kyl-substituted α-amino acid esters to give complexes **2–6**, (2) the hydroxylated amino acid esters Ser(OEt) and Tyr(OEt) to give **7** and **8**, (3) the mercaptan Cys(OEt) to give **9**, (4) the disulfide and sulfide Cys-Cys$(OMe)_2$ and Met(OEt) to give **10** and **11**, (5) the carboxy amino acid diester Asp$(OMe)_2$ to give **12**, and (6) the basic amino acids His(OMe), Trp(OEt), and various lysine derivatives to give complexes **13–19**. Of these diverse functional groups, only the acidic hydroxyl group of tyrosine interfered with the Schiff-base condensation in CH_2Cl_2 solution. However, in DMF solution, the condensation of Tyr(OEt) proceeds in good yield. Complexes **2–16** are now available as α-amino-protected amino acid residues, which can be incorporated into larger peptides by normal coupling procedures.[1]

Condensation of **1** with ethyl L-lysinate affords a 1:1 mixture of **15** and **16** where either the α- or ε-amino groups have reacted to form a rhena β-keto imine. An important objective of our effort to label biologically important molecules with heavy atoms is the type of distal labeling shown in complexes **16–19**. In these compounds, the rhena β-keto imine label is appended onto the amino acid side chain, R, thereby not interfering with chemical modifications at the N or C termini of the amino acid residue. Compounds **16–19** have the C terminus protected as the ethyl ester, while the N terminus is either unprotected or protected by acetyl, *t*-BOC, or CBZ groups.

Since peptides such as N^{α}-Ac-N^{ϵ}-Ac-L-Lys-D-Ala-D-Ala are known to bind to antibiotics such as vancomycin (presumably through the D-Ala-D-Ala moiety[9]), the distal-labeled tripeptide N^{α}-Ac-N^{ϵ}-[Re]-L-Lys-D-Ala-D-Ala is expected to bind similarly. Work on these more ambitious projects is in progress.

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Registry No. **1**, 59299-78-4; *inter*-**4**, 87681-84-3; *intra*-**4**, 87727-40-0; *inter*-**5**, 87681-85-4; *intra*-**5**, 87727-41-1; *inter*-**6**, 87681-86-5; *intra*-**6**, 87727-42-2; *inter*-**7**, 87681-87-6; *intra*-**7**, 87758-26-7; *inter*-**8**, 87681-88-7; *intra*-**8**, 87727-43-3; *intra*-**9**, 87681-89-8; *intra*-**10**, 87681-90-1; *inter*-**11**, 87681-91-2; *intra*-**11**, 87727-44-4; *inter*-**12**, 87681-92-3; *intra*-**12**, 87758-27-8; *intra*-**13**, 87681-93-4; *inter*-**14**, 87681-94-5; *intra*-**14**, 87727-45-5; *intra*-**15**, 87681-95-6; *inter*-**16**, 87681-96-7; *intra*-**16**, 87727-46-6; *inter*-**17**, 87681-97-8; *intra*-**17**, 87727-47-7; *inter*-**18**, 87681-98-9; *inter*-**19**, 87696-30-8; *intra*-**19**, 87758-28-9; L-valine methyl ester, 4070-48-8; L-leucine ethyl ester, 2743-60-4; L-phenylalanine ethyl ester, 3081-24-1; L-serine ethyl ester, 4117-31-1; L-tyrosine ethyl ester, 949-67-7; L-cysteine ethyl ester, 3411-58-3; L-cystine dimethyl ester, 1069-29-0; L-methionine ethyl ester, 3082-77-7; DL-aspartic acid dimethyl ester, 40149-67-5; L-histidine methyl ester, 1499-46-3; L-tryptophan ethyl ester, 7479-05-2; L-lysine ethyl ester, 4117-33-3; N^2-acetyl-L-lysine methyl ester, 6072-02-2; N^2-[(1,1-dimethylethoxy)carbonyl]-L-lysine ethyl ester, 87681-83-2; N^2-[(phenylmethoxy)carbonyl]-L-lysine ethyl ester, 52396-41-5.

