The preparation of supramolecular structures by self-assembly is a subject of much current interest as an approach to materials with novel physicochemical properties. This strategy takes its lead from nature, which utilizes noncovalent or metal–ligand interactions to organize molecules into large assemblies. This facilitates the construction of molecular architectures, the size and complexity of which would often be impossible to imagine using traditional organic syntheses involving covalent bonds. Bioinorganic chemists have long since recognized the importance and usefulness of metal–ligand interactions, since nature uses metals in a multitude of roles, and organic chemists are slowly recognizing the practicalities of self-assembly strategies involving noncovalent bonding.

One approach to supramolecular architectures is metal-ion-assisted self-assembly. There are many reported examples of coordination of metal ions by polybipyridine ligands to generate interesting two- and three-dimensional arrays including rods, grids, helices, ladders, and rings. Bipyridines are neutral ligands, which produce charged complexes upon coordination to metals at any oxidation state (> M²⁺). Consequently, counterions are needed to generate neutral species, but unfortunately such counterions often give rise to disorder in the solid state, rendering X-ray crystallography useless if crystals of adequate quality cannot be grown. Additionally, the resulting salts are frequently difficult to purify using chromatography.

Multi-porphyrin architectures have also been reported, albeit sometimes created through the use of covalent interactions, which show promise in electronic and photonic applications. A recent report has suggested the possible application of self-assembled crystalline porphyrin lattices with nano-dimension channels running through them as alternatives to inorganic zeolites. Porphyrins

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are useful ligands for complexion reactions since they generate resonance stabilized dianions which readily coordinate to metal ions to give metalloporphyrins. However, the difficulties often encountered in the preparation of functionalized porphyrins and the structural limitations of the tetra-pyrrolic ring itself inhibits the usefulness of porphyrins in self-assembly strategies.

Dipyrromethenes are essentially the building blocks of porphyrins, but possess greater diversity and flexibility as a result of their nonmacrocyclic nature. Our use of these molecules as ligands for supramolecular complexation reactions has allowed us to prepare new and interesting architectures. We herein present a detailed report of some of our work in this area and discuss some of the features which control the self-assembly process.

The dipyrromethene unit 1 is a fully conjugated flat monoanionic ligand, useful in metal chelation reactions. Consequently, dipyrromethene moieties linked by a bridging unit are useful as ligands for the formation of well-defined architectures through self-assembly. Fuhrhop et al. reported that a mixture of 1:1 and 2:2 octaethyl formylbiliverdinate/zinc complexes could be separated by hand and X-ray crystallographic analysis showed that the 2:2 complex existed in a helical conformation. Similarily, the X-ray structure of 1,2,3,7,8,12,13,17,18,19-decamethylbiladiene-a,c revealed a helical structure. As part of our ongoing studies to investigate the use of bis(dipyrromethene) ligands in self-assembly strategies we have previously shown that similar ligands (n = 3, 4, 6, 8, 12), with octyl rather than ethyl β-substituents, form dinuclear and mononuclear complexation products depending upon the length of the linking alkyl chain.

Reaction of benzyl 2,4-dimethylpyrrole-5-carboxylate with acidified aqueous formaldehyde in methanol gave the key intermediate 8. Removal of the benzyl group gave the corresponding acid which then underwent decarboxylation and in-situ coupling with 3-ethyl-2-formyl-4-methylpyrrole in the presence of hydrobromic acid to give ligand 2 as shown in Scheme 1. All reactions proceeded in excellent yield, with extremely facile isolation procedures.

Ligands 2–16 each contain two dipyrromethene units separated by an alkyl chain (n = 1–6). We wished to investigate the structure and geometry of the complexes resulting from reaction of these ligands with metal ions. We have previously shown that similar ligands (n = 3, 4, 6, 8, 12), with octyl rather than ethyl β-substituents, form dinuclear and mononuclear complexation products depending upon the length of the linking alkyl chain.

The factors dominant in the coordination algorithm operating during self-assembly.

Ligands 2–16 each contain two dipyrromethene units separated by an alkyl chain (n = 1–6). We wished to investigate the structure and geometry of the complexes resulting from reaction of these ligands with metal ions. We have previously shown that similar ligands (n = 3, 4, 6, 8, 12), with octyl rather than ethyl β-substituents, form dinuclear and mononuclear complexation products depending upon the length of the linking alkyl chain.

