Double-Helical Dinuclear Bis(dipyrromethene) Complexes Formed by Self-Assembly

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Bis(dipyrromethene) ligands linked by an alkyl spacer between β and β' positions are shown to give helical dimers or monomers, dependent upon the length of the alkyl linker, upon complexation. Ligands consisting of methylene, ethylene, and propylene linkers $-(CH_2)_n-$ ($n = 1$, 2, and 3) give helical dimers, while longer linking chains ($n = 4$, 5, or 6) give monomers or mixtures of dimers and monomers. X-ray crystal structures of the dimeric zinc complexes ($n = 1$, 2, and 3) reveal that the angles between dipyrromethene planes and the extent of helicity in the complexes differ as the length of the linker varies. The extent of helicity was assessed and found to be dependent upon the length and, specifically, the conformational preferences of the alkyl spacer unit. The presence of an ethylene linker gave complexes of greatest helicity. The use of a methylene spacer gave less helical structures upon complexation, while propylene spacers gave only slightly helical complexes. Our studies identify the crucial importance that the conformational preferences of the β-β' alkyl spacer group plays in the coordination algorithm of self-assembly to form dipyrromethene based complexes.

The preparation of supramolecular structures by self-assembly is a subject of much current interest as an approach to materials with novel physicochemical properties.[1] This strategy takes its lead from nature which typically 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.[2] There are many reported examples of coordination of metal ions by polybipyridine ligands to generate interesting two and three-dimensional arrays including rods,[3] grids,[4] cages,[5] helices,[6] ladders,[7] and rings.[8] Bipyridines are neutral ligands, which produce charged complexes upon coordination to metals at any oxidation state (> M^0). 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.[9] 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.[10] Porphyrins

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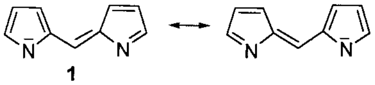
are useful ligands for complexation reactions since they generate resonance stabilized dianions which readily coordinate to metal ions to give metalloporphyrins. However, the difficulties often encountered in the preparation of functionalized porphyrins and the structural limitations of the tetra-pyrrolic 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.[11] 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.



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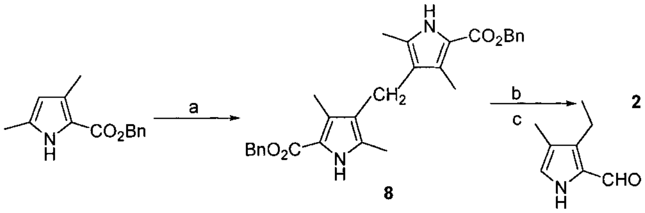
The dipyrromethene unit **1** is a fully conjugated flat monoanionic ligand, useful in metal chelation reactions.[12] Consequently, dipyrromethene moieties linked by a bridging unit are useful as ligands for the formation of well-defined architectures through self-assembly. Fuhrop et al. reported that 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 as a dinuclear helix.[13] Similarly, the X-ray structure of 1,2,3,7,8,12,13,17,18,19-decamethylbiladiene-*a,c* revealed a helical structure.[14] As part of our ongoing studies to investigate the use of bis(dipyrromethene) ligands in self-assembly strategies we have recently shown that ligands consisting of two dipyrromethene units linked at the α- or β-positions generate either trinuclear, dinuclear, or mononuclear helical structures upon complexation,[11] depending upon the exact structure of the dipyrromethene ligands used. This followed original work by one of us in 1965 which suggested that a 2:2 bis(dipyrromethene) ligand/Co^{II} complex existed in a helical conformation.[15] The purpose of our current study is to investigate the effects of varying length of spacer between β-linked dipyrromethene units upon the structure of resultant complexes and determine the factors dominant in the coordination algorithm operating during self-assembly.

Scheme 1[a]



[a] Key: (a) HCHO (aq), MeOH, HCl (concd), 90%; (b) H_2, Pd/C, THF, Et_3N; (c) HBr (aq), MeOH, 60% over two steps.

Ligands **2**−**7**[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.[11]

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 **3**−**4** were prepared as shown in Scheme 2.[16] 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 CH_2Cl_2 catalyzed by $SnCl_4$ under carefully controlled conditions gave the required intermediate **11**. Work up was achieved by addition of 10% $NaHSO_3$, since aqueous HCl, NaOH or neutral workup gave homologated coupling products. It is unclear why workup using $NaHSO_3$ solution is so successful. Reduction, debenzylation 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.[16]

The ligands were each reacted with excess Zn^{II} and Co^{II} in the presence of NaOAc, as described in the Experimental Section and shown in Scheme 3. Ligand **2** was also reacted with Cu^{II}. 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 λ_{max} 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 CH_2Cl_2 or $CHCl_3$ were stable for >6 months in the dark, but very slow photobleaching was observed

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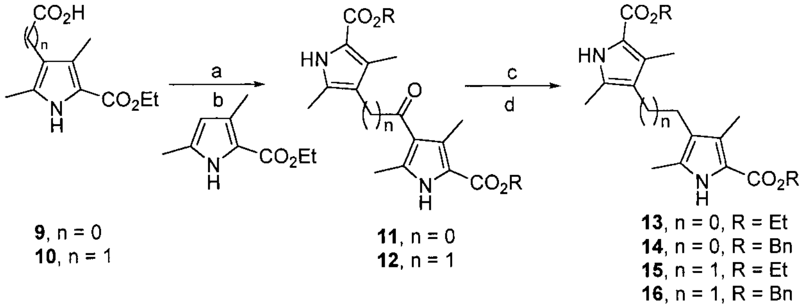
Scheme 2[a]