Supplementary Material Available: Tables of microanalytical data and IR and ^1H NMR spectroscopic data for compounds **4–19** (5 pages). Ordering information is given on any current masthead page.

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Axial Ligand Derivatives of a Zinc(II) Tetraimine Macrocyclic Complex

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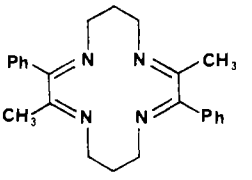
The synthesis of axial ligand derivatives of the macrocyclic complex (2,9-dimethyl-3,10-diphenyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)zinc(II) with one axial ligand (Cl^-, Br^-, I^-, pyridine, or dimethylbenzimidazole) or two axial ligands (both I^-) is reported. The compounds were characterized by elemental analyses, conductivity measurements, and spectral measurements (infrared, UV–visible, proton and carbon-13 NMR, and mass spectra). The major difference between the zinc complexes and the iron, cobalt, and nickel complexes of the same macrocyclic ligand is the reduced importance of metal–ligand π back-bonding. With the exception of the imine carbon resonances, the NMR spectra of the derivatives are insensitive to changes in axial ligation and coordination number. The imine carbon chemical shifts, however, span a range of 5 ppm and are affected most by coordination number and to a lesser extent by axial ligand.

Introduction

The template condensation of α-diketones with 1,3-diaminopropane in the presence of divalent iron, cobalt, nickel, or copper leads to 14-membered-ring macrocyclic complexes containing two α-diimines. A number of complexes of this class, derived from biacetyl,[1-3] 1-phenyl-1,2-propanedione,[4-6] benzil,[7,8] and substituted benzils[4] have been prepared. Under the template reaction conditions with 1-phenyl-1,2-propanedione as ketone, zinc(II) behaves differently, causing rapid polymerization of the reagents and leading ultimately to deep red polymers but no macrocyclic complex. Therefore, a nontemplate method similar to that reported by Gagné[9] was used by Coltrain[6] to prepare the zinc complex of MePhTIM.



MePhTIM

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Table I. Elemental Analysis and Conductivity Data for Zn(MePhTIM) Derivatives

compd	elemental analyses[a]			conductivity	
	% C	% H	% N	Λ_m[b]	solvent
$[Zn(MePhTIM)Cl]PF_6$	46.62, 46.15	4.56, 4.40	9.06, 9.15	69	CH_3NO_2
$[Zn(MePhTIM)Br]PF_6$	43.49, 43.55	4.27, 4.02	8.45, 8.52	84	CH_3NO_2
$[Zn(MePhTIM)I]PF_6$	40.62, 40.89	3.98, 3.68	7.89, 7.95	90	CH_3NO_2
$[Zn(MePhTIM)I_2]$	41.67, 41.54	4.09, 4.12	8.10, 8.06	5	CH_2Cl_2
$[Zn(MePhTIM)py](PF_6)_2$	43.16, 43.05	4.13, 4.09	8.68, 8.74	327	CH_3CN
$[Zn(MePhTIM)Me_2BIM](PF_6)_2$	45.35, 45.18	4.38, 4.60	9.62, 9.36	221	CH_3CN

[a] Calculated, found. [b] Units Ω^{-1} cm^2 mol^{-1}, for 1×10^{-3} M solutions.

The method involves a reductive transmetalation reaction in which $[Cu(MePhTIM)]^{2+}$ is reduced by metallic zinc to give $[Zn(MePhTIM)]^{2+}$ and metallic copper. In this paper we report the preparation and characterization of several five-coordinate derivatives and a six-coordinate derivative of $[Zn(MePhTIM)]^{2+}$. Our aim was to determine whether the NMR spectra (proton and carbon-13) are sensitive to changes in the coordination sphere about zinc that must accompany variations in coordination number and type of axial ligand. In addition, the data for the zinc complexes will be compared with that for the MePhTIM complexes of other metals.

