Bimetallic Reactivity. General Synthesis of Binucleating Macrocyclic Ligands Containing 6- and 4-Coordinate Sites

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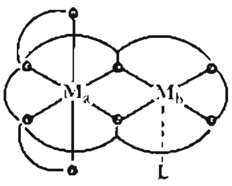
General methods are described for the synthesis of binucleating macrocyclic ligands containing 6- and 4-coordinate sites. The procedure involves the formation of a mononuclear complex containing two appropriately positioned aldehyde groups followed by acid-catalyzed condensation with a diamine to give the isolated complexes of the type $[M(\text{ligand})(H^+)_2]^{n+}$ where the 4-coordinate site is occupied by two protons. The following diamines were incorporated in the 6- and 4-coordinate sites; ethylenediamine, trimethylenediamine and *S*-1,2-propylenediamine. Eight of the diamine combinations were isolated and characterized. The monometallic complexes are ideal precursors for the synthesis of site-specific heterobimetallics under mild conditions. When *S*-1,2-propylenediamine is present at the 6-coordinate site only one chiral topology is induced in the complex but an *S*-1,2-propylenediamine link at the 4-coordinate site induces little or no diastereomeric selection. The stereochemistry of monometallic and bimetallic complexes was deduced by ^{1}H NMR data, X-ray crystallography, and circular dichroism spectra. The first two methods indicate that when the macrocycle contains ethylenediamine links in both the 6- and 4-coordinate sites, the ligand cannot accommodate two metals in a planar geometry. The ideal ring size for the incorporation of two metals in a C_2 symmetric topology requires trimethylenediamine links in both sites. The circular dichroism spectra are generally not useful in assigning absolute configurations without information about the conformation of the ligand. The Co(III)/Co(II) redox couples of complexes of the type $[Co(\text{ligand})ZnCl]^{n+}$ indicate that the Co(III) state is readily accessible when the 6-coordinate site incorporates an ethylenediamine link but not when trimethylenediamine is present at this site. It is probable that this difference reflects, in the latter complexes, the inability of the ligand to accommodate the structural requirements of Co(III).

Numerous binucleating ligands and their bimetallic complexes have been prepared and characterized.[1] These studies had a number of objectives including finding structural analogues of metalloproteins, studying the cooperative physical behavior of contiguous metals and a general interest in exploring metal compounds of new ligand types. We recently introduced a binucleating ligand of the general formulation **1**[2-5] which in its general macrocyclic framework contains a sexadentate compartment (closed-site) and a contiguous quadridentate compartment (open-site). This ligand system was designed in order to explore the possibility of binding a substrate to the open-site metal and using the reducing power of both metals to reduce the bound substrate. For example, it is conceivable that dioxygen bound to the open-site metal could be reduced to peroxide by using one electron from each metal. Similarly, an oxo ligand transferred from a oxo-transfer reagent could bind to the open-site metal after oxidizing each of the metals by one unit. By use of different metal combinations, distinct reactivity patterns might be expected and new catalysts may ensue.



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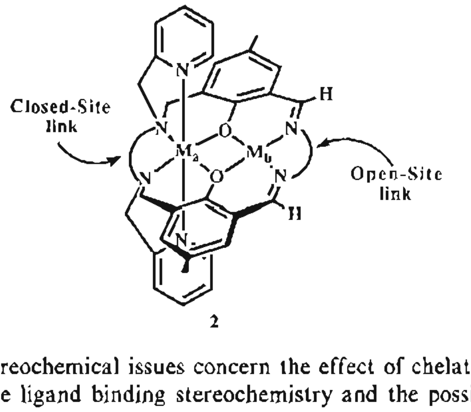
This paper describes the evolution of such systems which require a number of characteristics to be embodied. The constant features of our binucleating ligand are illustrated in **2**. We wished to investigate the influence of the closed- and open-site links on the stereochemistry of bimetallic systems and on the redox properties of the closed-site metal. Further, we sought to develop general, reliable synthetic methods for preparing heterobimetallic complexes with labile metal ions.



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The stereochemical issues concern the effect of chelate link size on the ligand binding stereochemistry and the possibility

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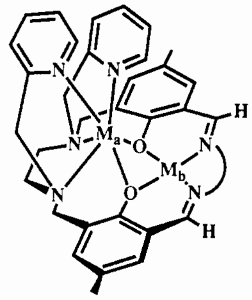
that chiral links may induce a single chiral topology of the ligand framework. We have noted previously[2,3] that when an ethylenediamine link is present in the closed-site, unsymmetrical *bimetallic* complexes of the structure **3** are generally formed irrespective of the span of the open-site link. Proper adjustment of the link sizes at the two sites may lead to the consistent formation of the C_2 symmetric bimetallic structures **2**. This objective involves more than a stereochemical exploration. Our ultimate interest is to avoid stereochemical ambiguity in asymmetric catalysis involving the open-site metal. Thus, using bimetallic complexes for asymmetric epoxidation of olefins[2,6,7] the oxo intermediate can form in two stereochemical environments in structure **3**, but in **2** the axial positions of the open-site metal are identical because of the C_2 axis. If the chiral topology of the bimetallic complex were the major source of chiral induction in these bimetallic systems, then it would be advantageous to fix the topological chirality by introducing a chiral link. In this way resolutions are avoided and racemization suppressed regardless of the metal type, labile or otherwise. The solution of these stereochemical problems must be correlated with the redox properties of the bound metals, as the metals must have access to higher oxidation states in order to reduce a substrate. Previously, we found that the link size has a strong effect on the redox properties of the metals, particularly metals in the closed-site.[4,5] We explore the variation in the Co(III)/Co(II) redox couple in the closed-site with variations in link size.



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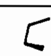
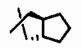
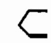
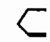
1. Scope and Nomenclature

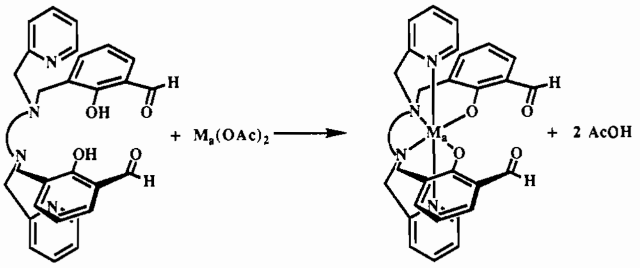
Table 1 lists ligands prepared and their names (see **2**). The names refer to the dianionic ligand and the closed-site link precedes the open-site link. Complexes are written as, for example, $[M_a(\text{enenim})M_bX]^{n+}$, where the closed-site metal, M_a, is written first, followed by the ligand, followed by the open-site metal, M_b, followed by the ligands on M_b. Our earlier nomenclature has been abandoned so that cyclim[2] becomes entnim, *S*,*S*-cypim[3,4] becomes *S*,*S*-encnim, and cytim[5] becomes tntnim. Work on these three ligands is described elsewhere, but they are included here for comparison.

Table 1. Nomenclature of the Macrocyclic Binucleating Ligands

entry	ligand name	closed-site link	open-site link
1	enen		
2	*S*-enpn		
3	entn		
4	*S*,*S*-encn		
5	*S*-pnen		
6	*S*-pntn		
7	tnen		
8	*S*-tnpn		
9	tntn		

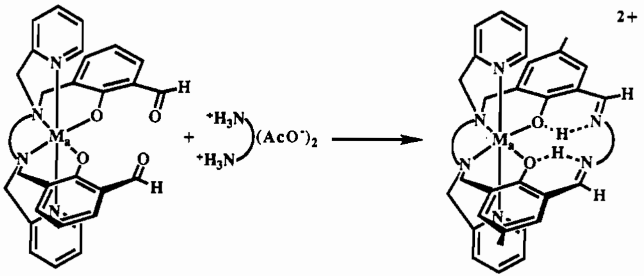
2. Synthesis

The dialdehyde precursors **4** were prepared by methods described previously.[2,3,5] The dialdehyde containing the *S*-1,2-propylenediamine[8] (*S*-pn) link was prepared by variation of the described synthesis.[2] Reaction of all of the dialdehydes, **4**, with zinc and cobalt acetates leads to the formation of very insoluble neutral species of the type **5**. When ethylenediamine and *S*-1,2-propylenediamine links are present the C_2 symmetric structures **5** appear to be produced,[2] but with a trimethylenediamine link the dialdehyde complexes appear to contain all three possible topological isomers of **5**. We discovered that irrespective of the link size of **5** these insoluble complexes reacted with diamines in the presence of 2 equiv of acetic acid to give the monometallic macrocyclic complexes **6a**. The yields are high, ranging from 60 to 80%. The two protons appear to reside in the open-site cavity.[3,5] This is supported by the broad ^1H NMR signals (in CD_3CN) of these protons which are coupled to the azomethine protons. Upon



4a: enalH$_2$
4b: tnalH$_2$
4c: S-pnalH$_2$

5a-c



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6a

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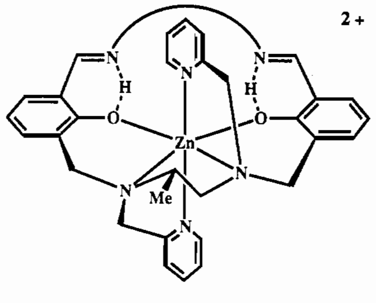
the addition of D_2O the signals corresponding to the protons in the open-site cavity disappear, and no coupling to the azomethine protons is detected.

The ^1H NMR spectra of all of the monometallic Zn(II) complexes of the type **6a** indicate that all of these complexes are C_2 symmetric as shown. Further, those complexes bearing an *S*-pn link at the closed-site give only a single diastereomer indicating that the chirality of the *S*-pn link specifies the topological chirality. This observation is analogous to that observed for *S*-propylenediaminetetraacetate complexes[9] which are stereospecifically formed. The requirement that the methyl group of the *S*-pn link be equatorially disposed leads to the conclusion that the Δ topological isomer is formed, namely, the diastereomer shown in **6b**. Acetonitrile solutions of the complexes $[Zn(S\text{-pnenim})(H^+)_2]^{2+}$ and of $[Zn(S\text{-pntnim})(H^+)_2]^{2+}$ are configurationally stable for 2 weeks as indicated by the constancy of the ^1H NMR spectrum at 25 °C.



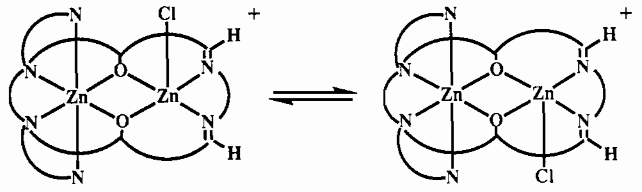
6b

The complexes $[Zn(S\text{-enpnim})(H^+)_2]^{2+}$ and $[Zn(S\text{-tnpnim})(H^+)_2]^{2+}$ were isolated as roughly equal mixtures of the two topological isomers. The ratio of these isomers remains constant in CD_3CN solutions for each complex. Fractional crystallization (CH_3CN–ethanol) of the $[Zn(S\text{-enpnim})(H^+)_2](PF_6)_2$ complex and mechanical separation of the crystals gave a sample consisting of a 6:1 mixture of diastereomers. When this mixture was dissolved in acetonitrile solution at 25 °C the diastereomeric mixture very slowly equilibrated to an almost equal mixture of diastereomers. The first order rate constant ($k_1 + k_{-1}$) for approach to equilibrium ($K = 1.08$) was found to be 1.0×10^{-5} s^{-1}, with a half-life for approach to equilibrium $t_{1/2}(k_1 + k_{-1}) =$ 18.7 h: $t_{1/2}(k_1) = 36.3$ h, and $t_{1/2}(k_{-1}) = 38.5$ h. Since in order to switch from one topological enantiomer to the other requires inversion at both of the tertiary amine ligands, and it is known that tertiary amines do not invert when bound to a metal,[10] the metal presumably is required to dissociate from these ligands. The precise nature of this putative occurrence is not known but it is possible that the zinc ion interchanges the sites of the binucleating ligand without fully dissociating. The slow rate of equilibration, however, indicates that even labile metals are relatively kinetically inert in the closed-site. This also implies that if sufficiently mild conditions are used, site-specific bimetallic complexes can be prepared from these monometallic precursors. It is intriguing that the complexes with an *S*-pn open-site link give almost equal amounts of the topological isomers because, as we reported earlier,[3] the $[M(S,S\text{-encnim})(H^+)_2]^{2+}$ complexes are formed as only one topological isomer. This difference presumably reflects the fact that the *S*,*S*-1,2-aminomethylcyclopentane link of *S*,*S*-encnim imparts a more pronounced twist to the ligand framework than does the open-site *S*-pn link.

