The sulfur atom of the 3-substituted compound is sterically incapable of coordination to the same metal atom that the oxygen coordinates. Thus, it is likely that the sulfur of 2-thenoyltrifluoroacetone does not coordinate.

Van Uitert[3] reported a value of 9.1 for the logarithm of the protonation constant for 2-thenoyltrifluoroacetone at 30° in 75 vol. % dioxane. He reported values of 9.5 and 8.0 for the average logarithm of the formation constants for both steps of the coordination reactions of copper(II) and nickel(II), respectively. The values reported in this study are lower in each case. In his pioneering work, Van Uitert based his calculations on only one point in each titration. He titrated with aqueous NaOH, using concentrated solutions of titrant so as not to deviate excessively from 75 vol. % dioxane. He could not determine the stepwise constants at the concentrations of reagents that he used, for the initial coordination in each formation constant titration was greater than $\bar{n} = 1$ before addition of any titrant.

In this work, many points were used in each titration to determine average values for each tabulated quantity. The titrant, tetramethylammonium hydroxide, was dissolved in 75 vol. % dioxane, so as not to change the solvent system during the titration. Use of dilute reagents and addition of perchloric acid together retarded the initial coordination enough to allow determination of stepwise formation constants.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Reaction of Iron Pentacarbonyl with Acetylacetone

BY J. W. FITCH, III, AND J. J. LAGOWSKI

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It has recently been reported that acetylacetone and iron pentacarbonyl react to form ferric acetylacetonate in low yield (8.5% based on iron pentacarbonyl).[1] The reaction was performed in the absence of a solvent and the isolation of the product involved its precipitation from acetone by the addition of water followed by subsequent recrystallization from benzene.

We have observed that iron pentacarbonyl reacts with acetylacetone in refluxing di-*n*-butyl ether to form, primarily, ferrous acetylacetonate (52% yield based on acetylacetone used), all manipulations being conducted in a nitrogen atmosphere. Isolation of the reaction product in air gives only ferric acetylacetonate in low yield.

Experimental

In a typical experiment acetylacetone (14.64 g., 0.1464 mole) and iron pentacarbonyl (28.60 g., 0.1460 mole) were dissolved together, under nitrogen, in 200 ml. of di-*n*-butyl ether. The mixture was refluxed for 15 hr. in the dark at 140°, after which time an orange precipitate had formed and the solution had turned dark red-brown. As the solution cooled under a slow stream of prepurified nitrogen more orange precipitate formed. The precipitate was filtered and washed twice with small portions of anhydrous diethyl ether and stored in a helium-filled drybox. The yield was 9.78 g. (52% based on acetylacetone used).

Anal. Calcd. for $FeC_{10}H_4O_4$: Fe, 21.98. Found: Fe, 22.07.

The magnetic susceptibility of the compound was determined with a Cheneveau balance and, after applying the diamagnetic correction, was found to correspond to 4.88 B.M. The spin-only moment for iron(II) is 4.90 B.M.[2]

The compound sinters at 177° and melts at 200–201° in an evacuated sealed capillary. Ferrous acetylacetonate is reported to sinter at 177° and to melt at 201°.[3] When determined in air, the compound melted at 178–181°, indicating that it had been converted into ferric acetylacetonate. Ferrous acetylacetonate is reported to be easily oxidized, especially when moist, to ferric acetylacetonate.[3]

Acknowledgment.—We wish to express our appreciation to the Robert A. Welch Foundation for supporting this investigation and to NASA for a fellowship (to J. W. F.).

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CONTRIBUTION FROM THE U. S. BORAX RESEARCH
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o-Carboranyl Derivatives of Boron Compounds

BY J. L. BOONE, R. J. BROTHERTON, AND L. L. PETTERSON

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The synthesis of many carborane derivatives has been accomplished by reaction of metallocarboranes with halo compounds.[1–3] In the present work, monolithio-*o*-carborane (I) was prepared from *o*-carborane and butyllithium in ether (eq. 1) and added to chlorobis(dimethylamino)borane (II) at 0° (eq. 2). The precipitate contained 84% of the theoretical amount of lithium chloride. Vacuum distillation of the solvent and recrystallization of the residue gave a 45% yield of the desired product, bis(dimethylamino)-*o*-carboranylborane (III). This compound melted at 46 ± 2° and slowly distilled under vacuum at 100° in a molecular still. The infrared spectrum of

$$o\text{-}HCB_{10}H_{10}CH + LiC_4H_9 \longrightarrow \underset{\text{I}}{o\text{-}HCB_{10}H_{10}CLi} + C_4H_{10} \quad (1)$$

$$\underset{\text{I}}{o\text{-}HCB_{10}H_{10}CLi} + \underset{\text{II}}{ClB[N(CH_3)_2]_2} \longrightarrow \underset{\text{III}}{o\text{-}HCB_{10}H_{10}CB[N(CH_3)_2]_2} + LiCl \quad (2)$$

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(1) For nomenclature consult R. Adams, *Inorg. Chem.*, **2**, 1087 (1963).