Results and Discussion

$[Zn(MePhTIM)Cl]PF_6$ was prepared from $[Cu(MePhTIM)]ZnCl_4$ by a previously reported[6] reductive transmetalation reaction:

$$[Cu(MePhTIM)]ZnCl_4 \xrightarrow[MeOH,\ N_2]{Zn\ metal} [Zn(MePhTIM)Cl]^+ + Cu^0$$

Upon addition of NH_4PF_6, the product precipitates in about 40% yield. $[Zn(MePhTIM)Cl]PF_6$ has been characterized previously.[6] The chloride axial ligand is strongly bound but rapidly exchanging in the solvents in which the compound is soluble. Other axial ligands in excess will only partially replace chloride. It was necessary to quantitatively remove chloride with Ag^+ in order to prepare pure derivatives containing other axial ligands. In the absence of suitable axial ligands, the four-coordinate zinc complex could not be isolated as a PF_6^- salt. Upon addition of excess axial ligand, the derivatives readily crystallized from acetonitrile/ethanol mixtures. Attempts to prepare derivatives with strongly binding axial ligands, CN^-, CNO^-, or 1-methylimidazole, led to significant demetalation of the macrocyclic complex. Only small amounts of these derivatives could be isolated. Elemental analyses and conductivity measurements support the formulations of the derivatives as shown in Table I. The monohalo derivatives are all 1:1 electrolytes,[10] and the py and Me_2BIM derivatives are 2:1 electrolytes[10] as expected.

$[Zn(MePhTIM)I_2]$ was prepared in order to compare the properties of five-coordinate, presumably pyramidal $[Zn(MePhTIM)I]^+$ with an analogous tetragonal derivative. Both conductivity measurements and electronic spectra of $[Zn(MePhTIM)I_2]$ in CH_2Cl_2 support its formulation as six-coordinate in solution. The molar conductivity in CH_2Cl_2 (1×10^{-3} M) is very low, 5 cm^2 Ω^{-1} mol^{-1}, and is comparable to that observed for the six-coordinate $[Cu(MePhTIM)X_2]$ derivatives where X = I, Br, or NCS.[6] Further evidence is derived from the fact that the UV–visible spectrum of $[Zn(MePhTIM)I_2]$ is different from that of $[Zn(MePhTIM)I]PF_6$ in CH_2Cl_2. In the range 800–200 nm, $[Zn(MePhTIM)I_2]$ has two maxima, 294 nm (ϵ_m = 8850 L mol^{-1} cm^{-1}) and 362 nm (ϵ_m = 3530 L mol^{-1} cm^{-1}). In contrast $[Zn(MePhTIM)I]PF_6$ exhibits only one maximum at 280 nm (ϵ_m = 5860 L mol^{-1} cm^{-1}). In both cases the bands are most likely Zn–I charge transfer, and no such bands are seen in any of the other derivatives. The other halide derivatives only have shoulders at about 270 nm on the side of the intense intraligand transitions that start at about 250 nm. The two iodide derivatives are yellow whereas all of the other derivatives are colorless.

The infrared spectra of all the Zn(MePhTIM) derivatives are very similar to those of the $[Cu(MePhTIM)X]^{n+}$ derivatives. Bands attributed to functional groups in the macrocycle are observed in the following regions (cm^{-1}): 3000–3100, aromatic ν_{C-H}; 2900–3000, aliphatic ν_{C-H}; 1640–1660, $\nu_{C=N}$ (asym) (w); 1609–1615, $\nu_{C=N}$(sym); 1590, $\nu_{C=C}$ (sh); ~710 and 740, C–H out of plane bending of phenyl. Weaker bands in the 900–1400-cm^{-1} region are also associated with the ligand framework. The sharp band seen for most TIM complexes at about 1200 cm^{-1} is observed for these complexes at 1220–1228 cm^{-1}. Extra bands due to axial ligands py and Me_2BIM could be identified in those derivatives. In comparison with the Fe(II), Ni(II), Co(III), and Cu(II) MePhTIM complexes,[5,6] the Zn complexes have C=N stretching bands that are more intense and shifted to slightly higher frequency. This effect indicates the decreased importance of π backbonding in the Zn complexes due to the filled d subshell.

