{NBFe}(\text{CO})_4]_n$ and 40 ml of pentane and pressurized to 90 atm. After stirring for one day excess CO was blown off from the cooled autoclave and all volatile material collected in a trap cooled to -196° . Some oily drops remained in the autoclave whose qualitative analysis was positive for boron and aminogroups only; since they showed reducing properties to silver ions and no BH-band in the ir-spectrum, it is most likely that they consisted of diethylaminopolyborons.

Fractionation of the yellow condensate yielded $\text{Fe}(\text{CO})_5$ in a trap held at -78° . Its purity was determined spectroscopically.

Reactions of $(\text{CH}_3)_2\text{NBFe}(\text{CO})_4$. a) Decomposition

(20) C. C. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 3552, 1959.

(21) N. N. Greenwood and J. Walker, *Inorg. Nucl. Chem. Letters*, 1, 65 (1965).

by *uv* light. 10 ml of an ethereal solution containing approximately 30 mg of $(\text{CH}_3)_2\text{NBFe}(\text{CO})_4$ contained in a pyrex flask attached to a high vacuum system was irradiated with *uv* light at -80° . Soon, a dark brown solution or suspension was formed. After four hours, the solid product was collected and the filtrate subjected to further irradiation. Virtually no CO gas was formed during the reaction. The ir spectrum of the product was identical with that obtained for $[(\text{CH}_3)_2\text{NBFe}(\text{CO})_4]_n$.

Analysis: Found Fe, 27.8; Calcd for $\text{C}_6\text{H}_6\text{BFFeNO}_4$ Fe, 25.07.

b) *Reaction with bromine* (2:1). Onto 0.08 g of $(\text{CH}_3)_2\text{NBFe}(\text{CO})_4$ (0.36 mmoles) were condensed 0.11 g Br_2 (0.72 mmoles) and 20 ccm of CCl_4 and the mixture slowly warmed up to room temperature with stirring. A red precipitate was identified as $(\text{CO})_4\text{FeBr}_2$; the solution contained $\text{Br}_2\text{BN}(\text{CH}_3)_2$ as evidenced by the ^{11}B nmr spectrum ($\delta^{11}\text{B}$: Found -25.5 ppm, lit.²² -25.7 ppm).

c) *Reaction with CO*. An ethereal solution of $(\text{CH}_3)_2\text{NBFe}(\text{CO})_4$ was prepared as described. It was transferred into an autoclave, which was pressurized to 90 atm. of CO. After stirring for one day, CO was slowly blown off and all volatiles collected; fractionation in vacuo yielded $\text{Fe}(\text{CO})_5$ trapped at -78° . The nonvolatile yellow oil obtained most likely consists of dimethylamino-polyboron compounds.

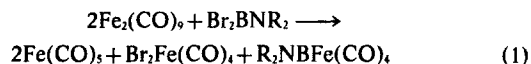
Discussion

Poly(dialkylamino)-boron compounds can be prepared by reductive dehalogenation of dialkylamino boron halides.²³ Active metals such as lithium, sodium, potassium or sodium potassium alloys are employed. The course of this reaction is still unknown; especially it is uncertain whether boron containing radicals are intermediates or dialkylaminoborane species.

Since a free R_2NB species was thought to be unstable, conditions had to be employed in its formation that allowed for a ready scavenging of this molecule by complex formation.

Amongst the various systems that were anticipated to function both as a reducing and scavenging agent diiron enneacarbonyl was found to be suitable.²⁴ It is the most reactive of the iron carbonyls, and it behaves in many respects as a donor of the $\text{Fe}(\text{CO})_4$ group. Since this group is unsaturated it may reduce a boron halide forming the well known tetracarbonyl iron dihalides or accept the R_2NB group with formation of $\text{R}_2\text{NBFe}(\text{CO})_4$.

Although $\text{Fe}_2(\text{CO})_9$ does indeed react with dialkylaminoborondibromide—the bromides being more reactive than the chlorides—the reaction itself is not straightforward as far as the stoichiometry is concerned due to decomposition of the products in this fairly slow reaction. Equation (1) describes the compounds formed, although it was not established quan-



titatively. The separation of the various products presented some problems. While $\text{Br}_2\text{Fe}(\text{CO})_4$ was readily obtained, the boron containing volatile products were difficult to remove from the ether (in case of $\text{R} = \text{CH}_3$) or $\text{Fe}(\text{CO})_5$. While it was possible to obtain $(\text{CO})_4\text{FeBN}(\text{CH}_3)_2$ virtually free from $\text{Fe}(\text{CO})_5$ and ether, since it is — surprisingly — more volatile than $\text{Fe}(\text{CO})_5$ but less than ether, $(\text{CO})_4\text{FeBN}(\text{C}_2\text{H}_5)_2$ could not be separated from the $\text{Fe}(\text{CO})_5$ formed. Therefore, reactions of the monomeric dialkylaminoborane-iron tetracarbonyls were studied only with the methyl derivative. The yields of these novel monomeric coordination compounds were very low, and this has precluded a more detailed investigation so far.²⁵