The mono-Co(II) complexes, $[Co(\text{ligand})(H^+)_2](PF_6)_2$, (ligand = enenim, *S*-pnenim, entnim, *S*-pntnim, tnenim, tntnim) were isolated and characterized. The complexes containing a 5-membered link at the closed site, that is complexes of the ligands enenim, *S*-pnenim, entnim, and *S*-pntnim, were oxidized to the Co(III) complexes $[Co(\text{ligand})(H^+)_2](PF_6)_3$ with ferrocenium hexafluorophosphate. Complexes with 6-membered chelate links at the closed-site, the tnenim and tntnim complexes, could not be oxidized. The ^1H NMR spectra of the Co(III) complexes indicate that all have the C_2 symmetric topology in which the pyridines are disposed trans (see **6a**). The complexes containing the *S*-pn link consist of one topological isomer indicating that the *S*-pn link induces the formation of the Δ-topological isomer exclusively. The ^1H NMR data are given in the Experimental Section for these and other complexes.

Bimetallic complexes incorporating zinc chloride in the open-site were prepared from the monometallic precursors under mild conditions by adding solutions of $ZnCl_2$ to solutions of the $[M(\text{ligand})(H^+)_2]^{n+}$ complexes in the presence of triethylamine. In this way the homobimetallic complexes $[Zn(\text{ligand})ZnCl]PF_6$ (ligand = entnim, tnenim, tntnim) were isolated, but we have not found conditions which give the di-Zn species of enenim, *S*-pnenim, and *S*-pntnim in a pure state. The Co(III) complexes $[Co(\text{ligand})ZnCl](PF_6)_2$ (ligand = enenim, entnim, *S*-pnenim, *S*-pntnim) and the Co(II) complexes $[Co(\text{ligand})ZnCl]PF_6$ (ligand = tnenim, tntnim) were prepared similarly.

The ^1H NMR spectra of the diamagnetic bimetallic complexes in CD_3CN solutions infer a number of interesting stereochemical features. The three di-Zn(II) complexes of entnim, tnenim, and tntnim show signals that are broad at 25 °C, and the number of resonances suggests that the molecules possess either a C_2 or a C_s axis on the ^1H NMR time scale. These same complexes in CD_2Cl_2 solutions at 25 °C show spectra which indicate that the molecules are devoid of symmetry elements. These results are consistent with the existence of the equilibrium depicted as **7** ⇌ **8** where the Cl^- ion interchanges from one side of the mean macrocyclic plane to the other. In CD_3CN solutions this process is fast on the ^1H NMR time scale, giving a broad, approximately symmetrical spectrum. In CD_2Cl_2 solutions this interchange occurs more slowly or not at all and results in an unsymmetrical spectrum. Consistent with the postulate that the interchange process occurs by dissociation are the facts that Cl^- is better solvated in CD_3CN than in CD_2Cl_2 and that CD_3CN is a better ligand. It should be noted that the molar conductivities of all of the bimetallic chloro–Zn(II) complexes in CH_3CN solutions are consistent with the presence of a coordinated Cl^- ligand (see Experimental Section) so that the standing concentration of uncoordinated Cl^- is low.



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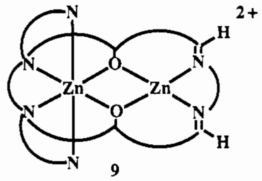
Removal of the bound Cl^- ligand with Ag^+ ions leads to the production of species which give ^1H NMR spectra that indicate symmetrical species of the type **9** or **10**, the latter of which could achieve C_s symmetry on the ^1H NMR time scale through conformational fluxionality. A crystal structure of [Zn-



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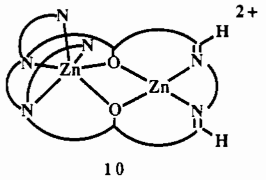

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[9] (a) Dwyer, F. P.; Garvan, F. L. *J. Am. Chem. Soc.* **1961**, *83*, 2610–2615. (b) Dwyer, F. P.; MacDermott, T. E. *J. Am. Chem. Soc.* **1963**, *85*, 2916–2919.

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(tntnim)Zn(OAc)]$^+$ shows the ligand topology shown in **9**,[5] and it is probable that structure **9** also obtains for the tnenim di-Zn(II) complex. Previous work[2,3] on complexes bearing an ethylenediamine link at the closed-site indicates that most of such bimetallic complexes containing stereochemically labile metals adopt the structure **10**. The number of resonances in the ^{1}H NMR spectrum of [Zn(entnim)ZnCl]$^+$ in CD_2Cl_2 solution indicates that an unsymmetrical complex is present. The two resolved signals due to the *p*-tolyl methyl protons and those due to the 5-pyridyl protons are of equal areas, respectively. This indicates that either the complex adopts the structure with trans pyridines, with the chloro ligand breaking the C_2 symmetry axis, or that the complex adopts the C_s symmetric structure with cis pyridines, with an equal distribution of the chloro ligands in the two distinct open-site coordination positions. We consider the latter case improbable since the two coordination positions have significantly different steric environments. Upon removal of the chloro ligand with Ag$^+$ ions to produce [Zn(entnim)Zn]$^{2+}$, a symmetric ^{1}H NMR spectrum is produced, which is consistent with either scenario. Unless one supposes that the structure **10** were to form the two possible chloro coordination isomers in equal proportions, these data suggest that the dizinc complexes of entnim have the trans pyridine C_2 symmetric structures in solution.

No ambiguities arise when the stereochemically rigid Co(III) is present in the closed site. The ^{1}H NMR spectra and previous work[2,3] on monometallic complexes bearing an ethylenediamine link at the closed-site strongly suggest that all of these monometallic Co(III) complexes have the structure **6a**. Incorporation of Zn(II) in the open-site will not change the overall stereochemistry.

The ^{1}H NMR spectra of [Co(ligand)ZnCl](PF$_6$)$_2$ (ligand = enenim, *S*-pnenim, entnim, *S*-pntnim) complexes in CD_3CN solutions at 25 °C are sharp and suggest that Cl$^-$ ligand interchange in these complexes is slow compared to that in the di-Zn(II) analogues. All of the ^{1}H NMR spectra for the Co(III) complexes were run in CD_3CN solutions at 25 °C. The ^{1}H NMR spectrum of [Co(entnim)ZnCl]$^{2+}$ indicates an unsymmetrical structure consistent with the presence of the Zn–Cl fragment, which removes the 2-fold axis of symmetry. Upon removal of the chloro ligand with Ag$^+$ ions, the spectrum is consistent with a C_2 symmetric structure. It is of interest to note that the preparation of this [Co(entnim)ZnCl]$^{2+}$ complex by ferrocenium ion oxidation of the Co(II) complex, [Co(entnim)ZnCl]$^+$, gives a product with an identical ^{1}H NMR spectrum. This suggests that the Co(II) precursor has the same topology as the Co(III) product. The [Co(*S*-pntnim)ZnCl]$^{2+}$ complex displays a spectrum which suggests the existence of two unsymmetric isomers in the ratio of ~7:1. Upon removal of the chloro ligand a single isomer is produced. Given that the *S*-pn link exists in a puckered conformation, the two isomers of the chloro complex are expected because the two axial Zn(II) sites are stereochemically different. Upon removal of the chloro ligand these axial sites become equivalent and a single diastereomer is formed. This, however, is not the case when the open-site bears an ethylenediamine link. The ^{1}H NMR spectrum of [Co(enenim)ZnCl]$^{2+}$ implies an unsymmetrical complex as expected. Upon removal of the chloro ligand, however, the spectrum remains unsymmetrical. A similar situation obtains for the [Co(*S*-pnenim)ZnCl]$^{2+}$ complex which exists as two isomers in a ratio of ~5:1. Upon removal of the chloro ligand the spectrum indicates that two isomers remain in the same ratio. We believe that the isomerism that is observed in the dechlorinated complexes arises from the coordination of the Zn(II), which lies out of the open-site coordination plane because the open-site cavity is insufficient to accommodate the Zn(II) when the ethylenediamine link is present. Expansion of this open-site link by one carbon atom allows the Zn(II) to coordinate in the mean macrocyclic plane, and hence this out-of-plane isomerism is not observed for the entnim and *S*-pntnim complexes. The fact that two out-of-plane isomers are observed in the [Co(*S*-pnenim)Zn]$^{3+}$ complex indicates that the Zn(II) neither dissociates intermolecularly nor passes through the open-site cavity by an intramolecular process on the NMR time scale.

Table 2. Crystal Parameters for [Co(enenim)ZnCl](PF$_6$)$_2$·EtOH

formula	$[CoC_{34}H_{36}N_6O_2O_2ZnCl][PF_6]_2 \cdot C_2H_5OH$
fw	1056.4
cryst syst	orthorhombic
space group	$P2_12_12_1$
a, Å	14.646(5)
b, Å	16.155(6)
c, Å	17.703(8)
V, Å^3	4188.8(29)
Z	4
D(calc), g cm^{-3}	1.675
μ(Mo Kα), cm^{-1}	12.07
temp, K	242
wavelength, Å	0.710 73
absolute structure	η = 1.14(12)
R,[a] %	7.45
R$_w$,[b] %	9.38

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$; $w^{-1} = \sigma^2 F_o + gF_o^2$.

Table 3. Selected Bond Distances and Angles for [Co(enenim)ZnCl](PF$_6$)$_2$·EtOH

	Bond Distances (Å)		
Zn–Co	3.033(3)	Co–O(1)	1.890(11)
Zn–Cl	2.196(6)	Co–O(2)	1.904(11)
Zn–O(1)	2.084(11)	Co–N(1)	1.961(14)
Zn–O(2)	2.102(11)	Co–N(2)	1.932(15)
Zn–N(5)	2.114(16)	Co–N(3)	1.945(13)
Zn–N(6)	2.033(17)	Co–N(4)	1.959(14)
	Bond Angles (deg)		
Co–Zn–Cl	113.4(2)	Zn–Co–N(2)	131.9(5)
Co–Zn–O(1)	37.9(3)	Zn–Co–N(3)	93.8(4)
Co–Zn–O(2)	38.4(3)	Zn–Co–N(4)	83.5(4)
Co–Zn–N(5)	114.2(4)	O(1)–Co–O(2)	85.6(5)
Co–Zn–N(6)	119.8(4)	O(1)–Co–N(1)	94.1(5)
Cl–Zn–O(1)	109.7(3)	O(1)–Co–N(2)	171.1(5)
Cl–Zn–O(2)	112.6(4)	O(1)–Co–N(3)	86.6(5)
Cl–Zn–N(5)	118.9(4)	O(1)–Co–N(4)	88.1(5)
Cl–Zn–N(6)	106.6(4)	O(2)–Co–N(1)	176.5(6)
O(1)–Zn–O(2)	76.0(4)	O(2)–Co–N(2)	90.4(6)
O(1)–Zn–N(5)	87.1(5)	O(2)–Co–N(3)	92.3(5)
O(1)–Zn–N(6)	143.3(5)	O(2)–Co–N(4)	89.1(5)
O(2)–Zn–N(5)	128.5(5)	N(1)–Co–N(2)	90.4(6)
O(2)–Zn–N(6)	85.5(5)	N(1)–Co–N(3)	84.2(6)
N(5)–Zn–N(6)	80.0(6)	N(1)–Co–N(4)	94.4(6)
Zn–Co–O(1)	42.7(3)	N(2)–Co–N(3)	101.5(6)
Zn–Co–O(2)	43.3(3)	N(2)–Co–N(4)	84.0(6)
Zn–Co–N(1)	136.7(4)	N(3)–Co–N(4)	174.4(6)

This isomer feature is supported by an X-ray structure of the [Co(enenim)ZnCl](PF$_6$)$_2$ crystal. The crystallographic data are collected in Table 2, and Table 3 lists selected bond length and angle data. The structure is shown in Figure 1. It can be seen that the Zn(II) ion lies above the plane defined by O(1), O(2), N(5), and N(6) by about 0.78 Å. The diagonal distances of the cavity are O(1)–N(6) = 3.9 Å and O(2)–N(5) = 3.8 Å which cannot accommodate Zn(II) in the mean plane because the Zn–N and Zn–O distances are each about 2.1 Å (Table 3). It will be noted that the topology about the Co(III) ion is that expected with trans-disposed pyridines. The phenolic residues are both tilted away from the Zn(II) ion as a consequence of the requisite out-of-plane coordination geometry. Usually with these ligands the phenolic residues adopt a twisted conformation, above and below the mean macrocyclic plane, when the pyridines are trans disposed. The out-of-plane Zn(II) ion forces the present conformation presumably in order to accommodate the directional properties of the four donor atom orbitals. The bond lengths and angles are otherwise unexceptional except to note that the interplay

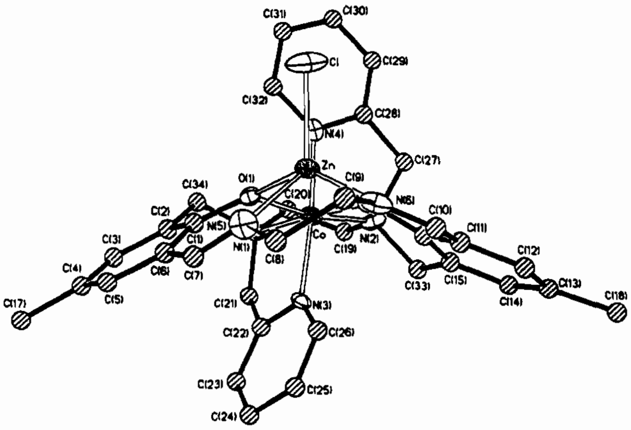

Figure 1. Side view of the molecular structure of [Co(enenim)ZnCl]-$(PF_6)_2 \cdot EtOH$ drawn with 35% probability ellipsoids, showing the placement of the Zn atom.

