and the volatilization of the molecular Pt_6Cl_{12}. The amount of Pt "missing" in the TG experiment has been observed to vary with sample size, heating rate, and gas flow rate. The thermodynamics and kinetics of these reactions have been studied via the reaction of Pt with Cl_2.[7]

Thermograms obtained at any heating rate from 1 to 30°/min in air or He show no plateaus corresponding to the composition $PtCl_4$. The constitutive water and HCl in the $(H_3O)_2(PtCl_6)$ cannot be removed below about 300 °C, and $PtCl_4$ begins to decompose to $PtCl_2$ and chlorine at this temperature.[9] Hence, it is not possible to prepare $PtCl_4$ in good yield in an inert atmosphere by a thermal decomposition of chloroplatinic acid. $PtCl_2$ does exhibit a narrow range of stability, from about 350 to 410 °C, and it should be possible to prepare the β-$PtCl_2$ in good yield by a thermal decomposition. Current preparation procedures for making $PtCl_2$ all suggest that thermal decomposition leads to impure products.[10,11] However, we have successfully prepared 10-g batches of pure, highly crystalline β-$PtCl_2$ by simple thermal decomposition of chloroplatinic acid in air using a tube furnace. The acid is spread into a thin layer (<5 mm thick) on the tube furnace boat, and a steady air purge through the tube is maintained, 200 mL/min, through a tube of approximately 1-L volume. The temperature is raised from room temperature to 350 °C in 50 °C steps over 3 h. The product in the furnace boat represents a 100% yield.

The volatility of Pt_6Cl_{12} in the thermal decomposition to metallic Pt offers an explanation for the ease of dispersing Pt as small crystallites on high surface area catalysts and catalyst supports.

Registry No. $[H_3O]_2[PtCl_6]\cdot xH_2O$, 26023-84-7.

References and Notes

(1) K. Kinoshita, K. Routsis, and J. A. S. Bett, *Thermochim. Acta*, **10**, 109 (1974).
(2) J. Escard, B. Pontvianne, M. T. Chenebaux, and J. Cosyns, *Bull. Chim. Soc. Fr.*, 2399 1975.
(3) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Wiley, New York, N.Y., 1972, pp 166–168.
(4) Matthey Bishop chloroplatinic acid, Lot No. 31455.
(5) K. Brodersen, G. Thiele, and H. G. von Schnering, *Z. Anorg. Allg. Chem.*, **337**, 120 (1965).
(6) V. Wiese, H. Schafer, H. G. von Schnering, C. Brendle, and K. Rinke, *Angew. Chem., Int. Ed. Engl.*, **9**, 158 (1970).
(7) A. Landsberg and J. L. Schaller, *J. Less-Common Met.*, **23**, 195 (1971).
(8) Powder patterns were calculated using POWD2 (D. K. Smith, UCRL-50264, 1967; *Norelco Rep.*, **15**, 57 (1968)) with the help of S. L. Lawton and D. H. Olson of the Mobil Laboratories.
(9) S. A. Shchukarev, M. A. Oranskaya, and T. S. Shemyakina, *Zh. Neorg. Khim.*, **1**, 17 (1956).
(10) W. E. Cooley and D. H. Busch, *Inorg. Synth.*, **5**, 208 (1957).
(11) A. J. Cohen, *Inorg. Synth.*, **6**, 209 (1960).

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A General Synthesis of Amine–Cyanoboranes

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The amine–cyanoborane $Me_3N\cdot BH_2CN$ is a precursor in the synthesis of $Me_3N\cdot BH_2COOH$, the protonated boron analogue of the dipolar amino acid betaine, $Me_3N^+CH_2COO^-$.[1] Both $Me_3N\cdot BH_2COOH$ and its *N*-ethylamide derivative have demonstrated significant antitumor and hypolipidemic activity in mice.[1,2] Furthermore, several amine–cyanoboranes have also shown similar biological activity.[2] Although a number of amine–cyanoboranes have been prepared,[3–6] the methods used either resulted in low yields[3–5] or were limited as to reaction scale.[6] Therefore, in view of the potential uses of amine–cyanoboranes and their derivatives, it was desirable to find a convenient large-scale preparation of these compounds.

