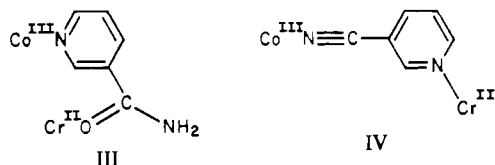


tautomerism is most unlikely with glycine because of the lack of activating organic groups, and it would not provide a conjugated system between metal centers because of the NH_2 group. In view of the great kinetic similarity of the glycine and cyanoacetate systems, the bridged-outer-sphere mechanism is the best way to rationalize the results.

The bridged-outer-sphere mechanism is difficult to distinguish from the inner-sphere mechanism, with electron transfer through the bridging group, because both result in ligand transfer to chromium(III). The outer-sphere path would only be expected when the substituent coordinated to chromium(II) is not in conjugation with the ligand atom bonded to cobalt(III) and when the bridged intermediate can attain a conformation in which chromium(II) and cobalt(III) have a normal outer-sphere interaction distance. Thus, the nicotinamide complex¹⁶ was found to give 70% ligand transfer and could be using a bridged outer-sphere intermediate such as III. Presumably



the cyanoacetamide complex does not do this because the amide group is much less basic and complex formation there

is unfavorable. On the other hand, with 3-cyanopyridine (IV),¹⁷ close contact of cobalt and chromium is not possible, and the observed 55% ligand transfer would seem to require electron transfer through the bridging ligand.

Taube and Gould¹⁸ observed that dicarboxylate bridging groups on cobalt(III) show an $[\text{H}^+]^{-1}$ term in the rate law for chromium(II) reduction only when there is potential for chelation between the remote and adjacent (to cobalt) carboxylates. But the chromium(III) products have extinction coefficients typical of monodentate carboxylate complexes. The ability to form a chelate with the adjacent carboxylate is tantamount to the ability to bring the remotely attached chromium(II) close to the cobalt(III). Thus, these observations could be explained by a bridged-outer-sphere mechanism without chelation in the transition state.

These few examples are just meant to illustrate some of the problems that the bridged-outer-sphere mechanism may raise and sometimes resolve.

Acknowledgment. We thank the National Science and Engineering Council of Canada for support of this work.

Registry No. $((\text{NH}_3)_5\text{CoNCCH}_3)(\text{ClO}_4)_3$, 15663-50-0; $((\text{NH}_3)_5\text{CoNCCH}_2\text{CH}_2\text{CN})(\text{ClO}_4)_3$, 78128-40-2; $((\text{NH}_3)_5\text{CoNCCH}_2\text{C}(\text{ONH}_2)(\text{ClO}_4)_3$, 78128-42-4; $((\text{NH}_3)_5\text{CoNCCH}_2\text{CO}_2\text{CH}_3)(\text{ClO}_4)_3$, 78128-44-6; $((\text{NH}_3)_5\text{CoNCCH}_2\text{CO}_2\text{H})(\text{ClO}_4)_3$, 77906-13-9; Cr^{2+} , 22541-79-3.

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Reaction between Epoxides and β -Diketonate Complexes of Low-Valent Vanadium and Molybdenum

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A series of epoxides were deoxygenated with the use of β -diketonate complexes of low-valent vanadium and molybdenum to give olefins and oxidized metallic species. Stereospecificity of deoxygenation was variable and was found to depend on the size of substituents on the oxirane ring and on the β -diketonate ligands. A mechanism is proposed for deoxygenation based on a metallooxetane intermediate.

Introduction

Deoxygenation of epoxides with the use of reagent systems obtained by reduction of metal halides is a subject of continuing interest in which attention has been focused historically on obtaining procedures attractive to the synthetic organic chemist.¹⁻¹⁰ The resulting lack of information concerning

either the metallic starting materials or the metallic products in utilized reagents, however, hampers rational evolution of new systems of enhanced utility. We have therefore studied deoxygenation reagent systems in which at least partial characterization of critical metallic species and systematic modification thereof can be accomplished and in which trends can be discerned relating parameters of the metallic complex starting material to the specificity of deoxygenation. In this context we describe the reaction between epoxides and β -diketonate complexes of V(II) and Mo(II) which have been prepared with reference to known routes.