Preparation of the ethylene linked ligand proved to be the most difficult with simple coupling reactions of benzyl 2,4-dimethylpyrrole-5-carboxylate with oxalyl chloride proving extremely messy. It was eventually found that reaction of the crude acid chloride generated from 9 with ethyl-2,4-dimethylpyrrole-5-carboxylate in CH2Cl2 catalyzed by SnCl4 under carefully controlled conditions gave the required intermediate 11. Work up was achieved by addition of 10% NaHSO3, since aqueous HCl, NaOH or neutral workup gave homologated coupling products. It is unclear why workup using NaHSO3 solution is so successful. Reduction, debenzylisation and coupling as before gave ligand 3. Ligand 4 was prepared using the same route but with higher yields due to a more facile coupling procedure and greater solubility of the intermediates (Scheme 2). Ligands 5–7 were prepared as previously reported using similar strategies.

The ligands were each reacted with excess ZnII and CdII in the presence of NaOAc, as described in the Experimental Section and shown in Scheme 3. Ligand 2 was also reacted with CuII. Yields of the resulting complexes were excellent in every case. The reactions were monitored by UV–vis spectroscopy and complexation was seen to occur immediately by an λmax red shift of 16–24 nm. Complete complexation also occurs when stoichiometric amounts of M(OAc)2 are used, but the reaction is much slower. The complexes were isolated as stable green/orange powders with a metallic luster. Solutions of the complexes in CH2Cl2 or CHCl3 were stable for >6 months in the dark, but very slow photobleaching was observed.

\[ \text{Scheme 1} \]

\[ \text{Scheme 2} \]

\[ \text{Scheme 3} \]


Oligomers were also observed. It is unclear whether the similar studies using MALDI spectrometry, higher order ion and the conformational preferences of the ligand. In both the coordination geometry requirements of the metal algorithm operates during self-assembly such as to satisfy such folding and instead give dinuclear complexes. We nuclear product. Shorter chain lengths are incapable of to fold around a single metal ion to generate a mono-
mononuclear complex becomes favored. Presumably, this of the spacer unit increases, so the formation of the from CoII complexation. Table 1 shows that as the length identically results were obtained for compounds obtained of the mono-nuclear complexes had been produced. The results for ZnII spectrometry, revealed that both dinuclear and mono-
higher order oligomers are merely artifacts of the ana-
lytical method used. The mono- and dinuclear complexes of ligands 5 and 6 were not separated, since TLC analysis showed that this would be extremely difficult via chromatography, and recrystallization proved unfruitful.

Crystals of 17–19 suitable for X-ray analysis were grown by slow diffusion of MeOH into chloroform solutions of the complexes. We thus present a series of X-ray structural studies and compare the conformations adopted by the complexes as the length of the alkyl spacing group is increased. In 17 and 19 disordered single molecules of CH₂Cl₂ and CHCl₃ respectively reside within the asymmetric unit, but this does not detract from our studies involving bulk structural comparison.

**Table 1. Oligomeric Ratios of Zn**II Complexes**

<table>
<thead>
<tr>
<th>ligand</th>
<th>n</th>
<th>product(s)</th>
<th>mononuclear/dinuclear</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1</td>
<td>17</td>
<td>0:1</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>18</td>
<td>0:1</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>19</td>
<td>0:1</td>
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<tr>
<td>5</td>
<td>4</td>
<td>20</td>
<td>1:2</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>21</td>
<td>2:1</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>22</td>
<td>1:0</td>
</tr>
</tbody>
</table>

* Oligomeric ratios were determined from EI m/s studies. Approximate values are given, since the relative affinities of the mono- and dinuclear species were not determined. a 2% trinuclear complex was also observed. b 2% dinuclear complex was also observed.

Higher oligomers are actually present in solution, although it should be noted that they are not observed using NMR spectroscopy. We strongly suspect that these higher order oligers are merely artifacts of the analytical method used. The mono- and dinuclear complexes of ligands 5 and 6 were not separated, since TLC analysis showed that this would be extremely difficult via chromatography, and recrystallization proved unfruitful.