The desorption/chemical ionization technique proved to be very successful for obtaining parent-ion mass spectra of the cations in all the complexes. Very little fragmentation was observed and could be interpreted in most cases in terms of loss of one or more axial ligands. The masses of the three most intense peaks in the parent ion pattern for each of the compounds are given in Table II. Also given are the formula and the calculated mass of the species that correlates best with the most intense peak. In most cases the observed masses and relative abundances of the other peaks agreed well with the predictions based on the species shown in the table. For $[Zn(MePhTIM)py](PF_6)_2$ the known abundances of Zn isotopes lead to the prediction that the peak at 515 amu should be most intense; however, in the observed spectrum the 517-amu peak is slightly larger. In the case of $[Zn(MePhTIM)Me_2BIM](PF_6)_2$, the intensity pattern follows the predicted relative abundances, but all peaks are shifted 1 amu lower than expected. This is consistent with the ionization process

$$[Zn(MePhTIM)Me_2BIM]^{2+} \rightarrow [Zn(MePhTIM)(Me_2BIM\text{–}H^+)]^+ + H^+$$

The two derivatives containing iodide give very different spectra. $[Zn(MePhTIM)I_2]$ shows no molecular parent ion, a small pattern corresponding to $[Zn(MePhTIM)I]^+$, and an intense pattern corresponding to $[Zn(MePhTIM)]^+$. In contrast $[Zn(MePhTIM)I]PF_6$ gives an intense parent-ion pattern and a weak one corresponding to $[Zn(MePhTIM)]^+$. The bromide and chloride derivatives both give spectra consistent with intact ionization.

The proton NMR spectra of Zn(MePhTIM) derivatives are analogous to those observed for other MePhTIM complexes.[5] In CD_3NO_2 solvent, the methyl resonances are singlets at 2.15–2.26 ppm relative to Me_4Si. The methylene groups β to nitrogen are a broad multiplet at 2.0–2.6 ppm, and the

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Table II. Mass Spectra of Zn(MePhTIM) Derivatives

compd	parent-ion spectrum		
	formula	mass	
		calcd	found
[Zn(MePhTIM)py](PF$_6$)$_2$	$^{64}Zn^{12}C_{29}{}^{1}H_{33}{}^{14}N_5$	515.2	515, 517, 519
[Zn(MePhTIM)Me$_2$BIM](PF$_6$)$_2$	$^{64}Zn^{12}C_{33}{}^{1}H_{38}{}^{14}N_6$	582.2	581, 583, 585
[Zn(MePhTIM)I$_2$]	$^{64}Zn^{12}C_{24}{}^{1}H_{28}{}^{14}N_4$	436.2	436, 437, 438
[Zn(MePhTIM)I]PF$_6$	$^{64}Zn^{12}C_{24}{}^{1}H_{28}{}^{14}N_4{}^{127}I$	563.1	563, 564, 565
[Zn(MePhTIM)Br]PF$_6$	$^{64}Zn^{12}C_{24}{}^{1}H_{28}{}^{14}N_4{}^{81}Br$ $^{66}Zn^{12}C_{24}{}^{1}H_{28}{}^{14}N_4{}^{79}Br$	517.1	515, 517, 519
[Zn(MePhTIM)Cl]PF$_6$	$^{64}Zn^{12}C_{24}{}^{1}H_{28}{}^{14}N_4{}^{35}Cl$	471.1	471, 473, 475

[a] Largest peak underlined. Only the three largest peaks are listed. Units are amu.