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III showed absorption characteristic of C–H (carborane) and B–H bonds at 3.25 and 3.85 μ, respectively, as well as absorption in the 6.8, 7.25, 9.10, and 13.9 μ regions. The reaction of monolithio-*o*-carborane with bromobis(dimethylamino)borane was also studied but the results were less definitive.

The reaction of methanol with III quantitatively liberated 2 moles of dimethylamine and 46% of the *o*-carborane calculated on the basis of eq. 3. Di-

$$o\text{-}HCB_{10}H_{10}CB[N(CH_3)_2]_2 + 3CH_3OH \longrightarrow o\text{-}HCB_{10}H_{10}CH + B(OCH_3)_3 + 2(CH_3)_2NH \quad (3)$$

methoxy-*o*-carboranylborane was not isolated. Hydrolysis of III in diethyl ether saturated with water gave only 70% of the theoretical dimethylamine and a viscous insoluble precipitate. Infrared analysis of the nonvolatile products showed that some *o*-carborane was formed in the reaction, but no dihydroxy-*o*-carboranylborane was isolated.

Lithium derivatives of *o*-carboranes were also used in attempts to prepare B-*o*-carboranylborazines. However, when B-trichloroborazine and monolithio-*o*-carborane were mixed in diethyl ether, side reactions occurred which converted large proportions (~53%) of the original monolithio-*o*-carborane into *o*-carborane. No *o*-carboranylborazine was isolated. Elimination of N–H bonds by the use of N-trimethyl-B-trichloroborazine did not prevent these side reactions and approximately 49% of the original monolithio-*o*-carborane was converted to *o*-carborane.

When N-trimethyl-B-trichloroborazine was mixed with C-monolithio-C′-*n*-butyl-*o*-carborane in an ether–*n*-heptane mixture, 95% of the theoretical lithium chloride precipitated (eq. 4). The solvent was removed from the filtrate and the residue was extracted with an ether–pentane mixture, giving a 64% yield of a light yellow, low-melting wax which was identified as B-tri(*n*-butyl-*o*-carboranyl)-N-trimethylborazine (IV). It showed infrared absorption at 3.25, 3.35, 3.82, 12.5, and 13.8 μ and broad absorption in the 6–10.5 μ region.

$$3o\text{-}B_{10}H_{10}C_2(n\text{-}C_4H_9)Li + (ClBNCH_3)_3 \longrightarrow \underset{\text{IV}}{[o\text{-}B_{10}H_{10}C_2(n\text{-}C_4H_9)BNCH_3]_3} + 3LiCl \quad (4)$$

Attempts to prepare tris-*o*-carboranylborane from boron trichloride and monolithio-*o*-carborane in ether were unsuccessful. Significant amounts of free *o*-carborane were obtained.

The reaction of acetylene derivatives with base adducts of decaborane is an established procedure for the preparation of *o*-carborane derivatives.[4–6] However, the reaction of dimethoxyethynylborane (V) with bis(diethyl sulfide)decaborane (VI) in refluxing benzene in an attempt to prepare dimethoxy-*o*-carboranylborane (VII) according to eq. 5 was unsuccessful.

$$\underset{\text{V}}{HC{\equiv}C\text{-}B(OCH_3)_2} + \underset{\text{VI}}{B_{10}H_{12}[S(C_2H_5)_2]_2} \not\longrightarrow \underset{\text{VII}}{o\text{-}HCB_{10}H_{10}B(OCH_3)_2} + 2S(C_2H_5)_2 + H_2 \quad (5)$$

Experimental

Preparation of Bis(dimethylamino)-*o*-carboranylborane.—A solution of monolithio-*o*-carborane was prepared in 50 ml. of anhydrous diethyl ether by the addition of 20.0 ml. of a *n*-heptane solution of butyllithium (56.2 mmoles) to 8.11 g. of resublimed *o*-carborane (56.2 mmoles). This solution was added dropwise at 0° during a 1-hr. period to a solution of 7.56 g. of chlorobis(dimethylamino)borane (56.2 mmoles) in 75 ml. of diethyl ether. The mixture was stirred at 0° for an additional 3 hr. and then at room temperature for 12 hr. The resulting precipitate (2.32 g.) was removed by filtration under a dry nitrogen atmosphere; halide analysis (71.9% Cl) indicated an 84.1% yield of lithium chloride. Removal of the volatile materials from the filtrate by vacuum distillation at room temperature left a viscous melt which slowly crystallized at room temperature. Recrystallization from an ether–pentane solution at −78° gave 6.1 g. of bis(dimethylamino)-*o*-carboranylborane (44.9% yield).