Crystals of 17–19 suitable for X-ray analysis were grown by slow diffusion of MeOH into chloroform solutions of the complexes. We thus present a series of X-ray structural studies and compare the conformations adopted by the complexes as the length of the alkyl spacing group is increased. In 17 and 19 disordered single molecules of CH₂Cl₂ and CHCl₃ respectively reside within the asymmetric unit, but this does not detract from our studies involving bulk structural comparison.

**Scheme 2**

![Scheme 2](image1.png)

**Scheme 3**

![Scheme 3](image2.png)

a Key: (a) Cl(COCI) reflux; (b) CH₂Cl₂, SnCl₄, 23%, n = 0, 85%, n = 1 over two steps; (c) borane, THF, 23%, n = 0, 94%, n = 1; (d) BnONa, BnOH, 209 °C, 94%, n = 0, 95%, n = 1.
Dinuclear Bis(dipyrromethene) Complexes

Table 2. Atom–Atom Distances for Complexes 17–19 and 24

<table>
<thead>
<tr>
<th>complex</th>
<th>N(1)–N(4) (Å)</th>
<th>N(2)–N(3) (Å)</th>
<th>Zn(1)–Zn(2) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>10.76</td>
<td>5.85</td>
<td>8.17</td>
</tr>
<tr>
<td>18</td>
<td>9.12</td>
<td>4.98</td>
<td>6.63</td>
</tr>
<tr>
<td>19</td>
<td>13.46</td>
<td>8.78</td>
<td>11.29</td>
</tr>
<tr>
<td>24</td>
<td>8.97</td>
<td>4.95</td>
<td>6.54</td>
</tr>
</tbody>
</table>

a Zn(1)–Zn(1) value. b Co(1)–Co(2) value.

Figure 1. One ligand plus zinc taken from crystal structures of 17, 18, and 19 and atoms Zn(1), N(1), and C(4) overlayed using HyperChem.

of the complexes. Each complex crystallizes in a helical dinuclear structure, with 18 showing greatest helicity, followed by 17 and then 19, which is only slightly helical. The Zn–N bond lengths for all complexes are in the range 1.96–2.00 (Å).

Analysis of the crystal structures reveals that the dipyrromethene units in one ligand of 17 is planar, as expected through conjugation, while the other ligand contains a dipyrromethene unit slightly distorted from planarity, the origin for which occurs at the methine positions. Zinc dinuclear complex 18 and cobalt dinuclear complex 24 have C2 symmetry and are essentially identical when the structures are overlayed. One dipyrromethene unit within each ligand is planar, while the other suffers slight distortion from planarity. Conversely, both dipyrromethene units within the ligands of 19, are essentially planar. This is presumably reflective of bond strain within the complexes containing methylene and ethylene spacers, as the coordination geometry requirements of the metal ion are met and the preferred ligand conformations are compromised. Conversely, the longer propylene spacer allows for satisfaction of the coordination geometry requirements of ZnII, while maintaining the preferred planar ligand conformation.

Table 2 shows some interesting atom–atom lengths for each of the complexes. Complex 19 has the longest N(1)–N(4) distance, followed by 17 and 18. This is easily appreciated by analysis of Figure 1, which shows a 3-atom overlayed view10 of one ligand plus ZnII from each of 17, 18 and 19 and clearly indicates the relative degrees of twist and bend within each of the three complexes. Complex 18 has the shortest N1–N4 distance. This is due to an angle of 36° between the two average planes defined by the dipyrromethene units of a single ligand, resulting in the near proximity of the dipyrromethene units and hence a short N(1)–N(4) distance. The angle of apparent twist along the axis of the molecule for 18 is 80°.19 Complex 17 has an angle of 90° between the two dipyrromethene defined planes of one ligand and an apparent twist angle of 60°. Complex 19 has an angle of 117° between the planes defined by the dipyrromethene units of one ligand and an apparent twist angle of 15°. Hence, the extent of helicity decreases in the order 18 > 17 > 19 as noted above and the N–N distances map this trend (Table 2).

Two major factors constitute the coordination algorithm of formation for these dipyrromethene complexes—the coordination geometry requirements of the metal ion and the preferred conformation of the ligand. The ligands only differ by length of the alkyl spacer unit and so the structural differences between the complexes formed must be due to the preferred conformation of the ligands involved. Each ligand contains largely equivalent dipyrromethene units, but consideration of the conformation of the alkyl bridging units serves to rationalize our observations. Complexes 17–19 all show slightly distorted tetrahedral geometry around the ZnII centers.