Table III. Carbon-13 NMR Chemical Shifts for Macrocycle Carbon Atoms[a]

assgnt[b]	[Zn(MePhTIM)Cl]$^+$	[Zn(MePhTIM)I]$^+$	[Zn(MePhTIM)I$_2$]	[Zn(MePhTIM)py]$^{2+}$	[Zn(MePhTIM)Me$_2$BIM]$^{2+}$
CH_3 (q)	18.18	18.27	18.95	18.68	18.69
β-CH_2 (t)	29.43	29.57	27.72	29.67	29.66
α-CH_2 (t)	53.48	53.48	52.62	53.77	53.77
α-CH_2 (t)	54.64	54.68	53.80	54.93	54.96
Ph (d)	128.19	128.24	127.74	128.34	128.22
Ph (d)	130.71	130.79	129.50	130.80	130.90
Ph (d)	131.88	131.97	130.56	132.33	132.33
Ph (s)	133.38	133.41	132.83	132.76	132.99
C=N (s)	168.41	168.06	167.38	171.53	170.91
C=N (s)	169.55	169.29	168.50	172.05	171.66
solvent	CD_3NO_2	CD_3NO_2	CD_2Cl_2	CD_3NO_2	CD_3NO_2

[a] All shifts in ppm from internal Me_4Si; PF_6^- salts used. [b] Assignment followed by off-resonance pattern in parentheses: s = singlet; d = doublet; t = triplet; q = quartet.

α-CH_2 groups are a well-resolved pair of triplets ($J \approx 4$ Hz) at 3.9 and 4.05 ppm. The phenyl pattern is a complex multiplet in the 7.4–7.9 ppm region. Additional resonances are observed for the py and Me_2BIM axial ligands in those derivatives. It was hoped that the α-CH_2 or CH_3 resonances would be sensitive to changes in axial ligand and possibly concomitant changes in pyrimidality. However, it is seen that these patterns remain remarkably constant over the range of derivatives.

The ^{13}C NMR assignments (given in Table III) indicate that for each derivative the methyl and phenyl substituents are trans to each other. No indication of other products was seen in any case. The chemical shifts of the methyl, methylene, and phenyl carbon atoms are remarkably constant. Even [Zn(MePhTIM)I$_2$], which has been characterized as six-coordinate in CH_2Cl_2 solution, shows no significant differences compared to the five-coordinate derivatives. Thus, it must be concluded that the chemical shifts of these carbon atoms are insensitive to the conformational and electronic changes concomitant with the variation of axial ligands. Others have found similar results. On the basis of the ^{13}C NMR spectra of *trans*-[Co(3,2,3-tet)(acido)$_2$] complexes, Brubaker and Johnson[11] found that the chemical shifts of carbon atoms in the six-membered rings are independent of axial ligand field strength. The carbon atoms of the five-membered rings, in contrast, are significantly correlated with axial ligand field strength. These results are in basic agreement with our observations.

The imine carbon chemical shifts of the Zn(MePhTIM) derivatives vary significantly among the derivatives, spanning a range of nearly 5 ppm. Due to their participation in the α-diimine chelate rings, these carbons would be expected to reflect the influences of metal–ligand bonding. In each derivative the difference between the two imine carbon chemical shifts is about 1.2 ppm and is attributed to the methyl and phenyl substituents. Between the derivatives, these resonances shift in tandem over a range of about 3.5 ppm. The lowest shifts are seen for [Zn(MePhTIM)I$_2$] and most likely indicate reduced interaction between zinc and the nitrogen donors due to the presence of two strongly interacting halide axial ligands. It is a general phenomenon in macrocyclic complexes seen from electronic spectra of cobalt complexes[12] that when the axial ligand field is increased the equatorial field strength decreases. Thus, for [Zn(MePhTIM)I]$^+$ the imine carbons are shifted downfield by about 1 ppm relative to [Zn(MePhTIM)I$_2$], indicating increased Zn–N interaction. Of course, part of this difference could also be due to differences in coordination geometry. The derivatives containing nitrogenous base axial ligands are shifted to lowest field, indicating greatest Zn–N interaction. This observation is consistent with the chemical behavior of the derivatives: Ag^+ is necessary to remove chloride from the zinc complex whereas proton NMR results indicate a modest binding constant for pyridine. Very small differences, less than 0.4 ppm, are seen for [Zn(MePhTIM)Cl]$^+$ compared with [Zn(MePhTIM)I]$^+$.