More readily accessible are brown microcrystalline materials of the same composition as the volatile material, which therefore must be oligomers of $\text{R}_2\text{NBFe}(\text{CO})_4$. Although these are soluble in ether or even better in tetrahydrofuran; their solubility in benzene near its freezing point was insufficient to reliably determine their molecular weight. The solubility behaviour seems to exclude a highly polymerized material and we believe that n equals 2 is a good assumption for $[\text{R}_2\text{NBFe}(\text{CO})_4]_n$. In analogy, the nonvolatile products $[\text{BrFe}(\text{CO})_4]_n$ and $[\text{IBFe}(\text{CO})_4]_n$ obtained by reacting $\text{Fe}_2(\text{CO})_9$ with BBr_3 and BI_3 respectively are most likely dimers as well.

The high volatility of $(\text{CH}_3)_2\text{NBFe}(\text{CO})_4$ and $(\text{C}_2\text{H}_5)_2\text{NBFe}(\text{CO})_4$ is indicative of a monomer, although we have failed to detect the molecular ion in the 70 eV mass spectrum of $(\text{CH}_3)_2\text{NBFe}(\text{CO})_4$.²⁶ Both monomers decompose readily, and dark brown products are formed. Although $(\text{CH}_3)_2\text{NBFe}(\text{CO})_4$ is stable below -40° , *uv* irradiation of its ethereal solution at -78° results in the formation of $[(\text{CH}_3)_2\text{NBFe}(\text{CO})_4]_n$. This reaction allows a differentiation of this compound from $\text{Fe}(\text{CO})_5$, which under the same conditions transforms to golden yellow $\text{Fe}_2(\text{CO})_9$ with evolution of CO, and the small amounts of CO evolved during the irradiation of $(\text{CH}_3)_2\text{NBFe}(\text{CO})_4$ may be due to a small contamination of the product with $\text{Fe}(\text{CO})_5$. While $(\text{CH}_3)_2\text{NBFe}(\text{CO})_4$ shows a clearly defined melting point, the oligomeric compounds $[\text{XBFe}(\text{CO})_4]_n$ all decompose at elevated temperatures without melting. The products of the decomposition have not been characterised.

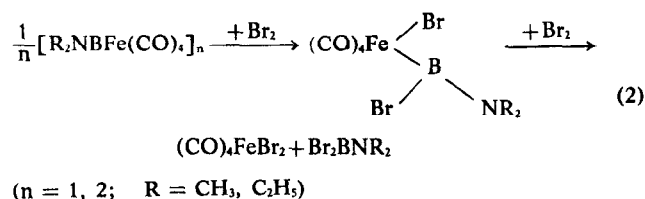
The presence of a metal boron bond in $(\text{CH}_3)_2\text{NBFe}(\text{CO})_4$ as well as in $[(\text{C}_2\text{H}_5)_2\text{NBFe}(\text{CO})_4]_n$ is demonstrated by the behaviour of these compounds towards bromine. The reaction in a 1:1 molar ratio yields a « Br_2 -adduct », which on further treatment with 1 mole of Br_2 leads to $\text{Br}_2\text{Fe}(\text{CO})_4$ and Br_2BNR_2 . This behaviour can be rationalized by equation (2).

(25) Variation in reaction time, temperature, concentration as well as the reaction of larger quantities did not improve yields. Also, reactions such as $\text{Na}_2\text{Fe}(\text{CO})_4 + \text{Cl}_2\text{BNR}_2 \rightarrow 2 \text{NaCl} + \text{R}_2\text{NBFe}(\text{CO})_4$ produced no volatile borine complex.

(26) At 70 eV binuclear, B-containing species such as $\text{Fe}_2(\text{CO})_9\text{BN}(\text{CH}_3)_2$ were found. Experiments at low electron energy were unfortunately not carried out during this study.

(22) H. Nöth und H. Vahrenkamp, *Chem. Ber.*, 99, 1049 (1966).
(23) K. H. Hermannsdörfer, E. Matejčiková, and H. Nöth, *Chem. Ber.*, 103, 516 (1970).

(24) $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$ were not very helpful in this respect.



In the case of monomeric (CH₃)₂NBFe(CO)₄ bromine adds first to the Fe–B bond while one of the two boron iron bonds of the R₂NB group in [(C₂H₅)₂NBFe(CO)₄]_n is cleaved by bromine. Also, the behaviour of (CH₃)₂NBFe(CO)₄ and [(C₂H₅)₂NBFe(CO)₄]_n towards CO is identical, Fe(CO)₅ being formed and most likely dialkylaminoborons as well, although the true nature of these products has not been established. The experiments demonstrate that the boron iron bond in these compounds is readily broken; this is easily understood for R₂NBFe(CO)₄, since in the case of the CO reaction this represents a simple ligand displacement, while for [R₂NBFe(CO)₄]_n, where we assume bridging R₂NB groups comprising Fe–B σ-bonds (*vide infra*), the uptake of CO must be accompanied by a redox process.