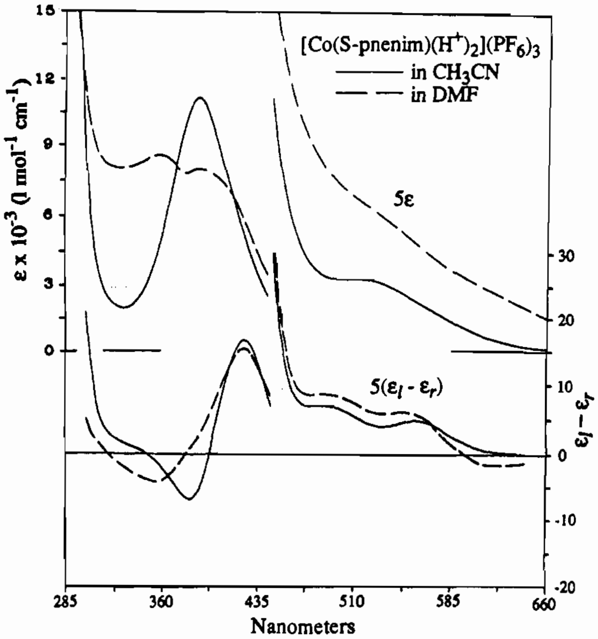

Figure 2. Absorption and circular dichroism spectra of Δ-[Co(*S*-pnenim)-$(H^+)_2]^{3+}$ in CH_3CN and DMF solutions.

of conformational accommodation to the out-of-plane Zn(II) ion causes minor distortions in bond lengths and angles (Table 2).

3. Circular Dichroism Spectra

We present a number of absorption and circular dichroism spectra of the chiral complexes in order to ascertain whether these can be used to assign the absolute configurations of these types of complexes. All have the Δ absolute configuration. The spectra of the Δ-[Co(*S*-pnenim)$(H^+)_2]^{3+}$ and Δ-[Co(*S*-pntnim)-$(H^+)_2]^{3+}$ complexes are strongly solvent dependent, and the spectra given in Figures 2 and 3 are taken in the solvents CH_3CN and DMF. Transitions at lower energies, at 516 nm (in CH_3CN solution) for the *S*-pnenim complex and at 532 nm (in CH_3CN solution) for the *S*-pntnim complex, represent the magnetic dipole allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ d–d transitions. These transitions are contiguous with overlapping, more intense, higher energy bands. Aside from the other d–d band, which is expected to carry weak circular dichroism, the intense transitions in the region 350–440 nm probably represent Co(III)–phenolate change transfer bands[11] and $\pi \rightarrow \pi^*$ azomethine transitions.[12] The latter are likely to be split by exciton coupling.[12,13] It will be noted that the solvent has a strong effect on these higher energy transitions. Solvent changes also affect the appearance of the circular dichroism spectra probably by shifting the positions and intensities of the circular dichroism component transition. These solvent effects are undoubtedly complex but they could arise from conformational changes, and in the case of the more intense transitions, from solvent interactions with the electric transition dipole moments. The circular dichroism couplets in acetonitrile solution seen at 426 and at 385 nm for both the *S*-pnenim and *S*-pntnim monometallic Co(III) complexes probably result from $\pi \rightarrow \pi^*$ exciton circular dichroism arising from coupling of the dissymmetrically disposed azomethine chromophores.[12,13] It is probable that the circular dichroism associated with the Co(III)–phenolic transition overlaps with these azomethine transitions causing changes in the net circular dichroism manifold with variation of solvent. Since the precise conformation of these complexes in solution is unknown, it is not possible to assign the absolute configuration of these complexes on the basis of these exciton couplets. The d–d circular dichroism associated with the $^1A_{1g} \rightarrow {}^1T_{1g}$ transitions of the two complexes is positive except that a weak negative band occurs at around 620 nm for the *S*-pnenim complex in DMF but not in CH_3CN. We note that although the $\pi \rightarrow \pi^*$ azomethine couplet has the same form, positive to lower energies–negative to higher energies,[3] for Δ-[Co(*S*,*S*-encnim)-$(H^+)_2]^{3+}$ as is observed for the present Δ-configuration complexes, the circular dichroism in the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of the *S*,*S*-encnim complex consists of a lower energy negative–higher energy positive couplet, each component having roughly equal intensity. Thus the circular dichroism under the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition is not a useful index of absolute configuration.

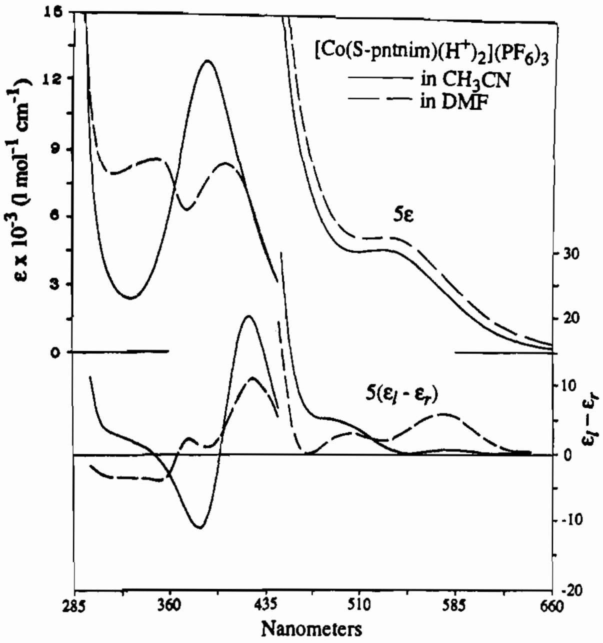

Figure 3. Absorption and circular dichroism spectra of Δ-[Co(*S*-pntnim)-$(H^+)_2]^{3+}$ in CH_3CN and DMF solutions.

This is confirmed by the d–d circular dichroism shown by Δ-[Co(*S*-pnenim)ZnCl]$^{2+}$ and by Δ-[Co(*S*-pntnim)ZnCl]$^{2+}$ (Figure 4). Although two isomers, due to the Zn–Cl unit, exist and may affect the circular dichroism to some extent, both complexes show net negative circular dichroism for the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. Furthermore, the azomethine $\pi \rightarrow \pi^*$ transitions do not show the clean resolved circular dichroism couplet displayed by the monometallic Co(III) complexes (Figures 2 and 3). This difference may arise from a different ligand conformation induced by the presence of the ZnCl in the open-site. It will be noted that

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[11] (a) Garbett, K.; Gillard, R. D. *J. Chem. Soc. A* **1968**, 979–987. (b) Yamamoto, Y.; Kudo, H.; Toyota, E. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1051–1056.

[12] Bosnich, B. *J. Am. Chem. Soc.* **1968**, *90*, 627–632.

[13] Bosnich, B. *Acc. Chem. Res.* **1969**, *2*, 266–273.

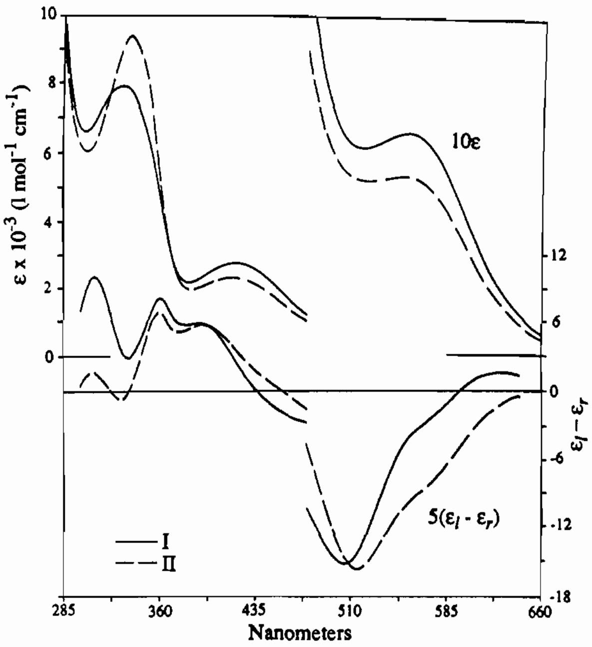

Figure 4. Absorption and circular dichroism spectra of Δ-[Co(*S*-pnenim)ZnCl]$^{2+}$ (I) and Δ-[Co(*S*-pntnim)ZnCl]$^{2+}$ (II) in CH_3CN solutions.

Table 4. Redox Potentials and Peak Separations for the Co(III)/Co(II) Couples in [Co(ligand)ZnCl]$^{n+}$ Complexes[a,b]

complex	E_f, V	$E_{pa} - E_{pc}$, V
[Co(enenim)ZnCl]$^{2+}$	−0.37	0.105
[Co(*S*-pnenim)ZnCl]$^{2+}$	−0.39	0.155
[Co(entnim)ZnCl]$^{2+}$	−0.37	0.102
[Co(*S*-pntnim)ZnCl]$^{2+}$	−0.37	0.099
[Co(*S*,*S*-encnim)ZnCl]$^{2+}$	−0.43	0.072
[Co(tnenim)ZnCl]$^{+}$	−0.10[c]	0.070
[Co(tntnim)ZnCl]$^{+}$	−0.11[c]	0.069

[a] Conditions: 5 × 10^{-4} M complex and 0.1 M nBu_4NBF_4 in CH_3CN; Pt-button working electrode; Pt-wire auxiliary electrode; Ag/AgCl reference electrode. [b] Potentials and peak separations are reported in V. Potentials are referenced versus a ferrocene/ferrocenium internal standard set equal to zero. [c] Ag/$AgNO_3$ reference electrode; ferrocene/ferrocenium external standard.

in these bimetallic complexes the $\pi \rightarrow \pi^*$ azomethine transition moves to higher energies compared to the monometallic complexes. This blue shift allows the previously obscured Co(III)–phenolate charge transfer band to be revealed at about 420 nm.

The complexity of these circular dichroism spectra clearly shows that assignment of absolute configurations of these types of complexes based on circular dichroism is an essay requiring considerable caution.

4. Redox Properties

Redox potentials of the Co(III)/Co(II) couples were measured by cyclic voltammetry in acetonitrile solutions and are quoted against the ferrocene/ferrocenium (Fc/Fc$^+$) couple as an internal standard where possible.[14] We found that the [Co(ligand)(H$^+$)$_2$]$^{n+}$ complexes did not give satisfactory reversible waves under a variety of scan rates. The bimetallic [Co(ligand)ZnCl]$^{n+}$ complexes, however, gave satisfactory quasi-reversible waves from which the Co(III)/Co(II) potentials were determined. These are listed in Table 4. It will be noted that all of the complexes bearing a 5-membered chelate link at the closed-site give essentially the same Co(III)/Co(II) redox couple except for the *S*,*S*-encnim complex which is slightly more negative. When a 6-membered chelate link is present at the closed-site the potentials become more positive by nearly 300 mV. The destabilization of the Co(III) state with increase in the length of the closed-site chelate link most probably reflects the inability of the whole molecular framework to adjust to accommodate the shorter bond lengths required by the Co(III) state.[15] Although the redox couples for the [Co(tnenim)(H$^+$)$_2$]$^{2+}$ and for the [Co(tntnim)(H$^+$)$_2$]$^{2+}$ were not accurately determined, their Co(III)/Co(II) couples are in the range of +0.05 V. These values explain why the monometallic Co(III) complexes of these ligands could not be oxidized by ferrocenium ion. Further, these monometallic couples indicate that although the presence of the Zn(II) ion in the open-site can affect the redox couple, the explanation for the large redox changes observed between 5- and 6-membered chelate closed-site bimetallic complexes should focus on the structures of the ligands.