The β,β'-methylene linkage between the two dipyrromethene binding units in 17 has limited conformational possibilities since sp3 hybridization must be maintained. In fact, the angle between the two dipyrromethene units across the methylene bridge in 17 is 114°, indicative of slight distortion from tetrahedral to accommodate the large dipyrromethene substituents. The dipyrromethene units in 18 experience a pseudo gauche interaction of angle 68° across the β-β' ethylene linkage. Clearly, the dipyrromethene units suffer significant steric interaction, but this is presumably a thermodynamically more stable conformation (for the whole molecule) than the alternative anti conformation which would result in immense strain in the N–Zn bonds and ligand conformation due to the relatively short ethylene linker. In 17 and 18 the dipyrromethene binding units are thus oriented such that complexation occurs on widely differing planes for each end of the molecule, resulting in twisted helical structures. The propylene linker in 19 has an anti anti conformation with anti angles of 178° and 176°. As a consequence, the dipyrromethene binding units are oriented on planes only 15° apart, thus leading to only slight twisting and a small extent of helicity in the resulting complex. The 2,4-dimethyl groups on the pyrroloato ring in all the dipyrromethene units are placed in effectively opposing positions either side of the β-linking position. Consequently their combined effect upon the adopted conformation is limited. We thus conclude that it is the conformational preferences of the alkyl linking units, rather than the length per se, which dominate the coordination algorithm and are responsible for the structures of the complexes obtained.

The ligands and ZnII complexes were also analyzed by 1H and 13C NMR spectroscopy. Further characterization and spectral assignment of ligand 2 and complex 17 was achieved by use of NOE spectroscopy and the results are shown in Table 3. These results were imperative to our novel use of chiral lanthanide shift reagents for 1H analysis of enantiomeric helical dipyrromethene complexes20 and reveal interesting features which support the presence of helical structures in solution.

(18) Using HyperChem 5.11, the atoms N1, C4 and Zn1 were overlayed in merged files containing single ligands plus metal from the crystal structures of 17, 18 and 19.

(19) The angle of apparent twist along the axis of the molecule is equivalent to the improper torsion angle of atoms N(4)–C(17)–N2–C6 for 18. Equivalent measurements for 17 and 19 were calculated using the improper torsion angle for atoms N4–C(16)–N2–C(6) and N(4)–C(18)–N(2)–C(6), respectively. This measurement serves as a method for comparing the structures of the complexes obtained.
ments showed that complexation of 2 to form 17 gave rise to upfield shifts for all $^1H$ signals. As expected, the $\alpha$-signals shift dramatically (0.54 ppm), while those further removed from the site of complexation experience less change upon complexation. Remarkably, the methyl signal at 2.62 ppm in ligand 2 shifts to 1.38 ppm in complex 17. Analysis of the X-ray crystal structure of 17 shows $\text{CH}_3$ to lie in a position such as to suffer anisotropic effects due to the ring current of a dipyrromethene moiety within the other ligand, as noted by others in analogous systems. Interestingly, $\text{CH}_3$-$\text{CH}_2$-$\text{F}^-$ NOE enhancements (Figure 2) are observed for both the ligand and the complex, indicative of steric interference between the two dipyrromethene units within a single ligand. This steric interaction presumably contributes to the coordination algorithm of self-assembly.

To examine some kinetic and thermodynamic properties of the complexation reaction, the complexation of ligand 2 with Zn$^{II}$ was conducted under a variety of conditions. Temperature variations (−78 to 60 °C), reaction time (5 min to 72 h) and order of addition did not affect the nature of products formed—in each case, dinuclear complex 17 was formed in quantitative yield, suggesting it to be both the thermodynamic and kinetic product.