Anal. Calcd. for $B_{10}C_2H_{11}B[N(CH_3)_2]_2$: C, 29.74; H, 9.57; B, 49.12; N, 11.57. Found: C, 28.05; H, 9.53; B, 48.72; N, 11.54.

Small portions of bis(dimethylamino)-*o*-carboranylborane were distilled slowly from an impure sample at 100° in a high-vacuum sublimation apparatus. The distillate was collected as fine white crystals on the cold finger, and impurities of *o*-carborane were sublimed from it by warming the cold finger to 35°. Further warming of the cold finger caused the purified sample to melt between 44 and 48°.

Solvolysis of Bis(dimethylamino)-*o*-carboranylborane. (a) **In Methanol.**—A redistilled sample of bis(dimethylamino)-*o*-carboranylborane (608.3 mg., 2.511 mmoles) was added with stirring to 50 ml. of anhydrous methanol. Methanol and dimethylamine were removed from the resulting clear solution by distillation at atmospheric pressure and were trapped in standardized aqueous hydrogen chloride. Four additional 25-ml. portions of methanol were added and distilled to dryness before the evolution of amine ceased. A total of 5.010 mequiv. of amine (calcd., 5.022 mequiv.) was collected, giving a molar ratio of dimethylamine to bis(dimethylamino)-*o*-carboranylborane of 1.995 (calcd., 2.000). *o*-Carborane (165 mg., 1.15 mmoles) which was sublimed from the residue under vacuum was equivalent to 46% of that possible from the complete methanolysis of the carborane–boron bond. Dimethoxy-*o*-carboranylborane was not isolated.

(b) **In Water.**—Addition of diethyl ether (75 ml.) saturated with water (28 mmoles) to bis(dimethylamino)-*o*-carboranylborane (3.55 mmoles) at room temperature gave a semisolid which would not dissolve in ether. Distillation of all volatiles at room temperature under vacuum and titration of the distillate with standardized hydrochloric acid gave only 69.5% of the theoretical amine.

Reaction of Monolithio-*o*-carborane with Bromobis(dimethylamino)borane.—Attempts to prepare bis(dimethylamino)-*o*-carboranylborane from monolithio-*o*-carborane and bromobis(dimethylamino)borane in diethyl ether were obviated by a side reaction between the bromoborane and diethyl ether. When bromobis(dimethylamino)borane was added to a toluene slurry of monolithio-*o*-carborane at 0° and stirred for 12 hr. at room temperature, 91% of the theoretical lithium bromide was isolated in the solid phase. Several small fractions of solid material were precipitated from the liquid phase by the addition of pentane, but their boron content was below the theoretical value. The infrared spectra of these solids, however, were the same as that of bis(dimethylamino)-*o*-carboranylborane (III). It is probable that the low boron analyses were due to the presence of lithium bromide.

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Preparation of B-Tri(*n*-butyl-*o*-carboranyl)-N-trimethylborazine.—*n*-Butyl-*o*-carborane was prepared by reaction of a 10% molar excess of *n*-butyl bromide with monolithio-*o*-carborane in an ether–heptane solution at 40° for 2.5 hr. The organic phase was washed with an aqueous solution of ammonium sulfate, dried, and distilled. The product (49% yield) was collected at 85° (0.20 mm.). Monolithio-*n*-butyl-*o*-carborane (23.8 mmoles) was prepared from butyllithium and *n*-butyl-*o*-carborane in an ether–heptane solution at 0–5° for 2.3 hr. and 25° for 16 hr. The resulting solution was added during 15 min. to 7.93 mmoles of B-trichloro-N-trimethylborazine in ether at 2°. The slurry was stirred for 2 hr. at that temperature and then for 4 hr. at 25°. Analysis of the precipitate showed that it contained a 95% yield of lithium chloride. The filtrate was reduced to dryness and partially redissolved in an ether–pentane mixture. The soluble fraction was dried under vacuum for 5 hr. at 80–130°, giving a 64% yield of a light yellow, low-melting wax identified as B-tri(*n*-butyl-*o*-carboranyl)-N-trimethylborazine.