A number of amine–boranes, amine·BH_3, have been prepared by the reaction of ammonium salts with lithium or sodium borohydride.[7] Using a similar procedure we have prepared a series of amine–cyanoboranes by the reaction of sodium cyanohydroborate and amine hydrochlorides in refluxing tetrahydrofuran (THF).[8]

$$NaBH_3CN + \text{amine}\cdot HCl \xrightarrow[65\ ^\circ C]{THF} \underset{\textbf{1-6}}{\text{amine}\cdot BH_2CN} + H_2 + NaCl$$

amine = Me_3N (**1**), Me_2NH (**2**), $MeNH_2$ (**3**), C_5H_5N (**4**), $PhNH_2$ (**5**), *p*-$MeC_6H_4NH_2$ (**6**)

In the cases of the reactions involving $Me_3N\cdot HCl$, $PhNH_2\cdot HCl$, and *p*-$MeC_6H_4NH_2\cdot HCl$, the crude products were solids which were readily purified by recrystallization or sublimation. Removal of the solvent from the reactions involving $Me_2NH\cdot HCl$ and $C_5H_5N\cdot HCl$, however, resulted in viscous oils which were difficult to crystallize or sublime. In these cases purification involved the dissolution of the oils in H_2O, followed by extraction of the amine–cyanoboranes into Et_2O, thereby removing the H_2O-soluble starting materials. The amine–cyanoboranes were then easily purified by sublimation. The purified products were obtained in good yields[9] and were identified by elemental analysis, IR and ^1H NMR spectroscopy, and melting point (Table I).

Although the amine–cyanoboranes were generally white crystalline solids, all attempts to crystallize or sublime **3**, the product of the reaction of $MeNH_2\cdot HCl$ and $NaBH_3CN$, were unsuccessful. Nevertheless, the viscous liquid obtained from the Et_2O extraction of the aqueous solution of the reaction products was found to have a satisfactory elemental analysis. Moreover, its ^1H NMR spectrum exhibited the expected triplet for the *N*-methyl protons due to coupling to the NH protons. Similar coupling was observed in the spectrum of $Me_2NH\cdot BH_2CN$.[6]

In a recent study of the isomers of $Me_3N\cdot BH_2(CN)$ Vidal and Ryschkewitsch[10] compared the C≡N infrared frequencies of the two isomers and found that the isocyano absorption at 2135 cm^{-1} was at least 50 cm^{-1} lower then the C≡N absorptions in the cyano isomer which range from 2185 to 2280 cm^{-1}. The lowest C≡N absorptions in the infrared spectra of the compounds that we have prepared range from 2180 to 2200 cm^{-1} which indicates that the cyano and not the isocyano isomers were formed. Further evidence for the cyano structure in these compounds is the thermodynamic preference of the boron–carbon bond over the boron–nitrogen bond as demonstrated by the easy isomerization of $Me_3N\cdot BH_2NC$ to $Me_3N\cdot BH_2CN$[10] and $NaBH_3NC$ to $NaBH_3CN$.[11] In view of the conditions of the above reactions (i.e., refluxing THF), it is unlikely that the isocyano isomers would be isolated.

In addition, it may be noted that qualitatively the relative rates of these reactions seemed to correlate with the pK_a of the corresponding ammonium cations. For example, the reactions involving the methylamine hydrochlorides (pK_a's range from 9.8 to 11)[12] required several days to go to completion, i.e., for evolution of hydrogen to cease. On the other hand, the reactions of the hydrochlorides of the weaker bases (aniline, pK_a = 4.6, and pyridine, pK_a = 5.3)[12] were much faster and in some cases evolution of hydrogen was so vigorous that it was necessary to combine the reagents quite slowly in order to control the reaction.

