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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The Reactions of Manganese(III) and Iron(III) Tetrapyridylporphines with Various Reducing Agents[1]

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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^-		$9.1 \pm 0.4 \times 10^5$		3050 ± 40
	Br^-		$4.2 \pm 0.3 \times 10^5$		*e*
	I^-		$4.0 \pm 0.2 \times 10^5$		*e*
	SCN^-		$2.3 \pm 0.2 \times 10^7$		$2.7 \pm 0.1 \times 10^5$
V(II)		1035 ± 35		145 ± 5	
	Cl^-		$3.2 \pm 0.3 \times 10^4$		$<10^{3\,g}$
	Br^-		$1.9 \pm 0.2 \times 10^4$		$<10^{3\,g}$
	SCN^-		$1.0 \pm 0.1 \times 10^7$		$4.2 \pm 0.1 \times 10^5$
$Cr(bipy)_3^{2+\,c-f}$		8660 ± 260		1290 ± 40	
$Eu(II)^e$		$1.5 \pm 0.2 \times 10^4$			

[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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