Experimental Section

Preparation of Starting Materials. Dichlorobis(β -diketonato)vanadium(IV) complexes were prepared according to published routes by reacting the corresponding bis(β -diketonato)oxovanadium(IV) compounds with thionyl chloride¹¹ or by reacting VCl_4 with β -diketonates.¹² Dihalobis(β -diketonato)molybdenum(IV) species were obtained from MoCl_5 and β -diketonates.¹³ Treatment of $\text{Cl}_2(\text{acac})_2\text{V}$

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Table I. Deoxygenation of Epoxides to Olefins^a

epoxide	reagent ^{b,c}	% olefin yield ^d	stereo-chemistry ^e	
			cis	trans
	V(acac) ₂	88	51	49
	V(dpm) ₂	~100	42	58
	V(tfa) ₂	41	44	56
	Mo(acac) ₂	61	72	28
	V(acac) ₂	45	41	59
	V(dpm) ₂	~100	43	57
	Mo(acac) ₂	66	25	75
	V(acac) ₂	44	43	57
	V(dpm) ₂	~100	43	57
	Mo(acac) ₂	95	83	17
	Mo(dpm) ₂	~100	77	23
	V(acac) ₂	88	32	68
	V(dpm) ₂	92	42	58
	Mo(acac) ₂	93	15	85
	Mo(dpm) ₂	98	22	78
	V(acac) ₂	82	47	53
	V(dpm) ₂	99	45	55
	V(tfa) ₂	56	41	59
	Mo(acac) ₂	99	84	16
	Mo(dpm) ₂	96	75	25
	V(acac) ₂	82	33	67
	V(dpm) ₂	~100	44	56
	Mo(acac) ₂	79	14	86
	Mo(dpm) ₂	83	19	81

^a For a continuation of Table I, see the paragraph on supplementary material. ^b Reagents were prepared from dihalobis(β-diketonato)metal complexes as described and were used without removal of Hg. ^c All reactions were run at 65–78 °C for 18–24 h; 4–5 equiv of metallic species were used. ^d Yields were determined by GLC using internal standards. ^e Olefinic products and oxirane starting materials are configurationally stable under the reaction conditions.

(acac = 2,4-pentanedionato) with 2 equiv of sodium (as a 2.4% amalgam) in DME at room temperature under N₂ resulted in a series of color changes, first to a dark green solution and finally to a deep blue one containing the V(II) species.^{14–16} (This compound could be rapidly air oxidized to VO(acac)₂.) A DME solution of this compound is stable under N₂ or argon for several days, even at 90 °C. Similar observations were made concerning reduction of V-(dpm)₂Cl₂ and V(tfa)₂Cl₂ (dpm = dipivaloylmethanato; tfa = 1,1,1-trifluoroacetylacetonato). In similar fashion, Na amalgam treatment of a suspension of Cl₂Mo(acac)₂ in DME resulted in a dark red-brown solution, presumably containing Mo(II)¹⁷ (which could then be air oxidized to afford a mixture of MoO₂(acac)₂ and Mo₂O₃(acac)₄^{18,19}).

Deoxygenation of Epoxides. A typical experimental procedure can be illustrated for the reduction of *cis*-4-methyl-2-pentene oxide with "Mo(acac)₂".^{16,17} A mixture of 0.556 g (1.5229 mmol) of Cl₂Mo(acac)₂ and 2.992 g (3.1219 mmol) of Na/Hg (2.4%) in 20 mL of DME was stirred at room temperature for 5 h to give a dark red-brown solution. To this solution (at room temperature) was added 0.472 mL (0.3045 mmol) of a 0.6455 M solution of *cis*-4-methyl-2-pentene oxide in DME. The mixture was stirred at 65 °C for 25 h. After 0.0117 g of pentane was added, the resulting mixture was evaporated under high vacuum. The obtained sample was analyzed by GLC (10%

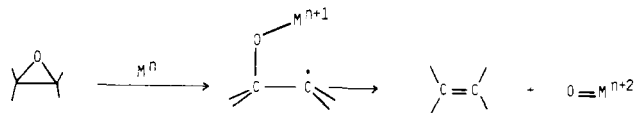


Figure 1.

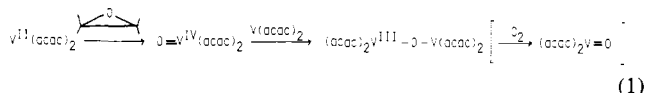
EDO-1) to determine total yield of olefin (95%) and (17% AgNO₃-EG) to determine the ratio of *cis*- and *trans*-4-methyl-2-pentenes (83:17). Similar reaction sequences were employed using vanadium species (see Table I).