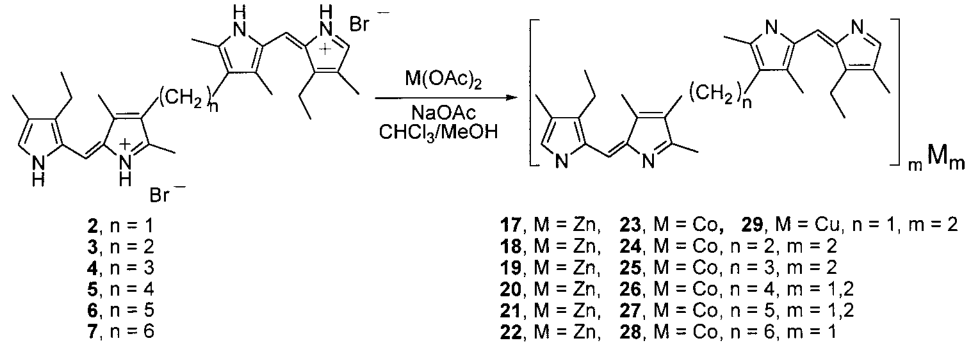
9, n = 0
10, n = 1

11, n = 0
12, n = 1

13, n = 0, R = Et
14, n = 0, R = Bn
15, n = 1, R = Et
16, n = 1, R = Bn

[a] Key: (a) ClC(O)Cl, reflux; (b) CH_2Cl_2, $SnCl_4$, 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%, $n = 1$.

Scheme 3



2, n = 1
3, n = 2
4, n = 3
5, n = 4
6, n = 5
7, n = 6

17, M = Zn, **23**, M = Co, **29**, M = Cu, n = 1, m = 2
18, M = Zn, **24**, M = Co, n = 2, m = 2
19, M = Zn, **25**, M = Co, n = 3, m = 2
20, M = Zn, **26**, M = Co, n = 4, m = 1,2
21, M = Zn, **27**, M = Co, n = 5, m = 1,2
22, M = Zn, **28**, M = Co, n = 6, m = 1

Table 1. Oligomeric Ratios of Zn^{II} Complexes

ligand	n	product(s)	mononuclear/ dinuclear[a]
2	1	**17**	0:1
3	2	**18**	0:1[b]
4	3	**19**	0:1
5	4	**20**	1:2
6	5	**21**	2:1
7	6	**22**	1:0[c]

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

to occur over a period of several weeks if the solutions were left exposed to light.

Analysis of the complexes, primarily by EI mass spectrometry, revealed that both dinuclear and mononuclear complexes had been produced. The results for Zn^{II} complexation reactions are given in Table 1. Practically identical results were obtained for compounds obtained from Co^{II} complexation. Table 1 shows that as the length of the spacer unit increases, so the formation of the mononuclear complex becomes favored. Presumably, this arises since the longer spacers are sufficiently flexible to allow the two dipyrromethene units within one ligand to fold around a single metal ion to generate a mononuclear product. Shorter chain lengths are incapable of such folding and instead give dinuclear complexes. We have previously reported that mononuclear complexes were generated using ligands with octylene and docecylene alkyl spacers.[11] In each case, the coordination algorithm operates during self-assembly such as to satisfy both the coordination geometry requirements of the metal ion and the conformational preferences of the ligand. In similar studies using MALDI spectrometry, higher order oligomers were also observed.[11] It is unclear whether the 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 oligomers 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** and **24** 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 crystal structures and compare the conformations adopted by the complexes as the length of the alkyl spacing group is increased.[17] In **17** and **19** disordered single molecules of CH_2Cl_2 and $CHCl_3$ respectively reside within the asymmetric unit, but this does not detract from our studies involving bulk structural comparison

