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# Metallosupramolecular Architectures Formed with Ferrocene-Linked Bis-Bidentate Ligands: Synthesis, Structures, and Electrochemical **Studies**

James A. Findlay, C. John McAdam, Joshua J. Sutton, Dan Preston, Keith C. Gordon, and James D. Crowley\*

Department of Chemistry, University of Otago, P.O. Box 56, Dunedin 9054, New Zealand

**S** Supporting Information

ABSTRACT: The self-assembly of ligands of different geometries with metal ions gives rise to metallosupramolecular architectures of differing structural types. The rotational flexibility of ferrocene allows for conformational diversity, and, as such, self-assembly processes with 1,1'-disubstituted ferrocene ligands could lead to a variety of interesting architectures. Herein, we report a small family of three bisbidentate 1,1'-disubstituted ferrocene ligands, functionalized with either 2,2'-bipyridine or 2-pyridyl-1,2,3-triazole chelating units. The self-assembly of these ligands with the (usually) fourcoordinate, diamagnetic metal ions Cu(I), Ag(I), and Pd(II) was examined using a range of techniques including <sup>1</sup>H and



DOSY NMR spectroscopies, high-resolution electrospray ionization mass spectrometry, X-ray crystallography, and density functional theory calculations. Additionally, the electrochemical properties of these redox-active metallosupramolecular assemblies were examined using cyclic voltammetry and differential pulse voltammetry. The copper(I) complexes of the 1,1'disubstituted ferrocene ligands were found to be coordination polymers, while the silver(I) and palladium(II) complexes formed discrete  $\begin{bmatrix} 1 + 1 \end{bmatrix}$  or  $\begin{bmatrix} 2 + 2 \end{bmatrix}$  metallomacrocyclic architectures.

# INTRODUCTION

The formation of self-assembled metallosupramolecular architectures has been studied extensively in the past 30 years.<sup>1</sup> The main factors determining the structures of these architectures are the coordination geometry preference of the metal ion(s) employed, the denticity of the ligands, and the length and flexibility of the linking units between binding sites on the ligands. The combination of a suitable metal ion with a rigid bridging ligand will reliably generate either macrocyclic or cage architectures. Conversely, bridging ligands with more flexibility provide less control on the outcome of the selfassembly process and can lead to mixtures or coordination polymers.<sup>2</sup> With the design principles required for the generation of discrete macrocyclic or cage architectures reasonably well understood, efforts are now focused on the development of applications for these multimetallic architectures. Indeed, metallosupramolecular systems with interesting biological,<sup>3</sup> photophysical,<sup>4</sup> and redox<sup>5</sup> properties have been generated. Recently, as part of the efforts to further enhance the potential applications of metallosupramolecular architectures, there has been considerable effort put into the development of more functionalized ligand systems<sup>6</sup> and heterometallic<sup>7</sup> complexes. Ferrocene (FcH), a well-known robust 18-electron organometallic sandwich complex,<sup>8</sup> displays several properties that potentially make it ideal for the development of both

functionalized ligands and heterometallic metallosupramolecular systems.<sup>9</sup> Ferrocene can be readily functionalized using a wide variety of standard organic transformations and will undergo reversible one-electron redox processes. These properties have been previously exploited in a range of areas including the development of electronic,<sup>10</sup> bioactive,<sup>11</sup> and stimuli-responsive materials<sup>12</sup> and redox sensors.<sup>13</sup> While a number of redox-active metallosupramolecular architectures have been generated with pendant Fc units,5,14 the self-assembly of systems that exploit ferrocene as a structural component remains rare. Presumably, the relative lack of interest in using 1,1'-disubstituted ferrocenes as components for metallosupramolecular self-assembly is connected to the rotational flexibility of ferrocene ligands (Figure 1). The multiple accessible conformers, arising from the ability of the cyclopentadienyl (cp) rings to rotate about the sandwiched Fe(II) ion, could potentially complicate the assembly process.

There are a number of reports on the exploitation of 1,1'disubstituted ferrocenes featuring monodentate heterocyclic donor groups for the assembly of both discrete metallomacrocyclic architectures and coordination polymers.<sup>15,16</sup>

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**Figure 1.** Cartoon representation of the rotational flexibility of 1,1'diaryl-substituted ferrocenes: (top) syn (stacked) conformer; (bottom) anti (open) conformer.