Conclusions

This work has served to illustrate some important preparative, stereochemical, and physical properties of this class of binucleating ligands which bears on our ultimate goal of finding cooperative bimetallic reactivity. The demonstration that monometallic complexes of the type [M(ligand)(H$^+$)$_2$]$^{n+}$ can be prepared in high yield for a wide variety of chelate links provides access to a large range of precursors to bimetallic combinations. The [M(ligand)(H$^+$)$_2$]$^{n+}$ complexes allow for the sequential incorporation of metals under very mild conditions. The fact that the [Zn(*S*-enpnim)(H$^+$)$_2$]$^{2+}$ complex undergoes epimerization with a half-life of about 18 *h* suggests that even labile metals in the closed-site undergo slow exchange. This slow exchange implies that site-specific heterobimetallic complexes can be made provided mild conditions are employed.

The observation that the *S*-pn link at the closed-site induces a single (Δ) topology of the complex provides a simple method of forming diastereomerically pure catalysts for asymmetric epoxidation of prochiral olefins even for systems incorporating stereochemically labile metals. The systematic variation of the chelate link size has indicated that binucleating macrocyclic ligands of this type require at least one of the chelate links to consist of three or more aliphatic carbon atoms in order to accommodate the open-site metal within the macrocyclic plane. As we have demonstrated previously[2–4] the presence of a 5-membered chelate link at the closed-site generally leads to distorted structures with cis pyridines in bimetallic but not in monometallic complexes. Expansion of the closed-site link tends to give C_2 symmetric bimetallic complexes.[5] The circular dichroism spectra associated with the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition manifold of these complexes has proved unreliable for assigning absolute configurations. The $\pi \rightarrow \pi^*$ azomethine exciton coupled transitions might prove to be a reliable guide provided these transitions are not heavily overlapped and the general conformation of the complex is known. At present it is not clear which conformations will be adopted by the ligands in different complexes. It seems, however, that if the circular dichroism under the $\pi \rightarrow \pi^*$ azomethine transitions is positive at lower energies and negative at higher energies the absolute conformation of the complex is Δ. This couplet is not always resolved because of overlap with other transitions. Finally, the Co(III)/Co(II) redox potentials are very sensitive to the chelate ring size at the closed-site. It is probable that this redox variation is coupled to the structure of the ligands which, when a trimethylenediamine link is present in the closed-site, cannot adjust to the required contractions of the bond lengths in going from the Co(II) to the Co(III) state. We believe that one of the major impediments to conformational adjustment is the presence of the azomethine groups. If these functionalities were reduced to amines, greater flexibility would ensue and the structural demands of the closed-site Co(III) could be met. Consequently, the Co(III) state would

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(14) Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854–2855.

(15) Wieghardt, K.; Schmidt, W.; Herrmann, W.; Küppers, H.-J. *Inorg. Chem.* **1983**, *22*, 2953–2956.

be stabilized when 6-membered rings are present at the closed-site. Indeed, we have recently reduced the azomethine groups in these complexes and have found that the Co(III) state becomes accessible when a 6-membered chelate link is present at the closed-site. We shall report on the reduced complexes shortly.

Experimental Section

Conductance measurements were made at 25 °C with a YSI Model 35 conductance meter on 0.001 M CH_3CN solutions of the complexes. The UV/vis solution spectra were obtained on a Varian (Cary) 2400 spectrophotometer using spectral grade CH_3CN or DMF. Reported values were obtained from CH_3CN solutions unless denoted otherwise. Circular dichroism spectra were recorded using a Jasco J-600 instrument and spectral grade solvents. Magnetic susceptibilities were measured on CD_3CN solutions at 20 °C according to the Evans NMR method[16] or on powdered solid samples using a Johnson–Mathey–Evans magnetic susceptibility balance. Cyclic voltammograms were recorded using a Bioanalytical Systems BAS 100 electrochemical analyzer on deaerated CH_3CN solutions which were 0.1 M in *n*-Bu_4NBF_4 supporting electrolyte and 5×10^{-4} M in sample. Redox couples were measured using a Pt button working electrode, either a Ag/AgCl aqueous or a $Ag/AgNO_3$ non-aqueous (CH_3CN) reference electrode, and a Pt-wire auxiliary electrode, and are tabulated versus a ferrocene standard.[14] All samples were dried to constant weight under high vacuum (0.25 mm) for at least 5 h prior to characterization. Solvents used in the preparative reactions were dried over K (THF) or $LiAlH_4$ (1,4-dioxane). Ethanol refers to absolute ethanol. Preparations of complexes of the *S,S*-encnim ligand[3,4] and of the tntnim ligand[5] have been reported previously.

Ligand Preparation. The dialdehyde ligands enalH_2[2] (**4a**) and tnalH_2[5] (**4b**) were prepared by the published methods.

***S*-1,6-Bis(2-pyridyl)-2,5-bis(2-hydroxy-3-formyl-5-methylbenzyl)-3-methyl-2,5-diazahexane (*S*-pnalH_2, 4c).** To *S*-1,2-diaminopropane[8] (1.59 g, 21.4 mmol) in methanol (12 mL) was added dropwise over 15 min 2-pyridinecarboxaldehyde (40.8 mL, 42.9 mmol) in methanol (4 mL). The yellow solution was stirred for 45 min and then was concentrated to dryness. The azeotropic removal of water with benzene (3 × 20 mL) was achieved by concentration under reduced pressure. The bis(2-pyridyl) diimine product was obtained as a yellow oil (5.41 g, 100%). To this diimine (5.41 g, 21.4 mmol) in THF (134 mL) at 0 °C, was added dropwise over 1 h borane–tetrahydrofuran complex (1.00 M in THF, 107 mL, 107 mmol). The resultant solution was stirred at 25 °C for 5 h. The reaction was then cooled to 0 °C and was quenched by slow addition of MeOH (26.1 mL, 643 mmol) over 30 min, and then with aqueous HCl (12 M, 17.9 mL, 214 mmol) over 30 min. The resultant cloudy solution was stirred for 12 h, and then it was concentrated to a yellow oil. The oil was dissolved in water (30 mL) and the solution was taken to pH ~10 with aqueous NaOH (1.00 N). It was then extracted with CH_2Cl_2 (5 × 30 mL). The extracts were dried over Na_2SO_4 and filtered, and were concentrated under reduced pressure to give the crude bis(2-pyridyl) diamine product as a yellow oil (6.62 g). The oil was fractionally distilled *in vacuo*. Pure product was obtained as a yellow oil (4.57 g, 83%) bp 138–160 °C (0.25 mm). [^1H NMR (300 MHz, $CDCl_3$): δ 1.11 (d, 6.3 Hz, 3 H), 2.24 (br s, 2 H), 2.64 (m, 2 H), 2.84 (m, 1 H), 3.93 (m, 4 H), 7.15 (m, 2 H), 7.34 (m, 2 H), 7.63 (m, 2 H), 8.54 (m, 2 H)]. The bis(2-pyridyl)diamine (4.57 g, 17.8 mmol) and 2-(allyloxy)-3-(chloromethyl)-5-methylbenzaldehyde dimethyl acetal[2] (12.07 g, 44.6 mmol) were coupled by the published method.[2] The bis(allyloxy)dialdehyde product was obtained as a viscous brown oil (11.59 g, ~100%). This product (11.59 g, 17.8 mmol) was deprotected by the published method.[2] The *S*-pnalH_2 ligand, **4c**, was obtained as a viscous brown oil (10.30 g ~100%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.02 (d, J = 6.5 Hz, 3 H), 2.19 (s, 3 H), 2.23 (s, 3 H), 2.36 (dd, J = 13.4, 5.7 Hz, 1 H), 2.85 (dd, J = 13.3, 8.5 Hz, 1 H), 3.67 (m, 9 H), 7.17 (m, 5 H), 7.39 (s, 1 H), 7.59 (m, 4 H), 8.53 (br t, J = 4.4 Hz, 2 H), 10.17 (s, 1 H), 10.25 (s, 1 H).

Monometallic Complexes. The complexes [Zn(enal)][2] and [Zn(tnal)][5] were prepared by the published methods.

[Zn(*S*-pnal)]. The mono Zn(II) complex was prepared by stirring the crude free *S*-pnalH_2 ligand, **4c**, (10.30 g, 18.6 mmol) with $Zn(OAc)_2 \cdot 2H_2O$ (4.91 g, 22.0 mmol) in ethanol solution (70 mL). Et_3N (5.18 mL, 37.0 mmol) was added to the heterogeneous mixture. After the mixture was stirred for ~12 h, the resulting yellow solid was collected, washed with ethanol (3 × 20 mL), Et_2O (2 × 10 mL) and pentane (2 × 10 mL), and then was dried in a vacuum desiccator to yield the pale yellow [Zn(*S*-pnal)] complex (3.87 g). A second crop of orange-yellow solid was obtained by concentration of the reaction filtrate and resuspension of the residue in a small volume of ethanol. The solid was collected and washed as above (1.07 g, 43% combined yield). ^1H NMR ($CDCl_3$–3 drops of CD_3OD): δ 1.61 (d, J = 5.3 Hz, 3 H), 2.13 (s, 3 H), 2.14 (s, 3 H), 2.81 (m, 3 H), 3.44 (m, 4 H), 3.84 (m, 2 H), 4.28 (m, 2 H), 6.64 (d, J = 7.9 Hz, 1 H), 7.04 (m, 3 H), 7.13 (m, 2 H), 7.29 (m, 2 H), 7.46 (td, J = 7.5, 1.5 Hz, 1 H), 7.68 (td, J = 7.4, 1.4 Hz, 1 H), 8.80 (d, J = 5.1 Hz, 1 H), 9.01 (d, J = 4.8 Hz, 1 H), 10.13 (s, 1 H), 10.38 (s, 1 H).

[M(ligand)(H^+)$_2$](PF_6)$_2$ Complexes. All of the monometallic Zn(II) and Co(II) complexes of ligands containing ethylenediamine or *S*-1,2-diaminopropane in the closed-site were prepared by the general method described for [Zn(enenim)(H^+)$_2$](PF_6)$_2$. All complexes containing 1,3-diaminopropane in the closed-site were prepared by the method described for [Zn(tnenim)(H^+)$_2$](PF_6)$_2$. The yields are calculated after recrystallization based on the metal dialdehyde precursors, [M(enal)], [M(*S*-pnal)], or [M(tnal)]. The physical data (conductance measurements, electronic absorption spectra, magnetic moments, and ^1H NMR data) are detailed for each complex. Each of these complexes showed an intense absorption at λ_{max} = 395–405 nm, $\epsilon = 1 \times 10^4$ L mol^{-1} cm^{-1}, in CH_3CN solution which is assigned to the $\pi \rightarrow \pi^*$ transition of the azomethine chromophore.[12] All Co(II) complexes were prepared and recrystallized under Ar using deaerated solvents. All complexes are air stable as solids.