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(17) Crystal data for **17**, $C_{59}H_{69}N_8Zn_2Cl_3$, 1125.35: red platelet, primitive triclinic, space group $P\bar{1}$ (#2), $a = 11.898(3)$ Å, $b = 14.766(3)$ Å, $c = 17.601(3)$ Å, $\alpha = 79.838(4)°$, $\beta = 74.264(2)°$, $\gamma = 79.171(2)°$, $V = 2897.5(9)$ Å^3, $Z = 2$, $T = -100$ °C, $2\theta_{max} = 50.2°$, Rigaku/ADSC CCD diffractometer, Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), R (on F, 7294 reflections with $I > 3\sigma(I)$) = 0.080, R_w (on F^2, all 9636 unique reflections) = 0.181, gof (F^2) = 1.87, 641 variables. Crystal data for **18**, $C_{60}H_{72}N_8Zn_2$, 1036.04: green platelet, C-centred monoclinic, space group $C2/c$ (#15), $a = 11.6977(7)$ Å, $b = 22.059(7)$ Å, $c = 21.994(1)$ Å, $\beta = 100.302(2)°$, $V = 5584(1)$ Å^3, $Z = 4$, $T = -93$ °C, $2\theta_{max} = 57.0°$, Rigaku/ADSC CCD diffractometer, Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), R (on F, $I > 3.00\sigma(I)$) = 0.048, R_w (on F, $I > 3.00\sigma(I)$, 2457 reflections) = 0.048, gof = 2.39, 316 variables. Crystal data for **24**, $C_{60}H_{72}N_8Co_2$, 1023.15: red-brown platelet, C-centred monoclinic, space group $C2/c$ (#15), $a = 11.630(1)$ Å, $b = 22.058(2)$ Å, $c = 21.949(2)$ Å, $\beta = 101.022(4)°$, $V = 5526.7(9)$ Å^3, $Z = 4$, $T = -93$ °C, $2\theta_{max} = 50.5°$, Rigaku/ADSC CCD diffractometer, Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), R (on F, 1920 reflections with $I > 3\sigma(I)$) = 0.063, R_w (on F^2, all 7159 unique reflections) = 0.181, gof (F^2) = 0.97, 316 variables. Crystal data for **19**, $C_{64}H_{78}N_8Zn_2Cl_6$, 1302.85: red block crystal, primitive monoclinic, space group $P2_1/a$ (#14), $a = 7.6470(9)$ Å, $b = 34.305(5)$ Å, $c = 12.577(3)$ Å, $\beta = 89.851(3)°$, $V = 3299.3(8)$ Å^3, $Z = 2$, $T = -100$ °C, $2\theta_{max} = 50.5°$, Rigaku/ADSC CCD diffractometer, Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), R (on F, 2197 reflections with $I > 3\sigma(I)$) = 0.072, R_w (on F^2, all 9671 unique reflections) = 0.186, gof (F^2) = 1.27, 357 variables.

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

complex	N(1)−N(4) (Å)	N(2)−N(3) (Å)	Zn(1)−Zn(2) (Å)
17	10.76	5.85	8.17
18	9.12	4.98	6.63[a]
19	13.46	8.78	11.29[a]
24	8.97	4.95	6.54[b]

[a] Zn(1)−Zn(1)* (Å) value. [b] Co(1)−Co(2)* (Å) value.

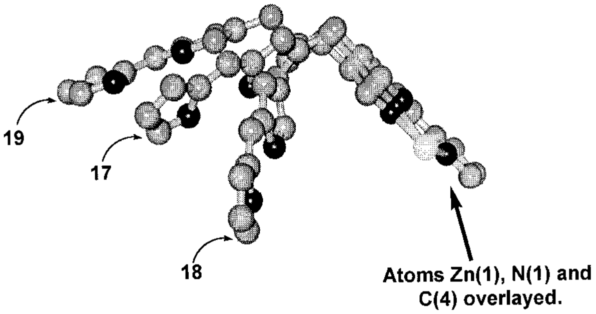

Figure 1. One ligand plus zinc taken from crystal structures of **17**, **18**, and **19** and atoms Zn(1), N(1), and C(4) overlayed using HyperChem.

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 (5) 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 Zn^{II}, 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 view[18] of one ligand plus Zn^{II} 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 Zn^{II} centers.

The β,β'-methylene linkage between the two dipyrromethene binding units in **17** has limited conformational possibilities since sp^3 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 pyrrolato 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 Zn^{II} complexes were also analyzed by ^1H and ^{13}C 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 complexes[20] and reveal interesting features which support the presence of helical structures in solution. Experi-

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(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−C(6) for **18**. Equivalent measurements for **17** and **19** were calculated using the improper torsion angle for atoms N4−C(16)−N(2)−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.

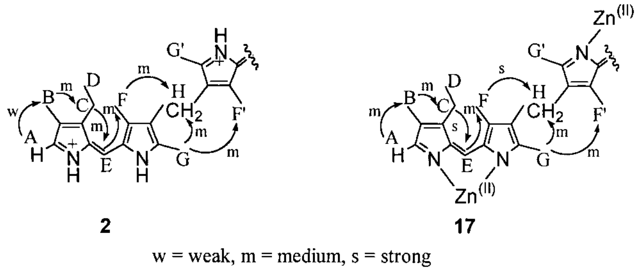

Figure 2. NOE correlations for **2** and **17**.

Table 3. ^{1}H NMR Signal Assignments for 2 and 17

signal	**2** δ (ppm)	**17** δ (ppm)
A	7.60	7.06
B	2.10	1.97
C	2.73	2.61
D	1.19	1.15
E	7.17	6.93
F	2.20	2.18
G	2.62	1.38
H	3.60	3.36

ments showed that complexation of **2** to form **17** gave rise to upfield shifts for all ^{1}H signals. As expected, the α-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 $-CH_3^G$ 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.[6] Interestingly, CH_3G-CH_3F' 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.[21] 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 $Zn(OAc)_2{\cdot}2H_2O$ under standard conditions. After 30 min, 0.5 equiv of of $Co(OAc)_2{\cdot}4H_2O$ 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 $Zn(OAc)_2{\cdot}2H_2O$ and 0.5 equiv of $Co(OAc)_2{\cdot}4H_2O$ 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 $Co(OAc)_2{\cdot}4H_2O$ in CH_3Cl/MeOH for 3 h. Similary, the Co:Co dinuclear complex was refluxed with 10.0 equiv of $Zn(OAc)_2{\cdot}2H_2O$ 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 $k_2 \gg k_{-2}$.