Additionally, 1.0 equiv of ligand 2 was reacted with 0.5 equiv of Zn(OAc)$_2$·2H$_2$O under standard conditions. After 30 min, 0.5 equiv of of Co(OAc)$_2$·4H$_2$O was added and the reaction continued for a further 30 min and then worked up as usual. EI mass spectrometry showed the Zn:Zn and Co:Co dinuclear complexes to be present in a 1:1 ratio, with the Zn:Co dinuclear species making up approximately 10% of the total yield. In another experiment, 1.0 equiv of ligand 2, 0.5 equiv of Zn(OAc)$_2$·2H$_2$O and 0.5 equiv of Co(OAc)$_2$·4H$_2$O were reacted under standard conditions. EI mass spectrometry showed a 1:2:1 ratio for the Zn:Zn, Zn:Co, and Co:Co dinuclear complexes, respectively. Furthermore, the Zn:Zn complex was refluxed with 10.0 equiv of Co(OAc)$_2$·4H$_2$O in CH$_3$Cl/MeOH for 3 h. Similarly, the Co:Co dinuclear complex was refluxed with 10.0 equiv of Zn(OAc)$_2$·2H$_2$O under identical conditions. In both cases, approximately 2% of the mixed Zn:Co complex was observed by EI mass spectrometry analysis of the products.

These experiments, although only qualitative since the relative affinities of the complexes under EI mass spectrometry conditions are unknown, reveal several important features of the complexation process. A schematic is shown in Figure 3. Although only the (productive) steps toward formation of the obtained dinuclear complex are shown, it is acknowledged that the dipyrromethene ligands may (and almost certainly do) complex metal ions in a variety of other, nonproductive, conformations. All alternative steps must be fully and readily reversible with complexation ultimately operating through $k_1$ and $k_2$ as shown, since a single dinuclear product 17 is obtained. From the experiments described above, it can be concluded that $k_2$ > $k_1$ and that $k_2$ > $k_{-2}$.

In summary, we have prepared a series of dipyrromethene based Zn$^{II}$ and Co$^{II}$ complexes of helical dinuclear and mononuclear architecture. The formation of four helical dinuclear complexes have been confirmed by X-ray crystallography and compared by overlay methods. The presence of helical structures in solution is supported by NMR spectroscopic results. The extent of helicity was assessed and found to be dependent upon the length and conformational preferences of the alkyl spacer unit between the two dipyrromethene moieties. Our studies have thus identified the crucial importance that the conformational preferences of the $\beta$-$\beta'$ alkyl spacer group plays in the coordination algorithm of self-assembly to form our dipyrromethene based complexes.

Current work is being directed toward the design and preparation of more exotic dipyrromethene based 3-dimensional complexes, and is guided by our understanding of the importance and nature of alkyl spacer conformational preferences. Additionally we are working toward the synthesis of dipyrromethene ligands connected by rigid spacer units. The physicochemical properties of dipyrromethene based ligands and complexes are currently under investigation.

**Experimental Section**

4,4'-Methylenebis[3,5-dimethyl-bis(phenylmethyl)ester]-1H-pyrrrole-2-carboxylate (8). To a solution of benzyl 2,4-dimethylpyrrrole-5-carboxylate$^{22}$ (250 mg, 1.09 mmol) in MeOH (20 mL) at room temperature was added 37% aqueous formaldehyde (2.6 equiv) and concentrated HCl (1 mL). After the mixture was stirred for 14 h, a white precipitate had appeared and TLC analysis showed the absence of starting material. The product was isolated by filtration, washed with MeOH (10 mL), water (10 mL), and MeOH (10 mL), and then air-dried (231 mg, 90%); mp > 230 °C; $\lambda_{max}$ (200 MHz; CDCl$_3$) 2.05 (3H, s), 2.23 (3H, s), 3.47 (1H, s), 5.29 (2H, s), 7.29—7.43 (5H, s), 8.48 (1H, br s); m/z EI 470 (M$^+$ + 1), 470.2212, C$_2$H$_2$N$_2$O$_2$ requires 470.2206. Anal. Calcld for C$_{29}$H$_{30}$N$_2$O$_4$: C, 74.04; H, 6.38; N, 5.96. Found: C, 73.92; H, 6.42; N, 6.10.

3,3'-Methanediyldibis[2,4-dimethyl-5-[1-ethyl-4-methyl-2H-pyrrrol-2-ylidene)methyl]-, Dihydrobromide 1H-Pyrrole (2). To a suspension of bipyrrole 8 (529 mg, 1.13 mmol) in THF (30 mL) were added NEt$_3$ (1 drop) and 10% Pd/C catalyst (20 mg). The reaction mixture was then exposed to 1 atm of hydrogen for 14 h, whereby all the starting material was seen to have dissolved and TLC indicated the absence of


(21) Although only shown in one direction for clarity, all NOE enhancements indicated in Figure 3 were observed in both directions.