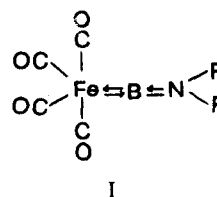
The high volatility of (CH₃)₂NBFe(CO)₄ clearly shows that the (CH₃)₂NB group has replaced a CO molecule in Fe(CO)₅. Thus the dimethylaminoborine group acts as a ligand presumably through its lone electron pair at the boron atom. This will impose sp hybridization at the boron atom. Therefore there are p-orbitals available at the boron atom for back bonding. Unfortunately we have so far been unable to obtain well resolved ir spectra in the range of 1800–300/cm for the monomers due to the ready decomposition of the compounds at room temperature, while it was possible, although with difficulties, to record good enough and reproducible spectra for the CO stretching region. This region is characterized by three bands in ethereal solution, the high frequency band is weak, the low frequency band of medium strength, while the band at 2035/cm is very strong. A comparison of these bands with those of other iron pentacarbonyl derivatives is made in Table I.

Table I. CO stretching frequencies of some iron pentacarbonyl derivatives (CO)₄FeL

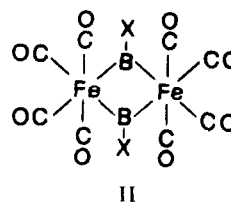
Compound	Solvent	νCO (cm ⁻¹)
(CH ₃) ₂ NBFe(CO) ₄	Ether	2112, 2035, 1935
CH ₃ CNFe(CO) ₄	Trichloromethane	2064, 1976, 1959 ⁽²⁷⁾
C ₂ H ₅ NFe(CO) ₄	Trichloromethane	2055, 1968, 1942 ⁽²⁷⁾
C ₂ H ₅ NFe(CO) ₄	Trichloromethane	2049, 1959, 1930 ⁽²⁷⁾
(C ₆ H ₅) ₃ PFe(CO) ₄	N-Hexane	2059, 1978, 1942 ⁽²⁷⁾

These data indicate that the (CH₃)₂NB ligand is a weaker electron donor than any of the other ligands listed. We regard this also as evidence that the (CH₃)₂NB group binds through its boron but not by its nitrogen atom to the Fe(CO)₄ group. Furthermore, the (CH₃)₂NB group seems to be a better acceptor

than CO, if the position of the first two bands is considered in connection with those of Fe(CO)₅. If this is so, then back bonding from iron to the boron atom is indicated and a fairly good shielding of the boron nucleus should be observed. The ¹¹B nmr spectrum shows a signal at –18.0 ppm; this is in agreement with the hypothesis of the R₂NB group acting as a good acceptor which results in a high electron density at the boron. As already mentioned, we assume that the boron atom in (CH₃)₂NBFe(CO)₄ is in an sp valence state, the p_y and p_z orbitals being available for back bonding both from the nitrogen and the iron atom as shown in I; for the latter the d_{xy} and d_{xz} orbitals are favourable for back bonding.



The instability of boron in the assumed sp-state reflects itself in the ready conversion of the highly volatile R₂NBFe(CO)₄ into nonvolatile [R₂NBFe(CO)₄]_n. We believe that oligomerisation of the monomer occurs via bridging R₂NB group where the boron atom is in the thermodynamically more favoured trigonal planar arrangement. The simplest formulation is a dimer of type II. For molecules of this symmetry (D_{2h}) three



IR active CO-stretching frequencies are to be expected, as is observed for all the [XBFe(CO)₄]_n compounds obtained (see Table).

Table II. CO stretching frequencies of [XBFe(CO)₄]_n and ¹¹B chemical shifts

	νCO (cm ⁻¹)	δ ¹¹ B(ppm)
[(C ₂ H ₅) ₂ NBFe(CO) ₄] _n	2040, 1980, 1960	–13.8
[BrBFe(CO) ₄] _n	2050, 2025, 2000	–15.3
[IBFe(CO) ₄] _n	2040, 2000, 1990	—

Although the XB group in a bridging position can be compared with a bridging CO group, we believe that it operates through two distinct two-electron two-center bonds as indicated in II; if it were to behave in this respect like a CO group the composition of binuclear borine substituted iron carbonyls should be (XB)₂Fe₂(CO)₇, two XB groups replacing two bridging CO groups in Fe₂(CO)₉. But this assumption can be discounted on the basis that no bridging CO group is indicated by the ir spectra.

(27) E. H. Schubert and R. K. Sheline, *Inorg. Chem.*, 5, 1071 (1966).

The ^{11}B chemical shift recorded in ether solution indicates fairly well shielded magnetically equivalent boron atoms. Although $[(\text{C}_2\text{H}_5)_2\text{NBF}(\text{CO})_4]_n$ and $[\text{BrBF}(\text{CO})_4]_n$ can be isolated from ether they may form adducts with the solvent in solution.

The dialkylaminoborane-iron-tetracarbonyls and their oligomers represent novel types of coordination compounds which impose very interesting valence and structural problems, and further work is in progress to clarify some questions raised by this paper as well

as to extend the scope of the reaction and to investigate other XB groups as ligands.

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