In summary, we have prepared a series of dipyrromethene based Zn^{II} and Co^{II} complexes of helical dinuclear and mononuclear architecture. The conformation 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 β-β' 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]-1*H*-pyrrole-2-carboxylate (8).[16] To a solution of benzyl 2,4-dimethylpyrrole-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; δ_H(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^+, 68); found M^+, 470.2212, $C_{29}H_{30}N_2O_4$ requires 470.2206. Anal. Calcd for $C_{29}H_{30}N_2O_4$: C, 74.04; H, 6.38; N, 5.96. Found: C, 73.92; H, 6.42; N, 6.10.

3,3′-(Methanediyl)bis[2,4-dimethyl-5-[(3-ethyl-4-methyl-2*H*-pyrrol-2-ylidene)methyl]-, Dihydrobromide 1*H*-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 1.0 atm of hydrogen for 14 h, whereby all the starting material was seen to have dissolved and TLC indicated the absence of

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(20) Thompson, A.; Dolphin, D. Nuclear Magnetic Resonance Studies of Helical Dipyrromethene-Zinc Complexes. *Org. Lett.* **2000**, 1315−1318.

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

(22) Robinson, J. A.; McDonald, E.; Battersby, A. R. *J. Chem. Soc.* **1985**, 1699−1709.

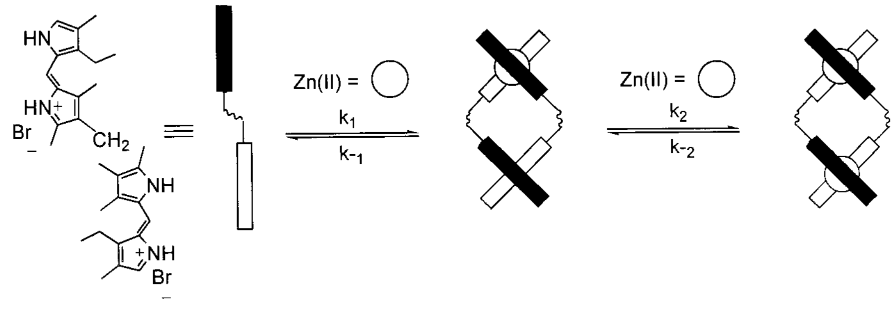

Figure 3. Schematic formation of dinuclear complex **17** from ligand **2** and Zn^{II}.

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 λ_{max}(CH_2Cl_2)/nm 498 (11, ϵ 199 000), 456 (4); δ_H(200 MHz; $CDCl_3$) 1.19 (3H, t, J = 7.6), 2.10 (3H, s), 2.20 (3H, s), 2.62 (3H, s), 2.73 (2H, q, J = 7.6), 3.60 (1H, s), 7.17 (1H, s), 7.60 (1H, s), 13.07 (1H, br s), 13.32 (1H, br s); δ_C(75 MHz; $CDCl_3$) 9.98 (CH_3), 10.71 (CH_3), 13.47 (CH_3), 16.21 (CH_3), 18.42 (CH_2), 19.59 (CH_2), 120.91 (CH), 124.39, 125.25, 126.27, 126.83, 141.06 (CH), 142.97, 148.53, 155.45; m/z EI 440 (M − 2HBr)$^+$, 67); found M$^+$, 440.2934, $C_{29}H_{36}N_4$ requires 440.2940. Anal. Calcd for $C_{29}H_{38}N_4Br_2$: C, 57.82; H, 6.36; N, 9.30. Found: C, 57.54; H, 6.33; N, 9.04.

Zinc, Bis[*m*-[[3,3′-(methanediyl)bis[5-[(3-ethyl-4-methyl-2*H*-pyrrol-2-ylidene-kN)methyl]-2,4-dimethyl-1*H*-pyrrolato-kN]](2-)]]di- (17). To a stirred solution of ligand **2** (100 mg, 0.17 mmol) in $CHCl_3$ (1 mL) at room temperature was added a solution of $Zn(OAc)_2{\cdot}2H_2O$ (182 mg, 0.83 mmol) and $NaOAc{\cdot}3H_2O$ (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_2Cl_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_2Cl_2 and then 1:10 MeOH/CH_2Cl_2 and removal of the solvents in vacuo gave the title compound as an orange powder with a green metallic luster (80 mg, 96%): mp dec >230 °C; UV−vis λ_{max}(CH_2Cl_2)/nm 522 (11, ϵ 220 000), 474 (4); δ_H(400 MHz; $CDCl_3$) 1.15 (3H, t, J = 7.6), 1.38 (3H, s), 1.97 (3H, s), 2.18 (3H, s), 2.61 (2H, q, J = 7.6), 3.36 (1H, s), 6.93 (1H, s), 7.06 (1H, s); δ_C(75 MHz; $CDCl_3$) 9.88 (CH_3), 10.00 (CH_3), 15.23 (CH_3), 16.50 (CH_3), 18.07 (CH_2), 20.44 (CH_2), 122.09 (CH), 122.78, 126.81, 135.77, 136.60, 138.02, 142.03, 146.03, (CH), 160.17; m/z EI 1008 (M$^+$, 100), 504 (M^{2+}, 22); found M$^+$, 1008.4102, $C_{58}H_{68}N_8{}^{64}Zn^{68}Zn$ requires 1008.4107. Anal. Calcd for $C_{58}H_{68}N_8Zn_2{\cdot}1.5H_2O$: C, 67.63; H, 6.46; N, 10.88. Found: C, 67.32; H, 6.61; N, 10.73.