Identification of Oxidized Metallic Species. A mixture of 0.500 g (1.562 mmol) of Cl₂V(acac)₂ and 3.07 g (3.203 mmol) of Na/Hg (2.4%) in 25 mL of DME was stirred for 5 h at room temperature under Ar to give a deep blue solution. To this solution was added excess 1-hexene oxide (10 equiv); the mixture was stirred at 59–62 °C for 4 days. The resulting dark brown solution was subjected to evaporation under high vacuum. The residue was dissolved in dry O₂-free toluene, and the solution was filtered under N₂. The filtrate was concentrated to afford a brown solid. The infrared spectrum of this brown solid displayed *no* absorption bands at 996 and 480 cm⁻¹ characteristic of VO(acac)₂.²⁰ This brown solid slowly turned dark green when dissolved in ethanol and exposed to air, and bands at 996 and 480 cm⁻¹ appeared. An infrared spectrum of this green sample was identical with that of an authentic sample of VO(acac)₂. The same brown solid was obtained by reacting V(acac)₂ (generated from Cl₂V(acac)₂ and Na/Hg) with VO(acac)₂.

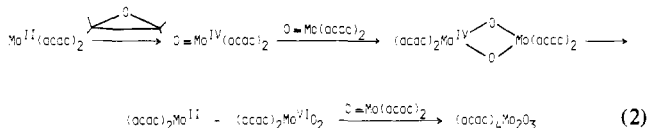
The dark red-brown solution, generated from Cl₂Mo(acac)₂ and Na/Hg, was treated with excess *cis*-4-octene oxide (5.2 equiv) at room temperature for 1 h and then at 58–60 °C for 76 h. Workup of the brown solids produced a mixture of MoO₂(acac)₂ (IR (Nujol) = 938, 911 cm⁻¹) and Mo₂O₃(acac)₄ (IR (Nujol) = 958, 930 cm⁻¹; UV (CH₂CN) 250, 322, 405, 482).¹⁸ This same mixture was obtained on air oxidation of "Mo(acac)₂".

Discussion

Either V(II) or Mo(II) β-diketonate complexes readily deoxygenate epoxides to give olefins. Both reduce both cyclic and acyclic epoxide species to give olefins in good to excellent yields as shown in Table I. It is likely that a V(III) binuclear complex²¹ is the ultimate product in deoxygenation of epoxides and is formed by reaction between V(II) and V^{IV}=O units according to reaction 1. Although MoO(IV) complexes are



not common,²⁸ MoO(acac)₂ is a reasonable candidate for the initial metallic product of deoxygenation; the origin of the isolated molybdenum oxo species may occur as shown below (reaction 2).



From an examination of the literature, one notes that metallic species capable of reducing epoxides to olefins can

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 (15) Pyridine complexes of V(acac)₂ have also been reported: Torii, Y.; Iwaki, H.; Inamura, Y. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1550.
 (16) We do not know if Cl⁻ ions remain ligated to the metal atom.
 (17) Mo(acac)₂ has been reported but not characterized: Svitych, R. B.; Buchachenko, A. L.; Yablonskii, O. P.; Petukhov, A. A.; Belyaev, V. A.; Kobayakov, A. K. *Kinet. Catal. (Engl. Transl.)* **1974**, *15*, 1149. The structure of this material remains to be determined.
 (18) Gehrke, H., Jr.; Veal, J. *Inorg. Chim. Acta* **1969**, *3*, 623.
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 (21) μ-Oxo-bridged binuclear complexes are well-known. For example: VOV⁴⁺,²² CrOCr⁴⁺,²³ FeOFe⁴⁺,²⁴ CrOV⁴⁺,²⁵ RuOV⁴⁺,²⁶ and FeOCr⁴⁺.²⁷
 (22) Newton, T. W.; Baker, F. B. *Inorg. Chem.* **1964**, *3*, 569. Kristine, F. J.; Shepherd, R. E. *J. Am. Chem. Soc.* **1977**, *99*, 6562; **1978**, *100*, 4398.
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 (28) For example, see: Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Hursthouse, M. G.; Motevalli, M. *J. Chem. Soc., Dalton Trans.* **1979**, 1603.