remaining starting material. The catalyst was removed by filtration and washed with THF (5 mL) and MeOH (5 mL). To the filtrate was added 3-ethyl-2-formyl-4-methylpyrrole (317 mg, 2.31 mmol), and the resultant mixture was stirred and briefly heated gently with a heat gun to ensure full dissolution. A solution of 50% HBr (1 mL) in MeOH (2 mL) was added to the reaction mixture and stirring continued for 30 min. Careful partial removal of the solvents in vacuo resulted in precipitation of the orange/red product, which was isolated by filtration and washed with cold MeOH (5 mL) (411 mg, 60%). mp dec. > 230 °C; UV – vis \( \lambda_{max} \) (CHCl\(_3\)) nm 498 (11, 199 000), 456 (4); \( \delta_{H} \) (200 MHz; CDCl\(_3\)) 1.39 (3H, t, J = 7.6), 2.10 (3H, s), 2.20 (3H, s), 2.62 (2H, s), 2.73 (2H, q, J = 7.6), 3.60 (1H, s), 7.17 (1H, s), 13.07 (1H, br s), 13.32 (1H, br s); \( \delta_{C} \) (75 MHz; CDCl\(_3\)) 19.88 (CH\(_3\)), 10.71 (CH\(_3\)), 13.47 (CH\(_3\)), 16.21 (CH\(_2\)), 18.42 (CH\(_3\)), 15.95 (CH\(_3\)), 120.91 (CH\(_3\)), 124.39, 125.25, 126.27, 126.83, 141.06 (CH\(_3\)), 142.97, 148.53, 155.45; m/z E I 440 (M – 2HBr)\(^+$), 67); found M\(^+\), 440.2934, C\(_{29}\)H\(_{36}\)N\(_4\) requires 440.2940.

Zinc, Bis[13,3′-(methanediyl)bis[5-[(3-ethyl-4-methyl-2H-pyrrolyl-2-yldiene-κN)methyl]-2,4-dimethyl-1H-pyrroloynitroso-kN]](2-)[di- (17). To a solution of ligand 2 (100 mg, 0.17 mmol) in CHCl\(_3\) (1 mL) at room temperature was added a solution of Zn(OAc\(_2\)) \( 2\)H\(_2\)O (182 mg, 0.83 mmol) and NaOAc-3H\(_2\)O (113 mg, 0.83 mmol) in MeOH (1 mL). The reaction mixture was stirred for 30 min, and the solvents were then removed in vacuo. CH\(_2\)Cl\(_2\) (10 mL) and water (10 mL) were then added, and the organic layer was separated, washed with water (10 mL), and dried over MgSO\(_4\). Filtration through a short plug of silica gel eluting with CH\(_2\)Cl\(_2\) and then 1:10 MeOH/CH\(_2\)Cl\(_2\) followed by filtration and washed with THF (5 mL) and MeOH (5 mL). To the filtrate was added 3-ethyl-2-formyl-4-methylpyrrole (317 mg, 2.31 mmol), and the resultant mixture was stirred and briefly heated gently with a heat gun to ensure full dissolution. A solution of 50% HBr (1 mL) in MeOH (2 mL) was added to the reaction mixture and stirring continued for 30 min. Careful partial removal of the solvents in vacuo resulted in precipitation of the orange/red product, which was isolated by filtration and washed with cold MeOH (5 mL) (411 mg, 60%). mp dec. > 230 °C; UV – vis \( \lambda_{max} \) (CHCl\(_3\)) nm 498 (11, 199 000), 456 (4); \( \delta_{H} \) (200 MHz; CDCl\(_3\)) 1.39 (3H, t, J = 7.6), 2.10 (3H, s), 2.20 (3H, s), 2.62 (2H, s), 2.73 (2H, q, J = 7.6), 3.60 (1H, s), 7.17 (1H, s), 13.07 (1H, br s), 13.32 (1H, br s); \( \delta_{C} \) (75 MHz; CDCl\(_3\)) 19.88 (CH\(_3\)), 10.71 (CH\(_3\)), 13.47 (CH\(_3\)), 16.21 (CH\(_2\)), 18.42 (CH\(_3\)), 15.95 (CH\(_3\)), 120.91 (CH\(_3\)), 124.39, 125.25, 126.27, 126.83, 141.06 (CH\(_3\)), 142.97, 148.53, 155.45; m/z E I 440 (M – 2HBr)\(^+$), 67); found M\(^+\), 440.2934, C\(_{29}\)H\(_{36}\)N\(_4\) requires 440.2940.