[Zn(enenim)(H^+)$_2$](PF_6)$_2$. To a stirred suspension of [Zn(enal)] (1.50 g, 2.49 mmol) in ethanol (50 mL) at 25 °C was added dropwise over 1 h a solution of ethylenediamine (168 μL, 2.49 mmol) and acetic acid (286 μL, 4.98 mmol) in ethanol (40 mL). Thirty minutes after the addition was complete, all starting material had dissolved. The resultant yellow solution was stirred for 1 h. A filtered solution of NH_4PF_6 (1.02 g, 6.23 mmol) in ethanol (~15 mL) was added to the reaction mixture. A yellow solid precipitated immediately. The solid was collected and was washed with ethanol (2 × 15 mL), Et_2O (2 × 5 mL), and pentane (2 × 5 mL) and was dried under vacuum. The yellow powder was recrystallized from CH_3CN–ethanol as follows. The crude salt was dissolved in a minimum volume of CH_3CN (~5 mL per 1 g of crude product) at room temperature and the solution was filtered. To the CH_3CN solution was added several aliquots of ethanol (~5 × 10 mL) over several hours. The crystalline complex was collected and washed as above. The [Zn(enenim)(H^+)$_2$](PF_6)$_2$ (2.05 g, 90%) was obtained as yellow needles. Λ_M = 277 Ω^{-1} mol^{-1} cm^2. ^1H NMR (300 MHz, CD_3CN): δ 2.20 (s, 6 H), 3.07 (m, 4 H), 3.79 (d, J = 12.3 Hz, 2 H), 4.12 (m, 10 H), 7.02 (m, 4 H), 7.19 (t, J = 6.3 Hz, 2 H), 7.36 (d, J = 1.8 Hz, 2 H), 7.66 (dt, J = 1.4, 7.7 Hz, 2 H), 8.41 (br s, 2 H), 8.52 (d, J = 5.1 Hz, 2 H), 15.54 (br s, 2 H). Anal. Calcd for $C_{34}H_{38}N_6O_2P_2F_{12}Zn$: C, 44.48; H, 4.17; N, 9.15; Zn, 7.12. Found: C, 44.64; H, 4.13; N, 9.03; Zn, 6.98.

[Zn(*S*-enpnim)(H^+)$_2$](PF_6)$_2$. To a stirred suspension of [Zn(enal)] (235.8 mg, 0.392 mmol) in ethanol (18 mL) at 25 °C was added dropwise over 30 min a solution of *S*-1,2-propylenediamine[8] (38.0 mg, 0.431 mmol) and acetic acid (44.8 μL, 0.783 mmol) in ethanol (12 mL). The reaction mixture was stirred for 18 h, and then it was filtered. A filtered solution of NH_4PF_6 (160 mg, 0.979 mmol) in ethanol (~5 mL) was added to the reaction mixture with stirring. A yellow solid precipitated immediately. The solid was collected and was washed with ethanol (2 × 5 mL), Et_2O (2 × 3 mL), and pentane (2 × 3 mL), and was dried under vacuum. This solid consisted of a mixture of diastereomers (as discussed in the text) in a 1.2:1 ratio (as determined by the ratio of the doublet signals at 1.54 and 1.48 ppm, respectively, corresponding to the methyl group on the diimine link in each diastereomer). Fractional crystallization from CH_3CN–ethanol produced two sets of crystals: yellow-orange needles (4%) which were enriched in the diastereomer corresponding to the methyl peak at 1.48 ppm (~5.7:1 ratio), and bright yellow plates (22%) which contained the diastereomers in a 1:1 ratio. Λ_M = 280 Ω^{-1} mol^{-1} cm^2. ^1H NMR (300 MHz, CD_3CN): δ 1.48 (d, J = 6.6 Hz), 1.54 (d, J = 6.7 Hz) (The signals at 1.48 and 1.54 taken together integrate to 3 H), 2.20 (s, 6 H), 3.08 (m, 4 H), 3.87 (m, 4 H), 4.26 (m, 6 H), 4.39 (m, 1 H), 7.02 (m, 4 H), 7.18 (m, 2 H), 7.37 (s, 2 H), 7.66 (m, 2 H), 8.51 (m, 4 H), 15.69 (br s, 2 H). The two isomers can only be distinguished by the doublets at 1.48 and 1.54 ppm, respectively. Anal. Calcd for $C_{35}H_{40}N_6O_2P_2F_{12}Zn$: C, 45.10; H, 4.33; N, 9.02; Zn, 7.01. Found: C, 45.30; H, 4.34; N, 8.97; Zn, 6.83.

Kinetic Experiment: Isomerization of [Zn(*S*-enpnim)(H^+)$_2$](PF_6)$_2$. The [Zn(*S*-enpnim)(H^+)$_2$](PF_6)$_2$ (5.28 mg, 5.67 μmol, 5.7:1 enriched sample) was weighed into an NMR tube and was dissolved in CD_3CN (0.5 mL). The isomerization was monitored by observing the change in the ratio of the doublets in the ^1H NMR spectrum at 1.48 and 1.54 ppm,

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[16] (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005. (b) Live, D. H.; Chan, S. I. *Anal. Chem.* **1970**, *42*, 791–792.

corresponding to the protons on the methyl groups on the diimine link in each diastereomer at 25 °C.

[Zn(*S*-pnenim)(H$^+$)$_2$](PF$_6$)$_2$. Cyclization of [Zn(*S*-pnal)] with ethylenediamine yielded [Zn(*S*-pnenim)(H$^+$)$_2$](PF$_6$)$_2$ as a microcrystalline solid after recrystallization. Yield: 81%. Λ_M = 269 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR (300 MHz, CD$_3$CN): δ 1.21 (d, J = 6.6 Hz, 3 H), 2.18 (s, 3 H), 2.21 (s, 3 H), 2.99 (m, 2 H), 3.18 (m, 1 H), 3.68 (d, J = 17.0 Hz, 1 H), 3.85 (d, J = 12.5 Hz, 2 H), 4.02 (d, J = 12.2 Hz, 1 H), 4.17 (m, 8 H), 6.86 (d, J = 7.9 Hz, 1 H), 6.95 (d, J = 0.9 Hz, 1 H), 7.09 (m, 3 H), 7.26 (t, J = 6.3 Hz, 1 H), 7.36 (d, J = 1.9 Hz, 1 H), 7.39 (d, J = 2.0 Hz, 1 H), 7.56 (dt, J = 1.6, 8.5 Hz, 1 H), 7.73 (dt, J = 1.5, 8.5 Hz, 1 H), 8.32 (m, 2 H), 8.46 (d, J = 12.1 Hz, 1 H), 8.70 (d, J = 5.1 Hz, 1 H), 15.23 (br s, 1 H), 15.79 (br s, 1 H). Anal. Calcd for C$_{35}$H$_{40}$N$_6$O$_2$P$_2$F$_{12}$Zn: C, 45.10; H, 4.33; N, 9.02; Zn, 7.01. Found: C, 45.14; H, 4.10; N, 8.99; Zn, 6.90.

[Zn(entnim)(H$^+$)$_2$](PF$_6$)$_2$. Cyclization of [Zn(enal)] with 1,3-diaminopropane yielded [Zn(entnim)(H$^+$)$_2$](PF$_6$)$_2$ as bright yellow blocks after recrystallization. Yield: 73%. Λ_M = 276 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR (300 MHz, CD$_3$CN): δ 2.18 (s, 6 H), 2.29 (m, 2 H), 2.94 (m, 4 H), 3.69 (d, J = 12.5 Hz, 2 H), 4.04 (m, 10 H), 6.99 (d, J = 1.5 Hz, 2 H), 7.05 (d, J = 7.9 Hz, 2 H), 7.25 (t, J = 6.4 Hz, 2 H), 7.30 (d, J = 2.1 Hz, 2 H), 7.71 (dt, J = 1.6, 8.4 Hz, 2 H), 8.18 (br s, 2 H), 8.61 (d J = 5.1 Hz, 2 H), 13.69 (br s, 2 H). Anal. Calcd for C$_{35}$H$_{40}$N$_6$O$_2$P$_2$F$_{12}$Zn: C, 45.10; H, 4.33; N, 9.02; Zn, 7.01. Found: C, 45.74; H, 4.32; N, 8.93; Zn, 6.65.

[Zn(*S*-pntnim)(H$^+$)$_2$](PF$_6$)$_2$. Cyclization of [Zn(*S*-pnal)] with 1,3-diaminopropane yielded [Zn(*S*-pntnim)(H$^+$)$_2$](PF$_6$)$_2$ as orange-yellow plates after recrystallization. Yield: 71%. Λ_M = 271 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR (300 MHz, CD$_3$CN): δ 1.13 (m, 3 H), 2.17 (s, 3 H), 2.19 (s, 3 H), 2.21 (m, 1 H), 2.35 (m, 1 H), 2.92 (br s, 3 H), 3.94 (m, 12 H), 6.84 (m, 2 H), 7.08 (s, 1 H), 7.12 (t, J = 5.3 Hz, 1 H), 7.20 (d, J = 7.9 Hz, 1 H), 7.28 (d, J = 2.1 Hz, 1 H), 7.36 (m, 2 H), 7.59 (dt, J = 1.6, 7.6 Hz, 1 H), 7.85 (dt, J = 1.6, 8.4 Hz, 1 H), 8.08 (d, J = 12.0 Hz, 1 H), 8.26 (d, J = 13 Hz, 1 H), 8.31 (d, J = 5.2 Hz, 1 H), 8.87 (d, J = 5.0 Hz, 1 H), 13.48 (br s, 1 H), 13.84 (br s, 1 H). Anal. Calcd for C$_{36}$H$_{42}$N$_6$O$_2$P$_2$F$_{12}$Zn: C, 45.70; H, 4.47; N, 8.88; Zn, 6.91. Found: C, 46.46; H, 4.73; N, 8.95; Zn, 6.81.

[Co(enenim)(H$^+$)$_2$](PF$_6$)$_2$. Cyclization of [Co(enal)] with ethylenediamine yielded [Co(enenim)(H$^+$)$_2$](PF$_6$)$_2$ as orange needles after recrystallization. Yield: 63%. Λ_M = 265 Ω^{-1} mol^{-1} cm^2. UV [$\lambda_{\max}$ in nm (ϵ in L mol^{-1} cm^{-1})]: 974 (8.5). μ_{eff}(25 °C) = 4.8 μ_B (Evans). Anal. Calcd for C$_{34}$H$_{38}$N$_6$O$_2$P$_2$F$_{12}$Co: C, 44.80; H, 4.20; N, 9.22; Co, 6.46. Found: C, 44.87; H, 4.22; N, 9.12; Co, 6.56.

[Co(*S*-pnenim)(H$^+$)$_2$](PF$_6$)$_2$. Cyclization of [Co(*S*-pnal)] with ethylenediamine yielded [Co(*S*-pnenim)(H$^+$)$_2$](PF$_6$)$_2$ as feathery orange needles after recrystallization. Yield: 70%. Λ_M = 270 Ω^{-1} mol^{-1} cm^2. UV [$\lambda_{\max}$ in nm (ϵ in L mol^{-1} cm^{-1})]: 978 (8). μ_{eff}(25 °C) = 4.8 μ_B (Evans). Anal. Calcd for C$_{35}$H$_{40}$N$_6$O$_2$P$_2$F$_{12}$Co: C, 45.42; H, 4.36; N, 9.08; Co, 6.37. Found: C, 45.59; H, 4.34; N, 8.94; Co, 6.30.

[Co(entnim)(H$^+$)$_2$](PF$_6$)$_2$. Cyclization of [Co(enal)] with 1,3-diaminopropane yielded [Co(entnim)(H$^+$)$_2$](PF$_6$)$_2$ as orange needles after recrystallization. Yield: 69%. Λ_M = 258 Ω^{-1} mol^{-1} cm^2. UV [$\lambda_{\max}$ in nm (ϵ in L mol^{-1} cm^{-1})]: 987 (11). μ_{eff}(25 °C) = 4.4 μ_B (Evans). Anal. Calcd for C$_{35}$H$_{40}$N$_6$O$_2$P$_2$F$_{12}$Co: C, 45.42; H, 4.36; N, 9.08; Co, 6.37. Found: C, 45.40; H, 4.21; N, 8.89; Co, 7.58.

[Co(*S*-pntnim)(H$^+$)$_2$](PF$_6$)$_2$. Cyclization of [Co(*S*-pnal)] with 1,3-diaminopropane yielded [Co(*S*-pntnim)(H$^+$)$_2$](PF$_6$)$_2$ as orange needles after recrystallization. Yield: 61%. Λ_M = 282 Ω^{-1} mol^{-1} cm^2. UV [$\lambda_{\max}$ in nm (ϵ in L mol^{-1} cm^{-1})]: 987 (12). μ_{eff}(25 °C) = 4.5 μ_B (Evans). Anal. Calcd for C$_{36}$H$_{42}$N$_6$O$_2$P$_2$F$_{12}$Co: C, 46.02; H, 4.50; N, 8.94; Co, 6.27. Found: C, 46.20; H, 4.46; N, 8.93; Co, 5.82.

