

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 Uitert³ 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.

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The Reaction of Iron Pentacarbonyl with Acetylacetone

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Received January 18, 1965

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

(1) T. G. Dunne and F. A. Cotton, *Inorg. Chem.*, **2**, 263 (1963).

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 FeC₁₀H₄O₄: 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.).

(2) B. N. Figgis and J. Lewis, "The Magneto-chemistry of Complex Compounds," in J. Lewis and R. G. Wilkins, Ed., "Modern Coordination Chemistry," Interscience Publishers Inc., New York, N. Y., 1960, p. 406.

(3) B. Emmert and R. Jarzynski, *Ber.*, **64**, 1072 (1931).

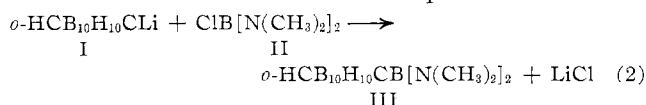
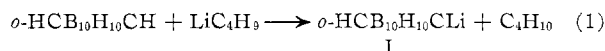
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o-Carboranyl Derivatives of Boron Compounds

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Received December 10, 1964

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 $46 \pm 2^\circ$ and slowly distilled under vacuum at 100° in a molecular still. The infrared spectrum of

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

(2) T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *ibid.*, **2**, 1097 (1963).

(3) D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *ibid.*, **2**, 1120 (1963).

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 C₂₁H₆₆B₃₃N₃: 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).

Acknowledgment.—The research reported in this publication was supported by Wright Air Development Division, Air Research and Development Command, United States Air Force, under Contract AF 33(616)-6722.

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The Reactions of Manganese(III) and Iron(III) Tetrapyrrolylporphines with Various Reducing Agents¹

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Received November 30, 1964

We wish to report the results of an investigation concerning the rates of the reduction of manganese(III)

Experimental

The tetrapyrrolylporphine 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 Sutin⁵ by following the decrease of the 398 mμ peak of the Fe(III)-TPyP ($\epsilon 9.1 \times 10^4$) or the 463 mμ peak of the Mn(III)-TPyP ($\epsilon 11.7 \times 10^4$) species as a function of time. The products were analyzed spectrophotometrically and identified as Fe(II)-TPyP (λ_{\max} 443 mμ, $\epsilon 12.5 \times 10^4$) or Mn(II)-TPyP (λ_{\max} 423 mμ, $\epsilon 15.3 \times 10^4$). 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 Plane.⁶

Results

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

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

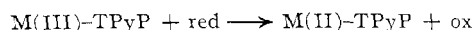
where X is a halide ion (Cl⁻, Br⁻, I⁻, or SCN⁻). Table I lists the set of rate constants k_1 and k_2 for various reducing agents. The product study with chromous ion as a reducing agent showed that the product of the chloride-catalyzed path was always Cr(H₂O)₅Cl²⁺. Because of the lability of both the 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, $\mu = 1.0$ (HClO₄-NaClO₄)

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

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

and iron(III) tetrapyrrolylporphine (TPyP) with various reducing agents. The stoichiometry of the reaction is



where "red" is the reducing agent.

(1) This research was supported by a grant from the Public Health Service.

(2) E. B. Fleischer, *Inorg. Chem.*, **1**, 493 (1962).

(3) J. Candlin, J. Halpern, and D. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

(4) A. I. Vogel, "Quantitative Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1961.

(5) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

(6) R. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3504 (1959).

(7) See the following for a discussion of activated complexes in electron-transfer reactions: G. Dulz and N. Sutin, *J. Am. Chem. Soc.*, **86**, 829 (1964); J. Halpern, *Quart. Rev. (London)*, **15**, 207 (1961).