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Table I. Physical and Spectroscopic Data for Amine–Cyanoboranes, amine·BH_2CN

compd	amine	reflux time, h	yield, %	mp, °C	% found (calcd)	^{1}H NMR data[a] (δ, multiplicity, J)	IR, cm^{-1}
1	Me_3N	48	82	63, lit. 63[3]		ref 6	ref 6
2	Me_2NH	86	58	54–55, lit. 57[6]	C 43.11 (42.93) H 10.57 (10.81) B 12.62 (12.88) N 33.17 (33.38)	ref 6	ref 6
3	$MeNH_2$	200	48		C 34.60 (34.36) H 9.92 (10.09) B 15.70 (15.47) N 40.06 (40.08)	BH_2 (2.0, q, J_{BH} = 100) Me (2.35, t, J_{HNCH} = 6) NH_2 (4.48, s)	3200 s, 3020 s, 2960 s, 2900 w, 2725 w, 2420 s, 2350 sh, 2300 sh, 2260 s, 2200 s, 1680 m, 1600 s, 1490 sh, 1460 s, 1420 w, 1325 s, 1160 s, 1100 s, 1050 s, 1015 m, 960 m, 880 m, 800 w
4	C_5H_5N	16	68	34–35[b]	C 60.98 (61.10) H 6.06 (5.98) B 9.28 (9.16) N 23.56 (23.75)	BH_2 (2.68, q, J_{BH} = 100) C_5H_5N (7.52, 7.97, 8.33, m)	3060 m, 2410 s, 2330 sh, 2200 w, 1620 m, 1485 m, 1455 m, 1340 w, 1250 w, 1205 w, 1160 sh, 1120 s, 1095 s, 1050 m, 1020 m, 835 m, 760 s, 725 s, 690 s
5	$PhNH_2$	19	60	152–154	C 63.58 (63.71) H 6.74 (6.87) B 8.37 (8.19) N 21.11 (21.23)	Ph (7.24, m) NH_2 (8.10, s) BH_2[c]	3010 s, 2390 s, 2350 sh, 2180 w, 1590 m, 1490 m, 1470 m, 1310 m, 1290 m, 1225 m, 1180 m, 1160 w, 1110 s, 1070 w, 1030 w, 1010 m, 915 w, 895 w, 835 m, 755 s, 685 m
6	p-$MeC_6H_4NH_2$	16	90	134	C 65.45 (65.81) H 7.93 (7.59) B 7.57 (7.40) N 18.81 (19.19)	Me (2.25, s) C_6H_4 (7.07, s) NH_2 (7.90, s) BH_2[c]	3350 m, 3150 s, 3070 s, 2910 sh, 2580 w, 2390 s, 2310 sh, 2190 m, 1890 w, 1660 w, 1585 s, 1500 m, 1420 m, 1290 s, 1210 m, 1165 m, 1090 s, 1010 w, 1000 m, 920 w, 890 m, 840 m, 800 s, 750 m, 730 w

[a] Chemical shifts in ppm from Me_4Si, coupling constants in Hz; d = doublet, t = triplet, q = quartet, m = multiplet. Solvent: CD_3CN for 3 and 4, Me_2SO-d_6 for 5 and 6. [b] See footnote 15. [c] Signal not observed.

There has been only one report of the preparation of the parent amine–cyanoborane $NH_3·BH_2CN$.[13] In other attempts to prepare this compound a novel complex, $[Na(NH_3·BH_2CN)_6]I$, was obtained.[14] Our attempts to prepare ammonia–cyanoborane via the reactions of either NH_4Cl or NH_4I with $NaBH_3CN$ were unsuccessful, resulting instead in unidentified colorless oils. Alternative synthesis of $NH_3·BH_2CN$ will be reported separately.

Experimental Section

Proton NMR spectra were recorded using JEOL-MH 100, Varian EM-360, or Varian T-60 spectrometers. Infrared spectra were run as KBr disks or as a neat liquid on Perkin-Elmer 137, 237, or 297 spectrophotometers. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., or by M-H-W Laboratories, Garden City, Mich. Sodium cyanohydroborate was purchased from Aldrich and used without further purification. The amine hydrochlorides were used as received from commercial sources. Tetrahydrofuran was dried by refluxing over and distilling from $LiAlH_4$. For reactions requiring long reflux periods, a round-bottom flask directly sealed to a reflux condenser was used to prevent the solvent from dissolving the stopcock grease. Hydrogen evolution was monitored by connection to a bubbler.