Cobalt, Bis[*m*-[[3,3′-(methanediyl)bis[5-[(3-ethyl-4-methyl-2*H*-pyrrol-2-ylidene-kN)methyl]-2,4-dimethyl-1*H*-pyrrolato-kN]](2-)]]di- (23). Following the general procedure as for **17**, ligand **2** (100 mg, 0.17 mmol) in $CHCl_3$ (1 mL) was reacted with $Co(OAc)_2{\cdot}4H_2O$ (207 mg, 0.83 mmol) and $NaOAc{\cdot}3H_2O$ (113 mg, 0.83 mmol) in MeOH (1 mL). Workup as for **17**, followed by filtration through a short plug of basic alumina eluting with CH_2Cl_2 and then 1:10 MeOH/CH_2Cl_2 followed by removal of the solvents in vacuo, gave the title compound as a metallic green powder (64 mg, 78%): mp dec >230 °C; UV−vis λ_{max}(CH_2Cl_2)/nm 522 (11, ϵ 188 000), 488 (5); m/z EI 994 (M$^+$, 100), 497 (M^{2+}, 18); found M$^+$, 994.4200 $C_{58}H_{68}N_8Co_2$ requires 994.4231.

Copper, Bis[*m*-[[3,3′-(methanediyl)bis[5-[(3-ethyl-4-methyl-2*H*-pyrrol-2-ylidene-kN)methyl]-2,4-dimethyl-1*H*-pyrrolato-kN]](2-)]]di- (29). Following the general procedure as for **17**, ligand **2** (60 mg, 0.10 mmol) in $CHCl_3$ (1 mL) was reacted with $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 0.50 mmol) and $NaOAc{\cdot}3H_2O$ (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 λ_{max}(CH_2Cl_2)/nm 520 (very broad, 5, ϵ 57 000), 494 (4); m/z EI 1004 (M$^+$, 67), 502 (M^{2+}, 1); found M$^+$, 1004.4149 $C_{58}H_{68}N_8 63Cu^{65}Cu$ requires 1004.4141.

4,4′-[2-Oxo-(1,2-ethanediyl)]bis[3,5-dimethylbis(ethyl)ester]-1*H*-pyrrole-2-carboxylate (11). Oxalyl chloride (3 mL) was added to pyrrole **9** (300 mg, 1.33 mL) and the reaction mixture refluxed for 2 h, after which time all of the starting material pyrrole had dissolved and effervescence was no longer apparent. The oxalyl chloride was removed in vacuo and any remaining traces of oxalyl chloride removed by successive addition and removal in vacuo of $CHCl_3$ (3 × 10 mL). The resulting crude acid chloride and ethyl-2,4-dimethylpyrrole carboxylate[36] (223 mg, 1.33 mmol) were dissolved in dry CH_2Cl_2 (4 mL) under N_2 and cooled to 0 °C. $SnCl_4$ (312 μL, 1.33 mmol) was then added dropwise. After 15 min, the dark red reaction mixture was poured onto a solution of 10% $NaHSO_3$ (30 mL), stirred for 15 min, and then extracted with CH_2Cl_2. The resultant solution was dried over $MgSO_4$, filtered and the solvent removed in vacuo. Purification was achieved by chromatography on silica gel eluting with 3:7 ethyl acetate/hexane to give the title product as a white powder (109 mg, 22%, 83% based on recovered ethyl-2,4-dimethylpyrrole carboxylate): mp 212−214 °C; δ_H(200 MHz; $CDCl_3$) 1.27−1.42 (6H, m), 2.16 (3H, s), 2.18 (3H, s), 2.51 (3H, s), 2.64 (3H, s), 3.79 (2H, s), 4.21−4.42 (4H, m), 8.69 (1H, br s), 9.05 (1H, br s); δ_c(75 MHz; $CDCl_3$) 10.85, 11.73, 12.99, 14.45, 14.57, 15.16, 38.37, 59.63, 60.43, 115.23, 117.14, 118.03, 123.39, 127.66, 128.88, 130.83, 138.10, 161.75, 195.10; m/z EI 374 (M$^+$, 13); found M$^+$, 374.1848; $C_{20}H_{26}N_2O_5$ requires 374.1842. Anal. Calcd for $C_{20}H_{26}N_2O_5$: C, 64.15; H, 7.00; N, 7.48. Found: C, 64.12; H, 7.01; N, 7.38.

4,4′-(1,2-Ethanediyl)bis[3,5-dimethylbis(ethyl)ester]-1*H*-pyrrole-2-carboxylate (13). To a suspension of bipyrrole **11** (400 mg, 1.07 mmol) under N_2 in THF (50 mL) and ethyl acetate (50 mL) was added $NaBH_4$ (65 mg, 1.71 mmol). $BF_3{\cdot}OEt_2$ (217 μL, 1.71 mmol) was then added dropwise. After 12 h at room temperature, much of the starting material was seen to remain undissolved. Nevertheless, the excess reagent was quenched by the cautious addition of acetic acid (1 mL) followed by water (20 mL). Removal of the organic solvents in vacuo, addition of CH_2Cl_2 (20 mL), separation of the organic layer, drying over $MgSO_4$, filtration, and removal of the solvent in vacuo gave the crude product, which was purified by chromatography on silica gel eluting with gradient 15:85 to 25:75 ethyl acetate:hexane (87 mg, 23%, 84% based on recovered starting material): mp > 230 °C; δ_H(200 MHz; $CDCl_3$) 1.33 (3H, t, J = 7.8), 1.92 (3H, s), 2.19 (3H, s), 2.44 (2H, s), 4.28 (2H, q, J = 7.8), 8.45 (1H, br s); δ_c(75 MHz; $CDCl_3$) 10.31, 11.01, 14.56, 24.82, 59.58, 116.54, 121.26, 127.33, 129.84; m/z EI 360 (M$^+$, 14); found M$^+$, 360.2049, $C_{20}H_{28}N_2O_4$ requires 360.2049)=. Anal. Calcd for $C_{20}H_{28}N_2O_4$: C, 66.64; H, 7.83; N, 7.77. Found: C, 66.70; H, 7.76; N, 7.74.