Copper, Bis[13,3′-(methanediyl)bis[5-[(3-ethyl-4-methyl-2H-pyrrolyl-2-yldiene-κN)methyl]-2,4-dimethyl-1H-pyrroloynitroso-kN]](2-)[di- (29). Following the general procedure for ligand 2 (60 mg, 0.10 mmol) in CHCl\(_3\) (1 mL) was reacted with Cu(OAc\(_2\)) \( \cdot \)H\(_2\)O (100 mg, 0.50 mmol) and NaOAc-3H\(_2\)O (68 mg, 0.50 mmol) in MeOH (1 mL). Workup as for 17 gave the title compound as a metallic green powder (43 mg, 86%); mp dec. > 230 °C; UV – vis \( \lambda_{max} \) (CHCl\(_3\))nm 520 (very broad, 5, \( \epsilon \) 57 000), 494 (4); m/z E I 1004 (M\(^+\), 67), 502 (M\(^+\)\(_2\)), 1; found M\(^+\), 1004.4149 C\(_{58}\)H\(_{68}\)N\(_8\)Cu\(_2\) requires 1004.4141.

**Figure 3.** Schematic formation of dinuclear complex 17 from ligand 2 and Zn\(^{II}\).
a drop in reaction mixture temperature was no longer observed upon addition. The solution was allowed to cool significantly and then poured onto a 1:1 mixture of MeOH/water (20 mL) and extracted with CH₂Cl₂; the organic fractions were then back-extracted with water (3 × 20 mL). The resulting organic fraction was dried over MgSO₄ and filtered, and the solvent was removed in vacuo to give the crude product. Purification by recrystallization from CH₂Cl₂/hexane gave clean crystals of the desired compound as needles: mp > 230 °C; 7876.454; EI 484 (85); found M⁺ 484.2375. Anal. Calcd for C₅₆H₆₀N₄O₂: C, 74.27; H, 6.84; N, 6.00. Found: C, 74.27; H, 6.84; N, 6.00.

1H-Pyrrole, 3,3-(1H,3-ethylpyrrol-2-ylidene)-2,4-dimethyl-1H-pyrrole-2-carboxylate (14). Following the general procedure as for 1, a solution of pyrrole 14 (100 mg, 0.21 mmol) in THF (10 mL) and NET₃ (1 drop), with catalyst 10% Pd/C (10 mg) was exposed to 1.0 atm hydrogen for 3 h. Workup as before was followed by the addition of 3-ethyl-2-formyl-4-methylpyrrole (439 mg, 3.20 mmol) and then poured onto a 1:1 mixture of MeOH/water (20 mL). The resulting organic fraction was dried over MgSO₄ and filtered, and the solvent was removed in vacuo to give the crude product. Purification was achieved via chromatography on silica gel eluting with gradient 25:75 to 35:65 ethyl acetate/hexane, to give the title product as a white powder (783 mg, 85%): mp 196–198 °C; δH (200 MHz; CDCl₃) 1.27–1.40 (6H, m), 2.21 (3H, s), 2.27 (3H, s), 2.48 (3H, s), 2.54 (3H, s), 2.69–2.90 (4H, m), 4.21–4.38 (4H, m), 8.52 (1H, br s), 8.85 (1H, br s); δC (75 MHz; CDCl₃) 10.67, 11.49, 12.79, 14.42, 16.36, 19.59, 21.83, 23.78, 26.15, 26.18, 28.21, 28.38, 123.33, 126.98, 129.05, 129.82, 138.05, 161.81, 197.54; m/z EI 388 (M⁺, 62); found M⁺, 388.200. Anal. Calcd for C₂₁H₂₇N₂O₂: C, 64.93; H, 7.27; N, 7.21. Found: C, 64.91; H, 7.28; N, 7.51.