[Zn(tnenim)(H$^+$)$_2$](PF$_6$)$_2$. To a stirred suspension of [Zn(tnal)] (1.00 g, 1.62 mmol) in ethanol (60 mL) at 25 °C was added dropwise over 1 h a solution of ethylenediamine (110 μL, 1.62 mmol) and acetic acid (186 μL, 3.25 mmol) in ethanol (40 mL). Two hours after the addition was complete, all of the starting material had dissolved. The resultant yellow solution was stirred for 1 h. A filtered solution of NH$_4$PF$_6$ (0.66 g, 4.06 mmol) in ethanol (~10 mL) was added to the reaction mixture. A yellow solid precipitated immediately. The solid was collected and was washed with ethanol (2 × 10 mL), Et$_2$O (2 × 5 mL), and pentane (2 × 5 mL) and was dried under vacuum. The yellow powder was recrystallized from CH$_3$CN–ethanol. The [Zn(tnenim)(H$^+$)$_2$](PF$_6$)$_2$ (1.06 g, 70%) was obtained as fine yellow needles. Λ_M = 290 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR (300 MHz, CD$_3$CN): δ 2.18 (s, 6 H), 2.28 (m, 2 H), 2.95 (m, 4 H), 3.32 (d, J = 12.1 Hz, 2 H), 3.81 (d, J = 17.5 Hz, 2 H), 4.11 (m, 6 H), 4.37 (d, J = 17.4 Hz, 2 H), 7.02 (m, 4 H), 7.20 (t, J = 6.3 Hz, 2 H), 7.36 (s, 2 H), 7.68 (dt, J = 8.5, 1.6 Hz, 2 H), 8.37 (d, J = 10.4 Hz, 2 H), 8.76 (d, 5.2 Hz, 2 H), 12.75 (br s, 2 H). Anal. Calcd for C$_{35}$H$_{40}$N$_6$O$_2$P$_2$F$_{12}$Zn: C, 45.10; H, 4.33; N, 9.02; Zn, 7.01. Found: C, 45.10; H, 4.54; N, 8.87; Zn, 7.16.

[Zn(*S*-tnpnim)(H$^+$)$_2$](PF$_6$)$_2$·C$_2$H$_6$O. To a stirred suspension of [Zn(tnal)] (258.6 mg, 0.420 mmol) in ethanol (18 mL) at 25 °C was added dropwise over 30 min a solution of *S*-1,2-propylenediamine (40.7 mg, 0.462 mmol) and acetic acid (48.1 μL, 0.840 mmol) in ethanol (12 mL). The reaction mixture was stirred for 18 h and then it was filtered. A filtered solution of NH$_4$PF$_6$ (171 mg, 1.05 mmol) in ethanol (~5 mL) was added to the reaction mixture with stirring. A yellow solid precipitated immediately. The solid was collected and was washed with ethanol (2 × 5 mL), Et$_2$O (2 × 3 mL), and pentane (2 × 3 mL), and was dried under vacuum. This solid consisted of a mixture of diastereomers (as discussed in the text) in a 1.5:1 ratio (as determined by the ratio of the doublet signals at 1.38 and 1.50 ppm, respectively). Fractional crystallization from CH$_3$CN–ethanol produced only fine yellow needles which effloresced when the product was dried under vacuum, and which contained the diastereomers in a 1:1 ratio. Λ_M = 283 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR (300 MHz, CD$_3$CN): δ 1.38 (d, J = 6.6 Hz), 1.50 (d, J = 6.7 Hz) (The signals at 1.38 and 1.50 taken together integrate to 3 H), 2.18 (s, 6 H), 2.27 (m, 2 H), 2.94 (m, 4 H), 3.33 (m, 2 H), 3.81 (m, 3 H), 4.15 (m, 3 H), 4.36 (m, 3 H), 7.04 (m, 4 H), 7.19 (m, 2 H), 7.37 (s, 2 H), 7.68 (m, 2 H), 8.36 (m, 2 H), 8.75 (m, 2 H), 15.30 (m, 2 H). Anal. Calcd for C$_{36}$H$_{42}$N$_6$O$_2$P$_2$F$_{12}$Zn·C$_2$H$_6$O (confirmed by ^{1}H NMR): C, 46.00; H, 4.88; N, 8.47; Zn, 6.59. Found: C, 46.03; H, 4.54; N, 8.27; Zn, 6.10.

[Co(tnenim)(H$^+$)$_2$](PF$_6$)$_2$. Cyclization of [Co(tnal)] with ethylenediamine yielded [Co(tnenim)(H$^+$)$_2$](PF$_6$)$_2$ as orange needles after recrystallization. Yield: 76%. Λ_M = 273 Ω^{-1} mol^{-1} cm^2. UV [$\lambda_{\max}$ in nm (ϵ in L mol^{-1} cm^{-1})]: 1023 (4.5). μ_{eff}(25 °C) = 4.6 μ_B (powder). Anal. Calcd for C$_{35}$H$_{40}$N$_6$O$_2$P$_2$F$_{12}$Co: C, 45.42; H, 4.36; N, 9.08; Co, 6.37. Found: C, 45.49; H, 4.38; N, 9.02; Co, 6.45.

[Co(ligand)(H$^+$)$_2$](PF$_6$)$_3$ Complexes. All of the [Co(ligand)(H$^+$)$_2$](PF$_6$)$_3$ complexes were prepared by the general procedure described for [Co(enenim)(H$^+$)$_2$](PF$_6$)$_3$·CH$_3$CN. The yields are based upon the [Co(ligand)(H$^+$)$_2$](PF$_6$)$_2$ starting materials. The appropriate physical data are included. All complexes showed an intense absorption at $\lambda_{\max}$ = 391–393 nm (ϵ = 1.15 × 10^4 L mol^{-1} cm^{-1}) in CH$_3$CN solution which is assigned to the $\pi \rightarrow \pi^*$ transition of the azomethine chromophore.[12]

[Co(enenim)(H$^+$)$_2$](PF$_6$)$_3$·CH$_3$CN. To a stirred solution of the [Co(enenim)(H$^+$)$_2$](PF$_6$)$_2$ (304 mg, 0.334 mmol) in deaerated CH$_3$CN (4 mL) under Ar was added [Cp$_2$Fe]PF$_6$ (111 mg, 0.335 mmol) in deaerated CH$_3$CN (5 mL). The resultant dark maroon solution was stirred under Ar for ~10 min, and then was opened to the air and was concentrated to dryness. The residue was triturated with Et$_2$O (3 × 5 mL) in order to remove Cp$_2$Fe. The residue was collected and was washed with ethanol (2 × 3 mL), Et$_2$O (2 × 5 mL), and pentane (2 × 5 mL) and was dried under vacuum. The dark maroon solid was recrystallized from CH$_3$CN–ethanol. The [Co(enenim)(H$^+$)$_2$](PF$_6$)$_3$·CH$_3$CN (312 mg, 85%) was obtained as maroon blocks. Λ_M = 392 Ω^{-1} mol^{-1} cm^2. UV [$\lambda_{\max}$ (ϵ in L mol^{-1} cm^{-1})]: 526 (8 × 10^2). ^{1}H NMR (300 MHz, CD$_3$CN): δ 2.29 (s, 6 H), 3.35 (m, 4 H), 3.46, 3.67 (syst AB, J_{AB} = 15.5 Hz, 4 H), 4.17 (br s, 4 H), 4.62, 4.79 (syst AB, J_{AB} = 18.9 Hz, 4 H), 7.44 (m, 8 H), 7.89 (d, J = 6.2 Hz, 2 H), 8.02 (t, J = 7.8 Hz, 2 H), 8.67 (d, J = 13.9 Hz, 2 H), 13.36 (br s, 2 H). Anal. Calcd for C$_{34}$H$_{38}$N$_6$O$_2$P$_3$F$_{18}$Co·CH$_3$CN: C, 39.39; H, 3.77; N, 8.93; Co, 5.37. Found: C, 39.36; H, 3.72; N, 8.48; Co, 5.51.

[Co(*S*-pnenim)(H$^+$)$_2$](PF$_6$)$_3$. The compound was obtained as maroon plates. Yield: 97%. Λ_M = 366 Ω^{-1} mol^{-1} cm^2. UV [$\lambda_{\max}$ 517 (6.5 × 10^2). UV [DMF; $\lambda_{\max}$ in nm (ϵ in L mol^{-1} cm^{-1})]: 360 (8.5 × 10^3), 391 (8.0 × 10^3), 518 (1.2 × 10^3). ^{1}H NMR (300 MHz, CD$_3$CN): δ 1.45 (d, J = 6.0 Hz, 3 H), 2.27 (s, 3 H), 2.29 (s, 3 H), 3.52 (m, 7 H), 4.19 (m, 5 H), 4.57 (d, J = 18.5 Hz, 1 H), 4.80 (m, 2 H), 7.45 (m, 8 H), 7.64 (d, J = 6.1 Hz, 1 H), 7.95 (t, J = 7.8 Hz, 1 H), 8.08 (t, J = 7.8 Hz, 1 H), 8.17 (d, J = 6.4 Hz, 1 H), 8.60 (d, J = 13.8 Hz, 1 H), 8.70 (d, J = 14.0 Hz, 1 H), 13.14 (br s, 1 H), 13.43 (br s, 1 H). Anal. Calcd for C$_{35}$H$_{40}$N$_6$O$_2$P$_3$F$_{18}$Co: C, 39.27; H, 3.77; N, 7.85; Co, 5.50. Found: C, 39.07; H, 3.61; N, 8.03; Co, 5.52.

[Co(entnim)(H$^+$)$_2$](PF$_6$)$_3$. The compound was obtained as maroon needles. Yield: 79%. Λ_M = 358 Ω^{-1} mol^{-1} cm^2. UV [$\lambda_{\max}$ in nm (ϵ in L mol^{-1} cm^{-1})]: 525 (7.5 × 10^2). ^{1}H NMR (300 MHz, CD$_3$CN): δ 2.24 (s, 6 H), 2.33 (m, 2 H), 3.29 (m, 4 H), 3.60 (m, 4 H), 4.00 (m, 4 H), 4.52, 4.65 (syst AB, J_{AB} = 18.6 Hz, 4 H), 7.29 (s, 2 H), 7.35 (s, 2 H), 7.46 (m, 4 H), 8.00 (t, J = 7.7 Hz, 2 H), 8.15 (d, J = 6.0 Hz, 2 H), 8.47 (d, J = 14.6 Hz, 2 H), 12.15 (br s, 2 H). Anal. Calcd for

$C_{35}H_{40}N_6O_2P_3F_{18}Co$: C, 39.27; H, 3.77; N, 7.85; Co, 5.50. Found: C, 39.06; H, 3.67; N, 7.76; Co, 5.50.

[Co(*S*-pntnim)(H$^+$)$_2$](PF$_6$)$_3$. The compound was obtained as maroon plates. Yield: 36%. Λ_M = 402 Ω^{-1} mol^{-1} cm^2. UV [λ_{max} in nm (ϵ in L mol^{-1} cm^{-1})]: 537 (8.3 × 10^2). UV [DMF; λ_{max} in nm (ϵ in L mol^{-1} cm^{-1})]: 353 (8.6 × 10^3), 407 (8.4 × 10^3), 518 (1.1 × 10^3). ^{1}H NMR (300 MHz, CD$_3$CN): δ 1.34 (d, *J* = 6.3 Hz, 3 H), 2.20 (s, 3 H), 2.26 (s, 3 H), 2.36 (m, 2 H), 3.19 (m, 1 H), 3.56 (m, 7 H), 4.00 (m, 4 H), 4.31 (d, *J* = 17.8 Hz, 1 H), 4.75 (m, 2 H), 7.16 (s, 1 H), 7.27 (m, 3 H), 7.36 (s, 1 H), 7.43 (d, *J* = 1.8 Hz, 1 H), 7.61 (m, 2 H), 7.69 (d, *J* = 6.0 Hz, 1 H), 7.82 (dt, *J* = 1.2, 7.7 Hz, 1 H), 8.13 (dt, *J* = 1.1, 7.7 Hz, 1 H), 8.32 (d, *J* = 14.6 Hz, 1 H), 8.59 (m, 2 H), 11.74 (br s, 1 H), 12.37 (br s, 1 H). Anal. Calcd for $C_{36}H_{42}N_6O_2P_3F_{18}Co$: C, 39.87; H, 3.90; N, 7.75; Co, 5.43. Found: C, 39.58; H, 3.98; N, 7.83; Co, 5.31.

Bimetallic Complexes. [Co(ligand)ZnCl](PF$_6$)$_2$ Complexes. All of the [Co(ligand)ZnCl](PF$_6$)$_2$ complexes were prepared by the general procedure described for [Co(enenim)ZnCl](PF$_6$)$_2$. The yields are based on the [Co(ligand)(H$^+$)$_2$](PF$_6$)$_3$ starting materials. Any variations from the general method are indicated. The appropriate physical data are included. All complexes show intense absorptions at λ_{max} = 333–340 nm (ϵ = 8 × 10^3 L mol^{-1} cm^{-1}) and λ_{max} = 417–422 (ϵ = 2.5 × 10^3 L mol^{-1} cm^{-1}) which are assigned to the $\pi \rightarrow \pi^*$ azomethine[12] and the Co(III)–phenolate charge transfer[11] transitions, respectively.