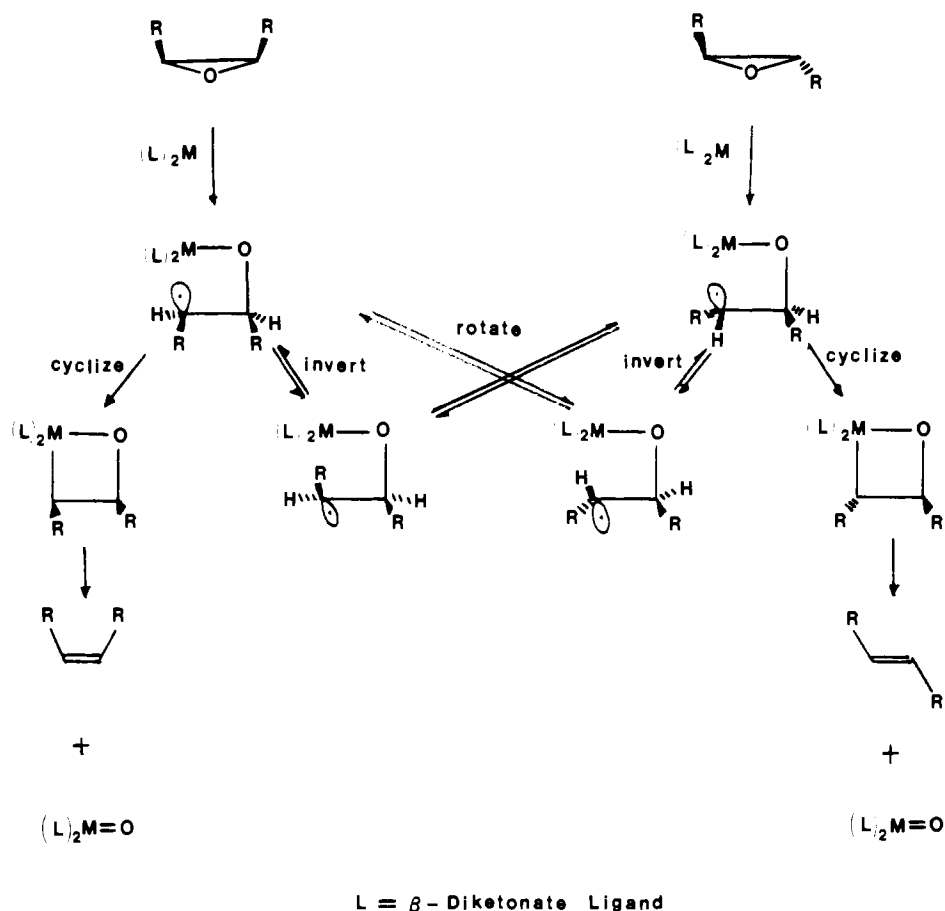


Figure 2.

be grouped broadly into two categories. (1) For class I species, the *same* mixture of cis and trans olefins is obtained from *either* cis or trans epoxides (nonspecific deoxygenation). Chromous ion,³ $TiCl_3$ -LAH,⁵ and WCl_6 -LAH⁶ reagent species belong to this group. (2) Class II species give rise to olefins with predominance of *retention* of stereochemistry from either cis or trans epoxide. Several tungsten reagents⁴ and many metallocenes⁷ belong in this group. As can be seen in Table I, these vanadium and molybdenum species are unusual in that, according to steric modification of the diketonate ligand environment, these reagents bridge class I or class II behavior; consequently, noting this ligand dependence can be used to help elucidate deoxygenation chemistry in general. For vanadium and for a given epoxide, a *decrease* in stereospecificity for deoxygenation is noticed as the steric size of ligands on the vanadium increases. For example, in the case of the 2-butene epoxides and $V(acac)_2$, some net retention occurs. However, when the $(dpm)_2V$ system is employed, no such specificity is maintained. All deoxygenation reactions involving molybdenum complexes proceeded with higher specificity than those for vanadium systems. As well, with these molybdenum complexes a greater degree of retention was noted for epoxides which had sterically *large* substituents on the three-membered ring than for those bearing small ones. Here, too, as was noted in the case of vanadium, changing *acac* to the somewhat bulkier *dpm* group resulted in a decrease in stereospecificity.

Class I and class II reagents have been discussed according to two extreme mechanisms. The first involves a stepwise deoxygenation mechanism involving diradicals in an "open" transition state and was postulated to explain nonstereospecificity of reduction of epoxides by Cr(II) and Ti(II) species.^{3,5} The other mechanism involves a postulated metallooxetane.^{8,10} Inherent in the concept of cycle formation is the notion of steric

interactions between substituents on the organic fraction of the metallooxetane and substituents on the metal. By virtue of ionic radii, molybdenum complexes, comparably ligated to those of vanadium, should be less sterically congested at the metal. As well, the introduction of bulky alkyl substituents on the diketonate ligands should introduce crowding about the metal site and, hence, impede metallooxetane formation. We propose that the initial product of reaction between the reduced metal species and the epoxide is an open-chain one which can be configurationally trapped by carbon-metal bond formation (closure to the metallooxetane, thence to yield olefin) competitive with carbon-carbon bond rotation (which would ultimately lead to nonspecific olefin formation) as shown in Figure 2. The critical feature, we conclude, in determining the stereospecificity of epoxide deoxygenation, then, would be the relative rate of metallooxetane ring formation vs. rotation about the C-C bond.²⁹ As has been shown in other cases, the presence of alkyl substituents on the C-C unit should be associated with a *decrease* of the C-C rotation rate as a