General Procedure. A solution of $NaBH_3CN$ (typically 250–500 mmol) and an excess of the appropriate amine hydrochloride in THF was allowed to reflux until evolution of hydrogen was complete. The reaction mixture was cooled and filtered, the solid (NaCl) was washed with THF, and the solvent was removed from the filtrate at reduced pressure leaving the amine–cyanoborane. In the case of the reaction of pyridine hydrochloride, evolution of hydrogen was extremely rapid and it was necessary to add a solution of $NaBH_3CN$ in THF slowly via an addition funnel to a stirred slurry of pyridine hydrochloride in THF before reflux was started.

Purification. Compound **5** was recrystallized from $EtOH/H_2O$, while **1** and **6** were purified by recrystallizing from THF–petroleum ether. Alternatively, **1** could be sublimed in vacuo. Compounds **2**, **3**, and **4** were dissolved in H_2O and the aqueous solution was extracted with Et_2O. The combined Et_2O extracts were dried over $MgSO_4$ and filtered, and the solvent was removed at reduced pressure. The residue was then sublimed in vacuo. Attempts to crystallize or sublime **3** were unsuccessful. Physical and spectroscopic data are given in Table I.

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Registry No. **1**, 30353-61-8; **2**, 51329-61-4; **3**, 66632-42-6; **4**, 66632-43-7; **5**, 66632-44-8; **6**, 66632-45-9; $NaBH_3CN$, 25895-60-7; $Me_3N·HCl$, 593-81-7; $Me_2NH·HCl$, 506-59-2; $MeNH_2·HCl$, 593-51-1; $C_5H_5N·HCl$, 628-13-7; $PhNH_2·HCl$, 142-04-1; p-$MeC_6H_4NH_2·HCl$, 540-23-8.

References and Notes

(1) B. F. Spielvogel, L. Wojnowich, M. K. Das, A. T. McPhail, and K. D. Hargrave, *J. Am. Chem. Soc.*, **98**, 5702 (1976).
(2) I. H. Hall, C. O. Starnes, B. F. Spielvogel, P. Wisian-Neilson, M. K. Das, and L. Wojnowich, submitted for publication in *J. Pharm. Sci.*
(3) (a) S. S. Uppal and H. C. Kelly, *Chem. Commun.*, 1619 (1970); (b) C. Weidig, S. S. Uppal, and H. C. Kelly, *Inorg. Chem.*, **13**, 1763 (1974).
(4) P. J. Bratt, M. P. Brown, and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 2161 (1974).
(5) D. R. Martin, M. A. Chiusano, M. L. Denniston, D. J. Dye, E. D. Martin, and B. T. Pennington *J. Inorg. Nucl. Chem.*, **40**, 9 (1978).
(6) O. T. Beachley and B. Washburn, *Inorg. Chem.*, **14**, 120 (1975).
(7) K. Beeker, "Gmelin Handbook of Inorganic Chemistry", K. Niedenzu and K.-C. Buschbeck, Ed., Springer-Verlag, New York, N.Y., 1977 [New Supplementary Series, Vol. 45, Part 14], and references cited therein.
(8) In one instance Kelly et al.[3b] have used this method to prepare *N*-methylmorpholine–cyanoborane.
(9) A reviewer has suggested that the lower yields obtained using a previous method[3] (i.e., addition of an amine to acidified THF solutions of $NaBH_3CN$) may be the result of a hydroboration reaction involving the CN group which is avoided using the method reported here. However, studies of the reaction of $NaBH_3CN$ and HCl in ether and THF have shown that only stable macrocyclic and polymeric $(BH_2CN)_n$ exist in the solutions [B. F. Spielvogel, R. F. Bratton, C. G. Moreland, *J. Am. Chem. Soc.*, **94**, 8597 (1972)]. The ^{11}B NMR studies of the addition of amine bases to solutions containing $(BH_2CN)_n$ in ether solvents show the disappearance of only the cyanoborane signal and appearance of only the amine–cyanoborane signal [B. F. Spielvogel, D. Denton, R. F. Bratton, and C. G. Moreland, paper in preparation]. Thus, the difference in yields is more likely ascribed to differences in isolation procedures used to obtain the final product.
(10) J. L. Vidal and G. E. Ryschkewitsch, *Inorg. Chem.*, **16**, 1898 (1977).
(11) R. C. Wade, E. A. Sullivan, J. R. Berschied, Jr., and K. F. Purcell, *Inorg. Chem.*, **9**, 2146 (1970).