It is interesting to note further that the imine carbon resonances of the Fe, Co, and Ni MePhTIM complexes[5] all occur at about 180 ppm, shifted about 12 ppm downfield from the zinc complexes. These complexes all have very strong metal–nitrogen interaction with some degree of π back-bonding. Their C=N stretching frequencies occur at slightly lower energy than the zinc complexes ($\sim$1600 as compared to 1610–1615 cm^{-1}), and the macrocyclic ligand is not removed by CN^- or strong acid as it is for the zinc complexes. The significance of the 12 ppm shift can be interpreted in view of results obtained for other complexes. For a large number of metal carbonyl[13] and cyano[14] complexes, the variations in ^{13}C

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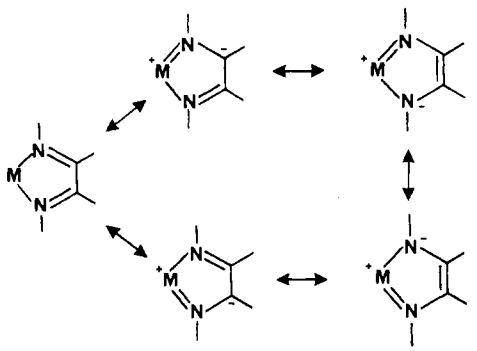
Scheme I



chemical shift have been attributed to the combined effects of changes in σ donation (an increase causing a downfield shift) and π acceptance (an increase causing an upfield shift). Neither of these effects is clearly dominant in determining trends. The observed shifts depend on the relative σ donor/π acceptor ability of the ligand and other factors such as metal electron configuration and oxidation state.[14] A consideration of the π back-bonding resonance structures for α-diimine complexes (Scheme I) indicates that the same bonding factors as for the cyano and carbonyl carbons should be important for the macrocycle imine carbons. Backbonding puts additional electron density on the imine carbons and decreases the CN bond order. The increased positive charge on the metal atom facilitates increased σ donation, which would be felt inductively by the imine carbons. Therefore, it is likely that both σ donation and π acceptance are significant in determining the imine carbon chemical shift. Since increased σ donation causes a downfield shift, this effect is dominant in determining the 12 ppm downfield shift of the Fe, Co, and Ni complexes as compared with the Zn complexes. However, increased electron density at the imine carbons and lowering of the CN bond order must also be important. The methyl substituent carbon chemical shifts may reflect this, since they move upfield by about 2 ppm in the Fe, Co, and Ni complexes relative to the Zn complexes. With the lack of structural information (no crystallographic results are available), there is no way to correlate these indications of bonding differences with possible structural variations.

Experimental Section

Preparations. [Cu(MePhTIM)]$ZnCl_4$ was prepared according to the procedure published in ref 15.

[Zn(MePhTIM)Cl]PF_6 was prepared from [Cu(MePhTIM)$ZnCl_4$ according to the procedure in ref 15.

[Zn(MePhTIM)Br]PF_6 was prepared from [Zn(MePhTIM)Cl]PF_6 by the following procedure. A 0.50-g sample of [Zn(MePhTIM)-Cl]PF_6 (8.1×10^{-4} mol) was dissolved in warm CH_3CN (15 mL) and filtered. Then a solution of 0.20 g of $AgBF_4$ (1.0×10^{-3} mol) in CH_3CN (10 mL) was added dropwise with stirring causing immediate precipitation of AgCl. The mixture was allowed to cool and then was stored in a refrigerator for a few hours. The AgCl was removed by filtration through fine filter paper. Then a solution of 0.25 g of NaBr (2.4×10^{-3} mol) in MeOH (40 mL) was added to the stirred solution. The resulting sparce precipitate of AgBr was removed by gravity filtration after cooling the mixture in a refrigerator for several hours. The filtrate was warmed to near boiling, and a solution of 0.40 g of NH_4PF_6 (2.5×10^{-3} mol) in MeOH (15 mL) was added, resulting in precipitation of [Zn(MePhTIM)Br]PF_6. The mixture was allowed to cool and was refrigerated for 24 h. The colorless crystalline product was collected by suction filtration, washed with absolute EtOH, and dried in vacuo over activated alumina. Yield: 0.33 g, 61%. More product can be obtained by rotoevaporation of the filtrate. If necessary, the product can be recrystallized from CH_3CN and MeOH.