4,4-(1,3-Propenediyl)bis[3,5-dimethylbis(phenylmethyl)ester]-1H-pyrrole-2-carboxylate (15). Following the procedure as for 13, a solution of pyrrole 15 (200 mg, 0.52 mmol) was dissolved in a mixture of THF (2 mL) and ethyl acetate (2 mL), and NaBH₄ (40 mg, 1.04 mmol) and 2H2O (132 µL, 1.04 mmol) were added. After being stirred at room temperature for 30 min, the excess reagent was quenched by the addition of acetic acid (1 mL) and water (10 mL). Removal of the organic solvents in vacuo, addition of CH₂Cl₂ (10 mL), separation of the organic layer, drying over MgSO₄, filtration, and removal of the solvent in vacuo gave the crude product, which was purified by recrystallization from CH₂Cl₂/hexane to give the title pyrrole 15 as a light brown powder (793 mg, 94%): 221–236 °C; δH (200 MHz; CDCl₃) 1.33 (3H, t, j = 7.9), 2.15 (3H, s), 2.22 (3H, s), 2.29–2.41 (4H, m), 4.28 (2H, q, j = 7.9), 8.67 (1H, br s); δC (75 MHz; CDCl₃) 10.54, 11.45, 14.56, 23.80, 31.72, 59.56, 116.70, 121.86, 129.67, 129.39, 161.75; m/z EI 374 (M⁺, 48); found M⁺, 374.2001. Anal. Calcd for C₂₁H₂₇N₂O₂: C, 67.35; H, 8.07; N, 7.48. Found: C, 66.97; H, 8.07; N, 7.35.

4,4-(1,2-Propenediyl)bis[3,3,5-dimethylbis(phenylmethyl)ester]-1H-pyrrole-2-carboxylate (16). Following the procedure as for 15, a solution of dihydrobromide (4) (200 mg, 0.51 mmol) in 2HCl (1 mL) was refluxed with oxalyl chloride (566 mg, 2.37 mmol) for 1 h. Following the procedure as described for the preparation of dihydrobromide (4), the title compound was isolated and benzylated. Workup and recrystallization as described for X gave white crystals of 16 (250 mg, 94%): mp 204–205 °C; δH (200 MHz; d6-DMSO) 2.13–2.54 (1H, m), 2.10 (3H, s), 2.12 (3H, s), 2.21–2.36 (2H, m), 5.24 (2H, s), 7.29–7.48 (5H, m), 11.10 (1H, br s); δC (75 MHz; d6-DMSO) 10.53, 10.87, 23.33, 31.58, 64.19, 115.36, 120.99, 126.24, 127.64, 128.39, 130.68, 137.09, 160.50; m/z EI 498 (M⁺, 25); found M⁺, 498.2510. Anal. Calcd for C₂₃H₂₇N₂O₂: C, 74.67; H, 6.87; N, 5.62. Found: C, 74.79; H, 6.99; N, 5.70.

1H-Pyrrole, 3,3-(1H,3-ethylpyrrol-2-ylidene)-2,4-dimethyl-1H-pyrrole-2-carboxylate (17). Following the general procedure as for pyrrole 14, dihydrobromide (4) (200 mg, 0.51 mmol) was benzylated. Workup and recrystallization as described for 17 gave the product as a dark red/brown powder (866 mg, 94%): mp 230 °C; UV–vis (CH₂Cl₂) λmax (75 MHz; CDCl₃) 193 000, 458 (3); found M⁺ 943.4420; C, 60H72N864Zn68Zn 94, 458 (5); 194 000, 484 (6); found M⁺ 943.4420; C, 60H72N864Zn68Zn 94, 458 (3).
1.97 (3H, s), 2.18 (3H, s), 2.19–2.25 (2H, m), 2.64 (2H, q, J = 7.6), 6.80 (1H, s), 7.04 (1H, s); δC(75 MHz; CDCl₃) 10.12 (2CH₃),
14.82 (CH₃), 16.67 (CH₃), 18.24 (CH₃), 23.45 (CH₂), 31.27 (CH₂),
122.15 (CH), 122.76, 129.02, 135.78, 136.91, 138.53, 141.95,
146.10 (CH), 159.41; m/z El 1064 (M⁺, 100), 532, (M²⁺ , 65);
found M⁺, 1064.4686, C₆₂H₇₆N₈Zn₂ requires 1064.4733.

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Supporting Information Available: Full X-ray crystallographic data and ORTEP diagrams for 17–19
 and 24. Experimental data for ligands 5–7 and complexes 20–22 and
 26–28. This material is available free of charge via the Internet at http://pubs.acs.org.

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