(12) "Handbook of Chemistry and Physics", 49th ed, CRC Press, Cleveland, Ohio, 1969.
(13) P. J. Bratt, M. P. Brown, and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 353 (1976).
(14) K. D. Hargrave, A. T. McPhail, B. F. Spielvogel, and P. Wisian-Neilson, *J. Chem. Soc., Dalton Trans.*, 2150 (1977).
(15) While this work was in progress, another preparation of **4** was reported[5] but no melting point was given since the compound was isolated as a green oil which was not sublimed or purified by any other methods.

Contribution from the Department of Chemistry, Howard University, Washington, D.C. 20059

Kinetics of the Reduction of Iron(III) Meso- and Deuteroporphyrin Esters by Chromium(II)

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Many kinetic studies have been done on the reduction to their divalent forms of cobalt(III), iron(III), and manganese(III) porphyrins by chromium(II),[1-4] vanadium(II),[1] europium(II),[1] dithionite,[5-7] hexaammineruthenium(II),[8] and tin(II).[9] The majority of this work has involved synthetic porphyrins of the *meso*-tetraphenyl type made water soluble by virtue of carboxylic acid, sulfonic acid, pyridinium, or *N*-methylpyridinium groups. In certain cases, this functionalization apparently provides pathways for electron transfer not available to natural porphyrins of the protoporphyrin type, and hence such synthetic adducts serve as poor models for heme-type proteins. Electron-transfer experiments on the reduction of iron(III) cytochrome *c*,[10-12] myoglobin,[13] and hemoglobin[13] have appeared. We report the kinetics of reduction of the iron(III) complexes of meso- and deuteroporphyrin IX dimethyl ester by chromium(II). These natural type porphyrins were solubilized and monomerized using the neutral detergent Triton X-100. Our results are compared with the kinetic behavior of related synthetic porphyrins.

Experimental Section

Meso- and deuteroporphyrin IX dimethyl ester (MPDME, DPDME) and their iron(III) dimer complexes were prepared by literature methods.[14] The iron porphyrins were dissolved in acetone and heated in a 2% Triton X-100 (spectroscopic grade, Research Products International Corp., Elk Grove, Ill.) solution until the acetone evaporated. The resulting solution was then filtered at room temperature through Metricel 0.45 μm filters and adjusted to the proper ionic strength.

Excellent isosbestic points were obtained in the Soret region from spectrophotometric acid–base titrations of the iron porphyrins in 2% Triton X-100, μ = 0.5 ($NaClO_4/HClO_4$) at 25 °C. The pK_1 for the hydrolysis reactions

$$H_2O\text{-}Fe^{III}P \leftrightarrow HO\text{-}Fe^{III}P + H^+ \quad K_1 \tag{1}$$

were determined by standard means.[15] pK_1 = 4.7 for Fe^{III}DPDME and 5.0 for Fe^{III}MPDME. "*n*", the number of protons dissociated, was 1.07 ± 0.07 for the iron meso complex and 0.99 ± 0.01 for the iron deutero ester.

The chromous solutions were prepared by zinc amalgam reductions of chromium(III) and analyzed spectrophotometrically by the permanganate method.[16] The kinetics were followed on a Durrum-Gibson stopped-flow apparatus using Hamilton gastight syringes to handle the air-sensitive, N_2 deaerated solutions. At pH 1, reoxidation by molecular oxygen of the chromium(II) reduced ferric porphyrins produced a mixture of the initial ferric porphyrin and the diprotonated porphyrin diacid, due to acid solvolysis of the iron(II) porphyrin form.

With the MPDME and DPDME iron(III) complexes, no evidence for ring reduction by Cr(II), as previously noted[6] in the Cr^{II}/M^{III}–tetrakis(4-*N*-methylpyridyl)porphyrin reactions, was found. In line with this observation, polarographic studies[9] in DMF/0.1 M *n*-Pr_4NClO_4 indicate that the free base form of tetrakis(4-*N*-methylpyridyl)porphyrin is reduced more easily ($E_{1/2}$ = −1.02 V vs. $Ag|Ag^+$ (0.1 M)) than either the corresponding H_2MPDME (−1.82 V) or H_2DPDME (−1.76 V).