(29) An alternative, *acyclic* mechanism to explain stereospecificity of deoxygenation as a function of alkyl group substitution on the epoxide, or of change in metal, involves a competition between carbon-carbon bond rotation and rupture of the carbon-oxygen bond with concomitant formation of $M=O$. We have noted how a change in alkyl group size would affect the rate of carbon-carbon bond rotation.³⁰ The rate of carbon-oxygen bond formation should correlate with the strength of the $M=O$ unit; the stronger the $M=O$ bond, the faster its formation should be and, hence, the greater the stereospecificity for olefin formation. Substitution on the β -diketonate ligands is known to affect $M=O$ bond strength: for vanadium oxo species $\nu_{V=O}$ has been measured for a series of β -diketonate ligands and has been correlated with the $V=O$ bond strength.²⁰ Noteworthy is the observation that for $(acac)_2V=O$ $\nu_{V=O} = 996\text{ cm}^{-1}$ and for $(dpm)_2V=O$ $\nu_{V=O} = 1006\text{ cm}^{-1}$. In other words, by this mechanism it would be predicted that $(dpm)_2V$ should deoxygenate epoxides with a *greater* degree of stereospecificity than would $V(acac)_2$, a prediction which stands *contrary* to the results observed.

function of the size of these alkyl substituents: smaller substituents should be able to pass one another readily³⁰ than should large ones. Hence, increasing the alkyl group size on the epoxide should lead to an increase in stereospecificity, provided that this increase in alkyl group size did not adversely affect the rate of ring closure. Clearly, reducing congestion about the metal (bigger ionic size, smaller ligands) would enhance this cyclization rate.

Acknowledgment. The authors acknowledge generous support for this work by the National Science Foundation (Grant No. CHE-79-00996). Y.H. thanks Mitsubishi Petrochemical Company (Japan) for financial support.

(30) For example, see: Doering, W. von E.; Barsa, E. A. *Tetrahedron Lett.* 1978, 2495 and references cited therein.

Registry No. *cis*-2,3-Dimethyloxirane, 1758-33-4; *trans*-2,3-dimethyloxirane, 21490-63-1; *cis*-2,3-epoxy-4-methylpentane, 3204-02-2; *trans*-2,3-epoxy-4-methylpentane, 2390-95-6; *cis*-2,3-dipropyloxirane, 1439-06-1; *trans*-2,3-dipropyloxirane, 1689-70-9; 7-oxabicyclo[4.1.0]heptane, 286-20-4; 8-oxabicyclo[5.1.0]octane, 286-45-3; ethyloxirane, 106-88-7; *cis*-2-ethyl-3-methyloxirane, 3203-99-4; *trans*-2-ethyl-3-methyloxirane, 3203-98-3; V(acac)₂, 14024-62-5; V(dpm)₂, 78624-81-4; V(tfa)₂, 78624-82-5; Mo(acac)₂, 34346-27-5; Mo(dpm)₂, 78624-83-6; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; *cis*-4-methyl-2-pentene, 691-38-3; *trans*-4-methyl-2-pentene, 674-76-0; *cis*-4-octene, 7642-15-1; *trans*-4-octene, 14850-23-8; cyclohexene, 110-83-8; cycloheptene, 628-92-2; 1-butene, 106-98-9; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8.

Supplementary Material Available: A table of deoxygenation of epoxides to olefins (1 page). Ordering information is given on any current masthead page.

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Characterization of the Thermolysis Products of Fe(TPTZ)₂Cl₂·nH₂O and the Related 2,4,6-Tris(2-pyridyl)-1,3,5-triazine Complexes Zn(TPTZ)Cl₂ and Fe(TPTZ)Cl₃

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Received February 4, 1981

A new five-coordinate ferrous complex, Fe(TPTZ)Cl₂, has been synthesized. The neat powder form of this species undergoes a slow, irreversible oxidation in the atmosphere at ambient temperature to the very strongly antiferromagnetically coupled ferric dimer [Fe(TPTZ)Cl₂]₂O. These complexes as well as the related Zn(TPTZ)Cl₂ and Fe(TPTZ)Cl₃ complexes are characterized by a variety of physical methods.