[Zn(MePhTIM)I]PF_6 was prepared by a procedure analogous to that used for [Zn(MePhTIM)Br]PF_6 by using NaI instead of NaBr.

[Zn(MePhTIM)I_2]. A 0.40-g sample of [Zn(MePhTIM)Cl]PF_6 (6.5×10^{-4} mol) was dissolved in acetone (15 mL), and the resultant mixture was filtered and warmed to 45 °C. A solution of 0.87 g of LiI (6.5×10^{-3} mol) in acetone (10 mL) also was warmed to 45 °C. Then the [Zn(MePhTIM)Cl]PF_6 solution was added dropwise with stirring to the LiI solution, resulting in a clear golden yellow solution. Diethyl ether (12–16 mL) was added dropwise until crystals began to form. The mixture was tightly stoppered and allowed to stand overnight. The yellow crystalline product was collected by suction filtration, washed with ether, and dried in a vacuo over activated alumina. Yield: 0.2 g, 40%. More product can be obtained by addition of ether to the filtrate. If necessary, the product can be recrystallized from acetone containing ether and a tenfold excess of LiI.

[Zn(MePhTIM)py]$(PF_6)_2$. A 0.50-g sample of [Zn(MePh-TIM)Cl]PF_6 (8.1×10^{-4} mol) was dissolved in warm CH_3CN (15 mL), and the resultant solution was filtered. Then a solution of 0.20 g of $AgBF_4$ (1.0×10^{-3} mol) in CH_3CN (10 mL) was added dropwise with stirring, causing immediate precipitation of AgCl. This mixture was allowed to cool and then was stored for a few hours in a refrigerator. The AgCl was removed by gravity filtration through fine filter paper. A 1-mL of portion of pyridine was added to the stirred solution followed by a solution of 0.40 g of NH_4PF_6 (2.5×10^{-3} mol) in MeOH (15 mL). The mixture was cooled in an ice bath for about 1 h, and any precipitate was removed by gravity filtration. Then 10 mL or more of MeOH was added, and the solution was evaporated on a rotary evaporator until it became cloudy. The mixture was allowed to stand at room temperature for several hours and then was stored in a refrigerator overnight. The colorless crystalline product was collected by suction filtration, washed with absolute ethanol, and dried under vacuum over activated alumina. The product was recrystallized from CH_3CN and EtOH containing excess pyridine.

[Zn(MePhTIM)Me_2BIM]$(PF_6)_2$ was prepared by using a procedure analogous to that used for the pyridine derivative. Three equivalents of diemthylbenzimidazole was used in place of pyridine.

Physical Measurements. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Conductivity measurements were made with an Industrial Instruments Model RCM-15B1 conductivity bridge and an immersion-type cell at room temperature. Infrared spectra were recorded on a Perkin-Elmer 1330 infrared spectrophotometer in the range 4000–400 cm^{-1}. Samples were prepared as mineral oil mulls on KBr plates. Proton NMR spectra were recorded on a Perkin-Elmer R32 spectrometer (90 MHz) at 35 °C. Carbon-13 NMR spectra were recorded by Dr. David L. Harris at the University of North Carolina at Chapel Hill using a Bruker WM-250 spectrometer. Mass spectra were acquired from a Ribermag R10-10 quadrupole mass spectrometer in the Department of Biochemistry at the Bowman Gray School of Medicine of Wake Forest University. The compounds were ionized by the desorption/chemical ionization technique using ammonia as reagent gas and a source temperature of 35 °C.

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Registry No. [Zn(MePhTIM)Cl]PF_6, 77153-92-5; [Zn(MePh-TIM)Br]PF_6, 87655-49-0; [Zn(MePhTIM)I]PF_6, 87655-51-4; [Zn-(MePhTIM)I_2], 87655-52-5; [Zn(MePhTIM)py]$(PF_6)_2$, 87681-06-9; [Zn(MePhTIM)Me_2BIM]$(PF_6)_2$, 87655-54-7.

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