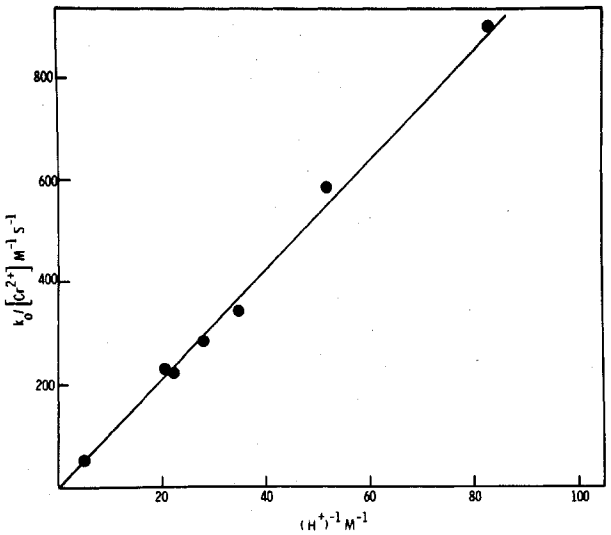

Figure 1. Plot of $k_{obsd}/(Cr^{2+})$ vs. $(H^+)^{-1}$ for the reaction of chromium(II) with iron(III) deuteroporphyrin dimethyl ester in 2% Triton X-100, 25 °C, μ = 0.5 ($NaClO_4/HClO_4$).

Results

The kinetics of the reduction of the iron(III) porphyrins by chromium(II)

$$Fe^{III}P + Cr^{2+} \rightarrow Fe^{II}P + Cr^{3+} \tag{2}$$

were studied at 25 °C, μ = 0.5 ($NaClO_4/HClO_4$) in 2% Triton X-100 between pH 0.2 and 2. Under pseudo-first-order conditions with at least 100-fold excess of Cr^{2+} to porphyrin, the reactions were first order in porphyrin over at least 2.5 half-lives. The reactions at constant pH were first order in chromium(II). The specific rate constant ($k_{obsd}/(Cr(II))$) increased with an increase in pH. Figure 1 shows a linear plot of the specific rate constant vs. $(H^+)^{-1}$ for Fe^{III}DPDME. The observed rate law is of the form $k_{obsd} = k(Cr(II))(H^+)^{-1}$. For Fe^{III}DPDME, k = 11.0 ± 0.3 s^{-1}, and for Fe^{III}MPDME, k = 1.6 ± 0.2 s^{-1}.

One overall mechanism for this reaction might be

$$H_2O\text{-}Fe^{III}P = HO\text{-}Fe^{III}P + H^+ \quad K_1 \tag{3}$$

$$Cr^{2+} + H_2O\text{-}Fe^{III}P \rightarrow \text{products} \quad k_1 \tag{4}$$

$$Cr^{2+} + HO\text{-}Fe^{III}P \rightarrow \text{products} \quad k_2 \tag{5}$$

The derived rate law would be

$$[k_{obsd}/(Cr(II))][1 + K_1/(H^+)] = k_1 + k_2K_1(H^+)^{-1} \tag{6}$$

If k_1 = 0 and, under our conditions, $[1 + K_1/(H^+)] = 1$, then our calculated rate constant, k, would equal k_2K_1. For Fe^{III}DPDME, $k_2 = 5.5 \times 10^5$ M^{-1} s^{-1} and for Fe^{III}MPDME, $k_2 = 1.7 \times 10^5$ M^{-1} s^{-1}.

Discussion

In terms of proton affinity (pK_3 for the monocation/free base equilibria), H_2MPDME (pK_3 = 5.9) is more basic[17] than H_2DPDME (5.5). It is thus not unexpected that H_2O–Fe^{III}MPDME (pK_1 = 5) is a weaker acid (more iron(II) porphyrin character) than the corresponding iron deuteroporphyrin (4.7). The more basic Fe^{III}MPDME is reduced the slowest by chromium(II), and similar results have been found for the dithionite[5] and tin(II)[9] reductions of manganese(III) and cobalt(III) porphyrins.

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