4,4′-(1,2-Ethanediyl)bis[3,5-dimethyl-bis(phenylmethyl)-ester]-1*H*-pyrrole-2-carboxylate (14).[16] To a solution of bipyrrole **13** (200 mg, 0.56 mmol) in BnOH (3 mL) at 209 °C was added a concentrated solution of BnONa in BnOH until 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 CH_2Cl_2; the organic fractions were then back-extracted with water (3 × 20 mL). The resulting organic fraction was dried over $MgSO_4$ and filtered, and the solvent was removed in vacuo to give the crude product. Purification by recrystallization from CH_2Cl_2/hexane gave the desired compound as white needles (253 mg, 95%): mp > 230 °C; δ_H(200 MHz; d_6-DMSO) 1.91 (3H, s), 2.11 (3H, s), 2.36 (2H, s), 5.24 (2H, s), 7.27−7.48 (5H, m), 11.07 (1H, br s); δ_C(75 MHz; d_6-DMSO) 10.30, 10.45, 24.60, 64.22, 115.19, 120.55, 126.68, 127.62, 127.77, 128.45, 131.26, 137.14, 160.55; *m/z* EI 484 (85); found M^+, 484.2357, $C_{30}H_{32}N_2O_4$ requires 484.2362. Anal. Calcd for $C_{30}H_{32}N_2O_4$: C, 74.36; H, 6.66; N, 5.78. Found: C, 74.27; H, 6.84; N, 6.00.

1*H*-Pyrrole, 3,3′-(1,2-Ethanediyl)bis[2,4-dimethyl-5-[(3-ethyl-4-methyl-2*H*-pyrrol-2-ylidene)methyl]-, Dihydrobromide (3). Following the procedure as for **2**, a solution of bipyrrole **14** (100 mg, 0.21 mmol) in THF (10 mL) and NEt_3 (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 (59 mg, 0.43 mmol) and 50% HBr (200 μL) in MeOH (1 mL). Isolation as for **2** gave the product as a dark red/brown powder (118 mg, 91%): mp dec >230 °C; UV−vis λ_{max}(CH_2Cl_2)/nm 494 (5, ϵ 161 000), 458 (3); δ_H(400 MHz; $CDCl_3$) 1.17 (3H, t, *J* = 7.7), 2.08 (6H, s), 2.58 (3H, s), 2.63 (2H, s), 2.67 (2H, q, *J* = 7.7), 7.10 (1H, s), 7.58 (1H, d, *J* = 3.3), 8.14 (1H, br s), 8.29 (1H, br s); *m/z* EI 454 ($(M - 2HBr)^+$, 57), 227 ($(M - 2HBr)^{2+}$, 100); found M^+, 454.3093, $C_{30}H_{38}N_4$ requires 454.3097. Anal. Calcd for $C_{30}H_{40}N_4Br_2{\cdot}1.5H_2O$: C, 57.61; H, 6.61; N, 8.86. Found: C, 57.93; H, 6.60; N, 8.87.

Zinc, Bis[*m*-[[3,3′-1,2-ethanediyl)bis[5-[(3-ethyl-4-methyl-2*H*-pyrrol-2-ylidene-kN)methyl]-2,4-dimethyl-1*H*-pyrrolato-kN]](2-)]]di- (18). Following the general procedure as for **17**, ligand **3** (110 mg, 0.18 mmol) in $CHCl_3$ (1 mL) was reacted with $Zn(OAc)_2{\cdot}2H_2O$ (196 mg, 0.89 mmol) and $NaOAc{\cdot}3H_2O$ (121 mg, 0.89 mmol) in MeOH (1 mL). Workup as for **17**, followed by rapid chromatography on basic alumina eluting with 3:7 CH_2Cl_2/hexane, gave the title compound as an orange powder with a metallic green luster (53 mg, 57%): mp >230 °C; UV−vis λ_{max}(CH_2Cl_2)/nm 518 (11, ϵ 242 000), 470 (6); δ_H(400 MHz; $CDCl_3$) 1.12 (3H, t, *J* = 7.6), 1.35 (3H, s), 1.88 (3H, s), 2.24 (3H, s), 2.34 (1H, d *J* = 10.0), 2.57 (2H, q, *J* = 7.6), 2.73 (1H, d, *J* = 10), 6.82 (1H, s), 6.92 (1H, s); δ_C(75 MHz; $CDCl_3$) 9.96 (CH_3), 10.10 (CH_3), 14.19 (CH_3), 16.55 (CH_3), 18.12 (CH_2), 25.31 (CH_2), 121.85 (CH), 122.78, 128.52, 135.53, 136.73, 138.96, 141.67, 145.87 (CH), 159.71; *m/z* EI 1552 (2), 1036 (M^+, 94), 517 (M^{2+}, 100); found M^+, 1036.4434, $C_{60}H_{72}N_8{}^{64}Zn{}^{68}Zn$ requires 1036.4420; found M^+, (trinuclear complex) 1552.6596, $C_{90}H_{108}N_{12}{}^{64}Zn_2{}^{68}Zn$ requires 1552.6652. Anal. Calcd for $C_{60}H_{72}N_8Zn_2{\cdot}H_2O$: C, 68.37; H, 7.08; N, 10.63. Found: C, 68.50; H, 6.81; N, 10.35.