[Co(enenim)ZnCl](PF$_6$)$_2$. To a stirred solution of the [Co(enenim)(H$^+$)$_2$](PF$_6$)$_3$ (76.5 mg, 0.0724 mmol) in CH$_3$CN (2.5 mL) was added Et$_3$N (20.2 μL, 0.145 mmol) followed by ZnCl$_2$ (10.1 mg, 0.0724 mmol) in ethanol (5 mL). The solution was stirred for 12 h and then was concentrated to dryness. The residue was collected and washed with ethanol (2 × 3 mL), Et$_2$O (2 × 3 mL), and pentane (2 × 3 mL), and was dried under vacuum. The dark maroon solid was recrystallized from CH$_3$CN–ethanol. The [Co(enenim)ZnCl](PF$_6$)$_2$ (56.4 mg, 77%) was obtained as dark maroon blocks. Crystals suitable for X-ray structure determination were obtained by crystallizing the [Co(enenim)ZnCl](PF$_6$)$_2$ complex by vapor diffusion of ethanol into an CH$_3$CN solution of the complex. These crystals retained one molecule of ethanol as a solvent of crystallization. Λ_M = 294 Ω^{-1} mol^{-1} cm^2. UV [λ_{max} in nm (ϵ in L mol^{-1} cm^{-1})]: 559 (6.7 × 10^2). ^{1}H NMR (300 MHz, CD$_3$CN): δ 2.20 (s, 3 H), 2.29 (s, 3 H), 2.68 (dt, *J* = 5.0, 11.0 Hz, 1 H), 2.99 (dd, *J* = 12.0, 3.7 Hz, 1 H), 3.69 (m, 7 H), 4.09 (m, 2 H), 4.39 (m, 3 H), 4.79 (d, *J* = 19.0 Hz, 1 H), 5.03 (d, *J* = 17.4 Hz, 1 H), 7.03 (d, *J* = 1.3 Hz, 1 H), 7.11 (m, 2 H), 7.23 (m, 2 H), 7.38 (m, 2 H), 7.61 (m, 2 H), 7.72 (dt, *J* = 1.0, 8.3 Hz, 1 H), 8.05 (d, *J* = 1.5 Hz, 1 H), 8.12 (dt, *J* = 1.0, 8.1 Hz, 1 H), 8.49 (d, *J* = 1.7 Hz, 1 H), 8.92 (d, *J* = 5.8 Hz, 1 H). Anal. Calcd for $C_{34}H_{36}N_6O_2ClP_2F_{12}CoZn$: C, 40.42; H, 3.59; N, 8.32; Cl, 3.51; Zn, 6.27; Co, 5.83. Found: C, 39.51; H, 3.57; N, 8.15; Cl, 3.46; Zn, 6.17; Co, 5.93. The appearance of two singlets at 2.20 and 2.29 ppm corresponding to the protons on the *p*-tolyl methyl groups, and one doublet at 8.92 ppm corresponding to one of the 5-pyridyl protons confirms the magnetic inequivalence of similar protons in the molecule and is consistent with C_1 symmetry.

[Co(enenim)Zn](PF$_6$)$_2$(NO$_3$). All [Co(ligand)ZnCl](PF$_6$)$_2$ complexes were dechlorinated by the following method. An excess of AgNO$_3$ was added to the [Co(enenim)ZnCl](PF$_6$)$_2$ in CD$_3$CN (0.6 mL) in an NMR tube, and the resultant mixture was shaken to precipitate AgCl. ^{1}H NMR (300 MHz, CD$_3$CN): δ 2.19 (br s, 3 H), 2.26 (br s, 3 H), 2.80 (m, 1 H), 3.12 (m, 1 H), 3.79 (m, 6 H), 4.11 (m, 3 H), 4.37 (m, 1 H), 4.54 (m, 2 H), 5.03 (t, *J* = 17.2 Hz, 2 H), 7.05 (br s, 1 H), 7.14 (m, 2 H), 7.31 (m, 4 H), 7.54 (m, 1 H), 7.63 (m, 1 H), 7.72 (m, 1 H), 8.11 (m, 2 H), 8.54 (br s, 1 H), 8.75 (br d, *J* = 5.5 Hz, 1 H). The appearance of the two singlets at 2.19 and 2.26 ppm corresponding to the protons on the *p*-tolyl methyl groups, and one doublet at 8.75 ppm corresponding to one of the 5-pyridyl protons, confirms the magnetic inequivalence of similar protons in the molecule and is consistent with the retention of C_1 symmetry on removal of the chloride.

[Co(*S*-pnenim)ZnCl](PF$_6$)$_2$·C$_2$H$_6$O. The complex was obtained as dark maroon blocks. Yield: 72%. Λ_M = 293 Ω^{-1} mol^{-1} cm^2. UV [λ_{max} in nm (ϵ in L mol^{-1} cm^{-1})]: 561 (6.6 × 10^2). ^{1}H NMR (300 MHz, CD$_3$CN): δ 1.27 (d, *J* = 6.3 Hz, 3 H), 2.19 (s, 3 H), 2.28 (s, 3 H), 3.05 (m, 1 H), 3.82 (m, 10 H), 4.36 (m, 2 H), 4.84 (d, *J* = 18.3 Hz, 1 H), 5.03 (d, *J* = 17.5 Hz, 1 H), 7.02 (m, 2 H), 7.14 (d, *J* = 1.8 Hz, 1 H), 7.20 (t, *J* = 6.9 Hz, 1 H), 7.35 (m, 3 H), 7.64 (m, 3 H), 8.07 (m, 2 H), 8.47 (d, *J* = 1.7 Hz, 1 H), 8.96 (d, *J* = 5.8 Hz, 1 H). Anal. Calcd for $C_{35}H_{38}N_6O_2ClP_2F_{12}CoZn \cdot C_2H_6O$ (confirmed by ^{1}H NMR): C, 41.51; H, 4.14; N, 7.85; Cl, 3.31; Zn, 6.11; Co, 5.50. Found: C, 41.60; H, 4.12; N, 7.78; Cl, 2.97; Zn, 6.53; Co, 5.33. The appearance of two singlets at 2.19 and 2.28 ppm corresponding to the protons on the *p*-tolyl methyl groups and one doublet at 8.96 ppm corresponding to one of the 5-pyridyl protons confirms the magnetic inequivalence of similar protons in the molecule and is consistent with C_1 symmetry. There is evidence of a second isomer at the following positions: major isomer, δ 1.27, 4.84, 5.03, 8.96; minor isomer, δ 1.60, 4.65, 4.87, 8.87. The ratio of isomers is ~5:1.

[Co(*S*-pnenim)Zn](PF$_6$)$_2$(NO$_3$). The [Co(*S*-pnenim)ZnCl](PF$_6$)$_2$ complex was dechlorinated by the standard method. ^{1}H NMR (300 MHz, CD$_3$CN): δ 1.30 (d, *J* = 6.3 Hz, 3 H), 2.20 (s, 3 H), 2.28 (s, 3 H), 3.15 (m, 1 H), 3.80 (m, 10 H), 4.41 (m, 2 H), 5.04 (m, 2 H), 7.05 (m, 2 H), 7.17 (s, 1 H), 7.23 (t, *J* = 6.5 Hz, 1 H), 7.36 (m, 3 H), 7.63 (m, 3 H), 8.11 (m, 2 H), 8.52 (d, *J* = 1.4 Hz, 1 H), 8.81 (d, *J* = 6.1 Hz, 1 H). The appearance of two singlets at 2.20 and 2.28 ppm corresponding to the protons on the *p*-tolyl methyl groups and one doublet at 8.81 ppm corresponding to one of the 5-pyridyl protons confirms the magnetic inequivalence of similar protons in the molecule and is consistent with the retention of C_1 symmetry on removal of the chloride. There is evidence of a second isomer at the following positions: major isomer, δ 1.30, 8.81; minor isomer, δ 1.61, 8.72. The ratio of isomers remains ~5:1.

[Co(entnim)ZnCl](PF$_6$)$_2$. Method 1. [Co(entnim)ZnCl](PF$_6$)$_2$ was prepared by the method described for [Co(enenim)ZnCl](PF$_6$)$_2$ except that the reaction mixture was stirred for only 30 min. [Co(entnim)ZnCl](PF$_6$)$_2$ (85%) was obtained as dark maroon needles.

Method 2. To a stirred solution of [Co(entnim)ZnCl]PF$_6$[2] (148.9 mg, 0.169 mmol) in deaerated CH$_3$CN (2.5 mL) under N$_2$ was added [Cp$_2$Fe]PF$_6$ (61.7 mg, 0.186 mmol) in deaerated CH$_3$CN (2.5 mL). The dark maroon solution was stirred for 30 min and then was opened to the air and was concentrated to dryness. The product was triturated with Et$_2$O (3 × 5 mL) in order to remove Cp$_2$Fe. The residue was collected and was washed with ethanol (2 × 3 mL), Et$_2$O (2 × 5 mL), and pentane (2 × 5 mL), and was dried under vacuum. The dark maroon solid was recrystallized from CH$_3$CN–ethanol. The [Co(entnim)ZnCl](PF$_6$)$_2$ (55.9 mg, 32%) was obtained as maroon needles. All physical properties were identical for the product obtained by either method. Λ_M = 260 Ω^{-1} mol^{-1} cm^2. UV [λ_{max} in nm (ϵ in L mol^{-1} cm^{-1})]: 554 (4.3 × 10^2). ^{1}H NMR (300 MHz, CD$_3$CN): δ 2.10 (m, 2 H), 2.22 (s, 3 H), 2.28 (s, 3 H), 2.66 (m, 1 H), 3.00 (m, 1 H), 3.74 (m, 7 H), 4.01 (m, 2 H), 4.14 (m, 2 H), 4.53 (d, *J* = 18.9 Hz, 1 H), 4.80 (d, *J* = 19.2 Hz, 1 H), 5.03 (d, *J* = 17.5 Hz, 1 H), 7.05 (s, 1 H), 7.17 (m, 2 H), 7.28 (m, 3 H), 7.56 (m, 2 H), 7.68 (d, *J* = 5.7 Hz, 1 H), 7.79 (m, 1 H), 8.07 (m, 2 H), 8.36 (br s, 1 H), 8.83 (d, *J* = 3.4 Hz, 1 H). Anal. Calcd for $C_{35}H_{38}N_6O_2ClP_2F_{12}CoZn$: C, 41.04; H, 3.74; N, 8.02; Cl, 3.46; Zn, 6.38; Co, 5.75. Found: C, 40.83; H, 3.67; N, 8.11; Cl, 3.26; Zn, 5.60; Co, 5.97. The appearance of two singlets at 2.22 and 2.28 ppm corresponding to the protons on the *p*-tolyl methyl groups and one doublet at 8.83 ppm corresponding to one of the 5-pyridyl protons confirms the magnetic inequivalence of similar protons in the molecule and is consistent with C_1 symmetry.

[Co(entnim)Zn](PF$_6$)$_2$(NO$_3$). The [Co(entnim)ZnCl](PF$_6$)$_2$ complex was dechlorinated by the standard method. ^{1}H NMR (300 MHz, CD$_3$CN): 2.10 (m, 2 H), 2.27 (s, 6 H), 3.36 (m, 4 H), 3.73, 3.84 (syst AB, J_{AB} = 14.8 Hz, 4 H), 3.94 (m, 4 H), 4.62, 4.84 (syst AB, J_{AB} = 18.6 Hz, 4 H), 7.24 (s, 4 H), 7.41 (m, 4 H), 7.96 (t, *J* = 7.6 Hz, 2 H), 8.13 (d, *J* = 6.0 Hz, 2 H), 8.26 (s, 2 H). The appearance of one singlet at 2.27 ppm corresponding to the protons on the *p*-tolyl methyl groups and one doublet at 8.26 ppm corresponding to the 5-pyridyl protons confirms the magnetic equivalence of similar protons in the molecule. This result is consistent with C_2 symmetry, which is achieved when the chloride is removed.