Introduction

Thermolysis of a series of six-coordinate low-spin bis(terpyridine) ferrous compounds, Fe(2,2',2''-terpyridine)₂X₂, produces complexes which are five-coordinate when X = Br⁻, I⁻, and NCS⁻ and high-spin by replacing one neutral tridentate ligand with two monovalent counteranions. The double salt [Fe(terpy)₂]²⁺[FeCl₄]²⁻ is obtained upon thermolysis of Fe(terpy)₂Cl₂.¹ The latter double salt complex contains a very stable low-spin, pseudooctahedral cation and a well-known pseudotetrahedral ferrous anion. Another bis(trimine)iron(II) compound has been thermolized in the present study in an attempt to add a chloride member to this series. Heating the navy blue, low-spin Fe(2,4,6-tris(2-pyridyl)-1,3,5-triazine)₂Cl₂·nH₂O (hereafter, Fe(TPTZ)₂Cl₂) does result in a new species, Fe(TPTZ)Cl₂. Unlike the mono(terpyridine) complexes, however, this gray blue TPTZ product is air sensitive and upon prolonged exposure to air oxidizes to a green complex, believed to be a μ-oxo dimer.

Zero- and high-field Mössbauer spectroscopy, magnetic susceptibility measurements, IR spectra, and X-ray powder and solution conductivity measurements are presented below as means to identify each of these new species. Schematic diagrams of the tris(pyridyl)triazine and 2,2',2''-terpyridine ligands are shown in Figure 1. The similarity of their tridentate nature is apparent.

Experimental Section

Preparation of [Dichloro]bis(2,4,6-tris(2-pyridyl)-1,3,5-triazine)iron Dihydrate. This compound and its thermolysis products were first prepared by M. Kahjehnessiri.² A solution of the TPTZ ligand in

absolute ethanol was added to freshly prepared FeCl₂·4H₂O in a 2.1:1 ligand to metal ratio. The navy blue salt was precipitated after reducing the volume of the solution to only a few milliliters and subsequently adding acetone. The product was recrystallized from absolute ethanol and acetone.

Preparation of Fe(TPTZ)Cl₂. The Fe(TPTZ)₂Cl₂·2H₂O starting material was placed in a thermolysis oven and heated under vacuum (~10 μm) to 180 °C for ~10 h. The ligand was observed to come off between 170 and 180 °C, and the final product represented ~60% weight loss. The original sample had turned grayish blue. Gravimetric factors for the calculation of the theoretical yield of the bis-to-mono conversion are in the range of 0.5843–0.5577 with the assumption of zero to two waters of hydration in the precursor. Anal. Calcd for FeC₁₈H₁₂N₆Cl₂: C, 49.16; H, 2.73; N, 19.12. Found: C 49.06; H, 2.87; N, 19.29.²

Preparation of [Fe(TPTZ)Cl₂]₂O·2H₂O. After exposure to air for several months, the gray-blue polycrystalline Fe(TPTZ)Cl₂ sample converts to a light green material. Prolonged vacuum thermolysis of this new material at T ≈ 200 °C had no effect, suggesting that the gray-blue to green conversion does not involve a readily reversible oxygenation. The progression of the conversion was monitored by Mössbauer spectroscopy. Spectral parameters and susceptibility results (to be discussed) show that the conversion involves oxidation of the ferrous centers. Anal. Calcd for [Fe(TPTZ)Cl₂]₂O·2H₂O: C, 46.42; H, 2.99; N, 18.05; Fe, 12.03. Found: C, 46.33; H, 2.46; N, 17.72; Fe, 12.4.

Preparation of Fe(TPTZ)Cl₃·1.5H₂O. In this preparation, a methanol solution of the ligand (2.56 mM) was added to a methanol solution of nominally anhydrous FeCl₃ (1.28 mM) under gaseous nitrogen. The yellowish orange product was filtered under vacuum and washed with absolute methanol twice. Anal. Calcd for [Fe(TPTZ)Cl₃]₂·3/2H₂O: C, 43.00; H, 2.99; N, 16.74. Found: C, 43.26; H, 2.53; N, 16.81.

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(2) M. Kahjehnessiri, Master Degree Thesis, Northeastern University, 1974.