Cobalt, Bis[*m*-[[3,3′-(1,2-ethanediyl)bis[5-[(3-ethyl-4-methyl-2*H*-pyrrol-2-ylidene-kN)methyl]-2,4-dimethyl-1*H*-pyrrolato-kN]](2-)]]di- (24). Following the general procedure as for **23**, ligand **3** (100 mg, 0.16 mmol) in $CHCl_3$ (1 mL) was reacted with $Co(OAc)_2{\cdot}4H_2O$ (202 mg, 0.81 mmol) and $NaOAc{\cdot}3H_2O$ (110 mg, 0.81 mmol) in MeOH (1 mL). Workup as for **23** gave the title compound as a green metallic powder (77 mg, 94%): mp dec >230 °C; UV−vis λ_{max}(CH_2Cl_2)/nm 516 (11, ϵ 193 000), 484 (6); *m/z* EI 1022 (M^+, 100), 511 (38, M^{2+}); found M^+, 1022.4523, $C_{60}H_{72}N_8Co_2$ requires 1022.4544.

4,4′-[2-Oxo-(1,2-ethanediyl)]bis[3,5-dimethyl-bis(phenylmethyl)ester]-1*H*-pyrrole-2-carboxylate (12).[16] Following the general procedure as for the preparation of **11**, pyrrole **10** (566 mg, 2.37 mmol) was refluxed with oxalyl chloride (5 mL) for 20 min to give the crude acid chloride. Isolation as previously, followed by reaction in dry CH_2Cl_2 (6 mL) with ethyl 2,4-dimethylpyrrolecarboxylate (396 mg, 2.37 mmol) and $SnCl_4$ (555 μL, 4.74 mmol) at 0 °C gave the coupled product after 15 min, as monitored by TLC. The reaction mixture was then poured onto 2 M HCl, stirred for 20 min, and then extracted with CH_2Cl_2 (50 mL). The reaction mixture was dried over $MgSO_4$ and filtered. Purification was achieved via chromatography over 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; δ_H(200 MHz; $CDCl_3$) 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); δ_C(75 MHz; $CDCl_3$) 10.67, 11.49, 12.79, 14.42, 14.56, 15.19, 18.52, 43.39, 59.67, 60.41, 116.88, 117.94, 120.85, 123.33, 126.98, 129.05, 129.82, 138.05, 161.81, 197.54; *m/z* EI 388 (M^+, 62); found M^+, 388.2000, $C_{21}H_{28}N_2O_5$ requires 388.1998. Anal. Calcd for $C_{21}H_{28}N_2O_5$: C, 64.93; H, 7.27; N, 7.21. Found: C, 64.91; H, 7.28; N, 7511.

4,4′-(1,2-Propanediyl)bis[3,5-dimethylbis(ethyl)ester]-1*H*-pyrrole-2-carboxylate (15). Following the procedure as for **13**, bipyrrole **12** (200 mg, 0.52 mmol) was dissolved in a mixture of THF (2 mL) and ethyl acetate (2 mL), and $NaBH_4$ (40 mg, 1.04 mmol) and $BF_3{\cdot}OEt_2$ (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 CH_2Cl_2 (10 mL), separation of the organic layer, drying over $MgSO_4$, filtration, and removal of the solvents in vacuo gave the crude product, which was purified by recrystallization from CH_2Cl_2/hexane to give the title product as fine white needles (183 mg, 94%): mp 211−213 °C; δ_H(200 MHz; $CDCl_3$) 1.33 (3H, t, *J* = 7.9), 2.15 (3H, s), 2.22 (3H, s), 2.29−2.41 (3H, m), 4.28 (2H, q, *J* = 7.9), 8.67 (1H, br s); δ_c(75 MHz; $CDCl_3$) 10.54, 11.45, 14.56, 23.80, 31.72, 59.56, 116.70, 121.86, 126.97, 129.39, 161.75; *m/z* EI 374 (M, 48); found M^+, 374.2001, $C_{21}H_{30}N_2O_4$ requires 374.2206. Anal. Calcd for $C_{21}H_{30}N_2O_4$: C, 67.35; H, 8.07; N, 7.48. Found: C, 66.97; H, 8.07; N, 7.35.