Anal. Calcd. for $C_{21}H_{66}B_{33}N_3$: C, 35.14; H, 9.27; B, 49.74; N, 5.85; mol wt., 718. Found: C, 36.42; H, 9.21; B, 47.6; N, 6.42; mol. wt., 720 (cryoscopic in benzene).

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
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The Reactions of Manganese(III) and Iron(III) Tetrapyridylporphines with Various Reducing Agents[1]

BY PETER HAMBRIGHT AND EVERLY B. FLEISCHER

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We wish to report the results of an investigation concerning the rates of the reduction of manganese(III) and iron(III) tetrapyridylporphine (TPyP) with various reducing agents. The stoichiometry of the reaction is

$$\text{M(III)–TPyP} + \text{red} \longrightarrow \text{M(II)–TPyP} + \text{ox}$$

where "red" is the reducing agent.

Experimental

The tetrapyridylporphine complexes were prepared as previously done and purified with chromatographic columns.[2] The preparation and standardization of the reducing agents and other reagents is described elsewhere in the literature.[3,4]

The kinetics were followed on a Cary Model 14 recording spectrophotometer or with a stopped-flow reactor similar to that described by Sutin[5] by following the decrease of the 398 mμ peak of the Fe(III)–TPyP (ϵ 9.1 × 10^4) or the 463 mμ peak of the Mn(III)–TPyP (ϵ 11.7 × 10^4) species as a function of time. The products were analyzed spectrophotometrically and identified as Fe(II)–TPyP (λ_{max} 443 mμ, ϵ 12.5 × 10^4) or Mn(II)–TPyP (λ_{max} 423 mμ, ϵ 15.3 × 10^4). The reactions were run under pseudo-first-order conditions by employing an excess of reducing agent. The resulting data gave first-order plots at least over three half-lives. The second-order rate constants were obtained by varying the concentration of the reducing agent over a five- to tenfold range. (Reducing agents were 10^{-3} to 10^{-5} *M* for Fe(III)–TPyP and 10^{-4} to 10^{-5} *M* for Mn(III)–TPyP and the porphyrin concentration was about 10^{-6} *M*. The anion concentrations were varied from 10^{-1} to 10^{-3} *M*. At high reductant concentrations (0.1 *M*) the porphyrin itself can be reduced.) The rates were found to be independent of pH from pH 1.0 to 3.5. The ionic strength was held constant with sodium perchlorate. The chromic product analysis was carried out by the method of Laswick and Planc.[6]

Results

The rates of formation of the divalent metallotetrapyridylporphine could in all cases be represented by

$$\text{rate} = k_1[\text{M(III)–TPyP}][\text{red}] + k_2[\text{M(III)–TPyP}][\text{red}][\text{X}]$$

where X is a halide ion (Cl^-, Br^-, I^-, or SCN^-). Table I lists the set of rate constants k_1 and k_2 for various reducing agents. The product study with chromous ion as a reducing agent showed that the product of the chloride-catalyzed path was always $Cr(H_2O)_5Cl^{2+}$. Because of the lability of both the iron and manganese ions a detailed mechanism cannot be deduced from the present data.[7]

TABLE I

RATE CONSTANTS FOR METALLOPORPHYRIN REDUCTIONS AT 25°, pH 2.0, μ = 1.0 ($HClO_4$–$NaClO_4$)

		Fe(III)–TPyP		Mn(III)–TPyP	
Reducing agent	Anion	$k_1{}^a$	$k_2{}^b$	$k_1{}^a$	$k_2{}^b$
Cr(II)		700 ± 10		840 ± 160	
	Cl^-		9.1 ± 0.4 × 10^5		3050 ± 40
	Br^-		4.2 ± 0.3 × 10^5		*e*
	I^-		4.0 ± 0.2 × 10^5		*e*
	SCN^-		2.3 ± 0.2 × 10^7		2.7 ± 0.1 × 10^5
V(II)		1035 ± 35		145 ± 5	
	Cl^-		3.2 ± 0.3 × 10^4		$<10^3$ [g]
	Br^-		1.9 ± 0.2 × 10^4		$<10^3$ [g]
	SCN^-		1.0 ± 0.1 × 10^7		4.2 ± 0.1 × 10^5
$Cr(bipy)_3{}^{2+}$ [c-f]		8660 ± 260		1290 ± 40	
Eu(II)[e]		1.5 ± 0.2 × 10^4			

[a] F^{-1} sec.^{1}. [b] F^{-2} sec.$^{-1}$. [c] μ = 0.1. [d] bipy/Cr(II) > 50. [e] Anion effects not studied. [f] Ref. 2. [g] Only upper limit.

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