[Co(*S*-pntnim)ZnCl](PF$_6$)$_2$. The complex was obtained as dark maroon needles. Yield: 56%. Λ_M = 296 Ω^{-1} mol^{-1} cm^2. UV [λ_{max} in nm (ϵ in L mol^{-1} cm^{-1})]: 556 (5.3 × 10^2). ^{1}H NMR (300 MHz, CD$_3$CN): δ 1.28 (d, *J* = 6.3 Hz, 3 H), 2.10 (m, 2 H), 2.20 (s, 3 H), 2.28 (s, 3 H), 2.97 (m, 1 H), 3.71 (m, 6 H), 3.99 (m, 4 H), 4.30 (m, 2 H), 4.94 (m, 2 H), 7.01 (s, 1 H), 7.23 (m, 5 H), 7.60 (m, 3 H), 7.74 (t, *J* = 7.4 Hz, 1 H), 8.01 (s, 1 H), 8.09 (t, *J* = 7.8, 1 H), 8.36 (s, 1 H), 8.88 (d, *J* = 5.9 Hz, 1 H). Anal. Calcd for $C_{36}H_{40}N_6O_2ClP_2F_{12}CoZn$: C, 41.64; H, 3.88; N, 8.09; Cl, 3.41; Zn, 6.29; Co, 5.67. Found: C, 41.51; H, 3.85; N, 8.08; Cl, 3.26; Zn, 5.91; Co, 5.76. The appearance of two singlets at 2.20 and 2.28 ppm corresponding to the protons on the *p*-tolyl methyl groups and one doublet at 8.88 ppm corresponding to one of the 5-pyridyl protons confirms the magnetic inequivalence of similar protons in the molecule and is consistent with C_1 symmetry. There is evidence of a second isomer at the following positions: major isomer, δ 1.28, 4.94, 8.88; minor isomer, δ 1.59, 4.64, 8.79. The ratio of isomers is ~7:1.

[Co(*S*-pntnim)Zn](PF$_6$)$_2$(NO$_3$). The [Co(*S*-pntnim)ZnCl](PF$_6$)$_2$ complex was dechlorinated by the standard method. ^{1}H NMR (300 MHz, CD$_3$CN): δ 1.37 (d, *J* = 6.3 Hz, 3 H), 2.12 (m, 2 H), 2.21 (s, 3 H), 2.26

(s, 3 H), 3.25 (m, 1 H), 3.80 (m, 9 H), 4.11 (m, 1 H), 4.23, 5.08 (syst AB, J_{AB} = 18.6 Hz, 2 H), 4.58, 4.96 (syst AB, J_{AB} = 17.9 Hz, 2 H), 7.10 (s, 1 H), 7.21 (m, 2 H), 7.33 (m, 3 H), 7.47 (m, 2 H), 7.78 (m, 2 H), 8.04 (td, J = 1.0, 7.7 Hz, 1 H), 8.14 (s, 1 H), 8.37 (s, 1 H), 8.50 (d, J = 5.9 Hz, 1 H). The appearance of two singlets at 2.21 and 2.26 ppm corresponding to the protons on the *p*-tolyl methyl groups and one doublet at 8.50 ppm corresponding to one of the 5-pyridyl protons confirms the magnetic inequivalence of similar protons in the molecule and is consistent with the retention of C_1 symmetry on the removal of the chloride. There is no evidence of a second isomer.

[Zn(ligand)ZnCl]PF$_6$ Complexes. All of the [Zn(ligand)ZnCl]PF$_6$ complexes were prepared by the general method described for [Zn(entnim)ZnCl]PF$_6$. The yields are based upon the [Zn(ligand)(H$^+$)$_2$](PF$_6$)$_2$ starting materials. Any variations from the preparation are indicated for the respective complexes. The appropriate physical data is included. All complexes showed an intense absorption at λ_{max} = 348–353 nm ($\epsilon = 1 \times 10^4$ L mol^{-1} cm^{-1}) in CH$_3$CN solution which is assigned to the $\pi \rightarrow \pi^*$ transition of the azomethine chromophore.[12]

[Zn(entnim)ZnCl]PF$_6$·0.5CH$_3$CN. To a stirred solution of [Zn(entnim)(H$^+$)$_2$](PF$_6$)$_2$ (151.6 mg, 0.163 mmol) in CH$_3$CN (2 mL) was added Et$_3$N (45.3 μL, 0.325 mmol) and ZnCl$_2$ (22.6 mg, 0.163 mmol) in ethanol (5 mL). The reaction mixture was stirred for 12 h and then was concentrated to dryness. The residue was slurried in ethanol (5 mL), and the solid was collected and was washed with ethanol (2 × 5 mL), Et$_2$O (2 × 3 mL), and pentane (2 × 3 mL) and was dried under vacuum. The crude product was recrystallized by vapor diffusion of Et$_2$O into an CH$_3$CN solution of the product. The crystalline [Zn(entnim)ZnCl]PF$_6$ (60.1 mg, 42%) was collected and was washed with Et$_2$O (4 × 5 mL) and pentane (4 × 5 mL), and was dried under vacuum. Λ_M = 119 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 1.91 (m, 1 H), 2.22 (s, 3 H), 2.23 (s, 3 H), 2.27 (m, 1 H), 2.49 (m, 1 H), 2.99 (m, 1 H), 3.26 (br s, 1 H), 3.62 (m, 3 H), 4.08 (m, 7 H), 4.38 (m, 2 H), 4.69 (m, 1 H), 6.75 (s, 2 H), 7.04 (m, 4 H), 7.33 (m, 2 H), 7.49 (s, 1 H), 7.86 (s, 2 H), 8.12 (s, 1 H), 8.28 (s, 1 H), 9.06 (s, 1 H). Anal. Calcd for C$_{35}$H$_{38}$N$_6$O$_2$ClPF$_6$Zn$_2$·0.5CH$_3$CN: C, 47.70; H, 4.40; N, 10.04; Cl, 3.91; Zn, 14.42. Found: C, 47.88; H, 4.33; N, 9.95; Cl, 3.46; Zn, 13.52. The appearance of two singlets at 2.22 and 2.23 ppm corresponding to the protons on the *p*-tolyl methyl groups and two broad singlets at 9.06 and 8.28 ppm corresponding to one of the 5-pyridyl protons confirms the magnetic inequivalence of similar protons in the molecule and is consistent with either C_1 symmetry or two isomers of C_s symmetry present in equal amounts.

[Zn(entnim)Zn](PF$_6$)$_2$. All [Zn(ligand)ZnCl]PF$_6$ complexes were dechlorinated by the following method. An excess of AgPF$_6$ was added to the [Zn(entnim)ZnCl]PF$_6$ in CD$_3$CN (0.6 mL) in an NMR tube, and the resultant mixture was shaken to precipitate AgCl (the complex was previously isolated by a different method[2]). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 2.13 (m, 2 H), 2.28 (s, 6 H), 2.88, 3.18 (syst AB, J_{AB} = 10.2 Hz, 4 H), 3.86, 4.24 (system AB, J_{AB} = 13.0 Hz, 4 H), 3.97 (m, 4 H), 4.10, 4.36 (syst AB, J_{AB} = 17.4 Hz, 4 H), 7.02 (s, 2 H), 7.13 (m, 4 H), 7.23 (t, J = 5.9 Hz, 2 H), 7.70 (t, J = 7.6 Hz, 2 H), 8.14 (s, 2 H), 8.46 (d, J = 4.9 Hz, 2 H). The appearance of one singlet at 2.28 ppm corresponding to the protons on the *p*-tolyl methyl groups and one doublet at 8.46 ppm corresponding to the 5-pyridyl protons confirms the magnetic equivalence of similar protons in the molecule. This result is consistent with C_2 symmetry.

[Zn(tnenim)ZnCl](PF$_6$)·H$_2$O. The complex was recrystallized from CH$_3$CN–ethanol. Yield: 88%. Λ_M = 114 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 2.10 (m, 2 H), 2.16 (s, 3 H), 2.25 (s, 3 H), 2.84 (m, 2 H), 3.11 (m, 2 H), 3.57 (m, 4 H), 4.23 (m, 8 H), 6.77 (m, 2 H), 7.06 (m, 4 H), 7.46 (m, 3 H), 7.93 (dt, J = 1.5, 7.7 Hz, 1 H), 8.00 (s, 1 H), 8.22 (d, J = 4.9 Hz, 1 H), 8.29 (m, 1 H), 9.29 (d, J = 5.0 Hz, 1 H). Anal. Calcd for C$_{35}$H$_{38}$N$_6$O$_2$ClP$_2$F$_{12}$Zn$_2$·H$_2$O (confirmed by ^{1}H NMR): C, 46.50; H, 4.47; N, 9.30; Cl, 3.92; Zn, 14.46. Found: C, 46.66; H, 4.20; N, 9.22; Cl, 3.79; Zn, 14.43. The appearance of two singlets at 2.16 and 2.25 ppm corresponding to the protons on the *p*-tolyl methyl groups and two doublets at 9.29 and 8.22 ppm corresponding to the 5-pyridyl protons confirms the magnetic inequivalence of similar protons in the molecule and is consistent with C_1 symmetry.

[Zn(tnenim)Zn](PF$_6$)$_2$. The [Zn(tnenim)ZnCl]PF$_6$ complex was dechlorinated by the standard method. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 2.09 (m, 2 H), 2.22 (s, 6 H), 2.91 (m, 2 H), 3.42, 4.31 (system AB, J_{AB} = 12.9 Hz, 4 H), 3.87 (m, 6 H), 4.10 (s, 4 H), 7.14 (m, 8 H), 7.73 (t, J = 7.2 Hz, 2 H), 8.25 (s, 2 H), 8.56 (s, 2 H). The appearance of one singlet at 2.22 ppm corresponding to the protons on the *p*-tolyl methyl groups and one doublet at 8.56 ppm corresponding to the 5-pyridyl protons confirms the magnetic equivalence of similar protons in the molecule. This result is consistent with C_2 symmetry which is achieved on removal of the chloride.

[Co(tnenim)ZnCl]PF$_6$. All procedures were conducted under Ar with deaerated solvents. To a stirred solution of [Co(tnenim)(H$^+$)$_2$](PF$_6$)$_2$ (131.2 mg, 0.142 mmol) in CH$_3$CN (0.5 mL) were added Et$_3$N (39.5 μL, 0.284 mmol) and ZnCl$_2$ (19.7 mg, 0.142 mmol) in ethanol (3 mL). Fine, pale orange needles precipitated within 5 min. Aliquots of ethanol (3 × 2 mL) were added to precipitate the complex. The crystals were collected and washed with ethanol (2 × 3 mL), Et$_2$O (2 × 3 mL), and pentane (2 × 3 mL) and were dried under vacuum. The crystals were recrystallized from CH$_3$CN–ethanol to give [Co(tnenim)ZnCl]PF$_6$ (80.4 mg, 74%) as pale orange needles. Λ_M = 121 Ω^{-1} mol^{-1} cm^2. UV [λ_{max} in nm (ϵ in L mol^{-1} cm^{-1})]: 482 (34), 545 (10), 1000 (6). μ_{eff}(25 °C) = 4.8 μ_B (powder). Anal. Calcd for C$_{35}$H$_{38}$N$_6$O$_2$ClPF$_6$CoZn: C, 47.79; H, 4.36; N, 9.56; Cl, 4.03; Co, 6.70; Zn, 7.43. Found: C, 47.63; H, 4.15; N, 9.44; Cl, 4.14; Co, 6.09; Zn, 7.54.

Crystallographic Analysis. Crystallographic data for the [Co(enenim)ZnCl](PF$_6$)$_2$·EtOH complex are collected in Table 2. Crystals were obtained from an CH$_3$CN/ethanol mixture. Preliminary photographic characterization showed *mmm* Laue symmetry, and systematic absences in the diffraction data uniquely established the space group as $P2_12_12_1$. The crystal was a thin plate, but azimuthal Ψ scans of six reflections and the low absorption coefficient indicated that absorption corrections were unnecessary.

The structure was solved by the Patterson method and completed by difference Fourier synthesis. All hydrogen and carbon atoms in the complex as well as all the atoms in the ethanol molecule and the fluorine atoms of the counter ions were refined with isotropic thermal parameters because of the limited amount of observed reflections; all other atoms were refined anisotropically. Computations were made with the SHELXTL PLUS (4.27) program library (G. Sheldrick, Siemens, Madison, WI).

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Supplementary Material Available: Top view of the structure and tables of detailed crystallographic data, complete bond distances and angles, anisotropic displacement parameters, hydrogen atom coordinates, and atomic coordinates (11 pages). Ordering information is given on any current masthead page.