4,4′-(1,2-Propanediyl)bis[3,5-dimethyl-bis(phenylmethyl)ester]-1*H*-pyrrole-2-carboxylate (16).[16] Following the procedure as for dipyrrole **14**, dipyrrole **15** (200 mg, 0.52 mmol) was benzylated. Workup and recrystallization as described for X gave white crystals of **16** (250 mg, 94%): mp 204−205 °C; δ_H(200 MHz; d_6-DMSO) 1.32−1.54 (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); δ_C(75 MHz; d_6-DMSO) 10.53, 10.87, 23.33, 31.58, 64.19, 115.36, 120.99, 126.24, 127.64, 127.74, 128.39, 130.68, 137.09, 160.50; *m/z* EI 498 (M^+, 25); found M^+, 498.2510, $C_{31}H_{34}N_2O_4$ requires 498.2519. Anal. Calcd for $C_{31}H_{34}N_2O_4$: C, 74.67; H, 6.87; N, 5.62. Found: C, 74.59; H, 6.99; N, 5.70.

1*H*-Pyrrole,3,3′-(1,3-propanediyl)bis[2,4-dimethyl-5-[(3-ethyl-4-methyl-2*H*-pyrrol-2-ylidene)methyl]-, Dihydrobromide (4). Following the procedure as for **2**, a solution of bipyrrole **16** (800 mg, 1.56 mmol) in THF (30 mL) and NEt_3 (1 drop) with catalyst 10% Pd/C (20 mg) was exposed to 1.0 atm of 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 50% HBr (1 mL) in MeOH (5 mL). Isolation as for **2** gave the product as a dark red/brown powder (866 mg, 88%): mp dec >230 °C; UV−vis λ_{max}(CH_2Cl_2)/nm 490 (11, ϵ 165 000), 460 (6); δ_H(400 MHz; $CDCl_3$) 1.38 (3H, t, *J* = 7.7), 1.53−1.64 (1H, m), 2.08 (3H, s), 2.25 (3H, s), 2.44 (2H, q, *J* = 7.7), 2.62−2.71 (5H, m), 7.13 (1H, s), 7.57 (1H, d, *J* = 3.5), 13.09 (1H, br s), 13.28 (1H, br s); δ_C(75 MHz; $CDCl_3$) 9.92 (CH_3), 10.45 (CH_3), 13.30 (CH_3), 16.22 (CH_3), 18.37 (CH_2), 23.78 (CH_2), 29.87 (CH_2), 120.60 (CH), 123.85, 125.80, 127.28, 128.87, 139.67 (CH), 143.19, 147.69, 156.58; *m/z* EI 468 ($(M - 2HBr)^+$, 12); found M^+, 468.3245, $C_{31}H_{40}N_4$ requires 468.3253. Anal. Calcd for $C_{31}H_{42}N_4Br_2{\cdot}H_2O$: C, 57.41; H, 6.84; N, 8.64. Found: C, 57.88; H, 6.54; N, 8.63.

Zinc, Bis[*m*-[[3,3′-(1,3-propanediyl)bis[5-[(3-ethyl-4-methyl-2*H*-pyrrol-2-ylidene-kN)methyl]-2,4-dimethyl-1*H*-pyrrolato-kN]](2-)]]di- (19). Following the general procedure as for **17**, ligand **4** (120 mg, 0.19 mmol) in $CHCl_3$ (1 mL) was reacted with $Zn(OAc)_2{\cdot}2H_2O$ (209 mg, 0.95 mmol) and $NaOAc{\cdot}3H_2O$ (130 mg, 0.95 mmol) in MeOH (1 mL). Workup as for **17** gave the title compound as an orange powder with a green metallic luster (112 mg, 90%): mp decomp >230 °C; UV−vis λ_{max}(CH_2Cl_2)/nm 506 (11, ϵ 240 000), 480 (6); δ_H(400 MHz; $CDCl_3$) 1.16 (3H, t, *J* = 7.6), 1.37−1.59 (1H, m), 1.61 (3H, s), 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); δ_C(75 MHz; $CDCl_3$) 10.12 (2CH$_3$), 14.82 (CH_3), 16.67 (CH_3), 18.24 (CH_2), 23.45 (CH_2), 31.27 (CH_2), 122.15 (CH), 122.76, 129.02, 135.78, 136.91, 138.53, 141.95, 146.10 (CH), 159.41; m/z EI 1064 (M^+, 100), 532, (M^{2+}, 65); found M^+, 1064.4686, $C_{62}H_{76}N_8{}^{64}Zn^{68}Zn$ requires 1064.4733. Anal. Calcd for $C_{62}H_{76}N_8Zn_2 \cdot 2H_2O \cdot 2CHCl_3$: C, 57.41; H, 6.17; N, 8.37. Found: C, 57.39; H, 5.80; N, 8.28.

Cobalt, Bis[*m*-[[3,3′-(1,3-propanediyl)bis[5-[(3-ethyl-4-methyl-2*H*-pyrrol-2-ylidene-kN)methyl]-2,4-dimethyl-1*H*-pyrrolato-kN]](2-)]]di- (25). Following the general procedure as for **23**, ligand **4** (100 mg, 0.16 mmol) in $CHCl_3$ (1 mL) was reacted with $Co(OAc)_2 \cdot 4H_2O$ (209 mg, 0.81 mmol) and $NaOAc \cdot 3H_2O$ (130 mg, 0.81 mmol) in MeOH (1 mL). Workup as for **23** gave the title compound as a metallic green powder (65 mg, 77%): mp dec >230 °C; UV−vis λ_{max}(CH_2Cl_2)/nm 512 (ϵ 210 000); m/z EI 1050 (M^+, 100), 525, (M^{2+}, 34); found M^+, 1050.4852, $C_{62}H_{76}N_8Co_2$ requires 1050.4860.

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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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