Of particular relevance, Lindner and co-workers have used 1,1'bis(3-pyridylethynyl)ferrocene and 1,1'-bis(4-pyridylethynyl)ferrocene to assemble discrete [2 + 2] metallomacrocycles with Ag(I), Pd(II), and Ni(II) ions.<sup>17</sup>

However, there are far fewer examples of self-assembly with 1,1'-disubstituted ferrocenes featuring bidentate ligands, where ferrocene forms an integral segment of the structure, as opposed to occupying a pendant role. Moutet and co-workers developed a family of 1,1'-disubstituted ferrocenes featuring two 2,2'-bipyridine (bipy) binding units linked to the ferrocene core via either ester or amide linkages. When these were reacted with Cu(I) ions, both a [1 + 1] metallomacrocycle<sup>18</sup> and a [2 + 2] double-stranded metallohelicate<sup>19</sup> could be observed crystallographically. Solution studies<sup>20</sup> indicated that the [1 + 1] metallomacrocycle was thermodynamically preferred at low concentrations, while the [2 + 2] double-stranded metallohelicate is the stranded metallohelicate.

Von Zelewsky and co-workers reported, in 2004, a series of bis-bidentate 1,1'-disubstituted ferrocene ligands with bipy binding pockets with appended variations of pinene groups.<sup>217</sup> Upon combination with Cu(I), Ag(I), and Zn(II) ions, the ligands all formed [2 + 2] double-stranded metallohelicates, where the metal ions each adopt a tetrahedral coordination geometry. The steric bulk of the pinene groups limits the ability of the ligand bipy groups to undergo significant  $\pi$ - $\pi$ -stacking interactions, thus promoting splaying of the binding sites and formation of the  $M_2L_2$  metallohelicate architecture. Similar results have been obtained by Wang et al.,<sup>23</sup> despite the use of more flexible linkers between the cp rings and the bidentate Schiff-base coordinating domain. In related work, Bera and coworkers have shown that 1,1'-dinaphthyridylferrocene ligands will form a variety of metallomacrocyclic complexes that react with Cu(I) or Zn(II) ions. While the 1,1'-dinaphthyridylferrocene is a bis-bidentate ligand, the lone pairs of electrons on the coordinating N atoms are parallel and thus not at ideal orientations for chelation of most metal ions. Nonetheless, interesting solid-state macrocyclic structures were reported including 1:1, 2:1, and 2:2 metal/ligand (M/L) complexes with the Cu(I) ions. Also, a  $M_4L_4$  macrocyclic architecture was formed upon the addition of 1 equiv of ZnCl<sub>2</sub>, where the "arms" of each ligand undergo  $\pi - \pi$  stacking and the two Cl ions bound to each Zn(II) ion act similarly to a bidentate capping unit,<sup>24</sup> directing formation of the discrete architecture.

As part of our long-standing interest in the use of ferrocene ligands for the development of stimuli-responsive molecular switches<sup>25–27</sup> and self-assembled metallosupramolecular archi-

tectures,<sup>28</sup> herein we examine the use of a series of 1,1'disubstituted ferrocene ligands featuring bidentate N–N metal binding domains for the generation of discrete metallosupramolecular systems and coordination polymers. The ferrocene ligands feature either two bipy units (L1), two 2pyridyl-1,2,3-triazole (pytri) units (L3), or one bipy and one pytri (L2) (Figure 2). The assemblies generated when the 1,1'-



Figure 2. 1,1'-Disubstituted ferrocene ligands L1–L3 in the folded/ stacked (syn) conformation and the model ligands L4 and L5.

disubstituted ferrocene ligands are treated with the diamagnetic Cu(I), Ag(I), or Pd(II) ions are examined using a battery of techniques including <sup>1</sup>H NMR spectroscopy, diffusion-ordered NMR spectroscopy (DOSY), high-resolution electrospray ionization mass spectrometry (HR-ESI-MS), X-ray crystallog-raphy, and density functional theory (DFT) calculations. Additionally, the electrochemical properties of the metal-losupramolecular assemblies are examined using cyclic voltammetry (CV).

### RESULTS AND DISCUSSION

**Ligand Synthesis.** We have previously reported the synthesis of L1 as part of our work on stimuli-responsive molecular actuators.<sup>26</sup> The new ligands L2 and L3 were synthesized using procedures analogous to those used to generate L1. A Pd(0)-catalyzed Sonogashira cross-coupling<sup>29</sup> in diisopropylamine between either 1,1'-diiodoferrocene<sup>30</sup> or 1-(5-ethynyl-2,2'-bipyridine)-1'-iodoferrocene<sup>25,26</sup> and 5-ethynyl-2-(1-hexyl-1H-1,2,3-triazol-4-yl)pyridine (S2) using microwave irradiation (200 W, 2 h, 100 °C) provided the ferrocene ligands in good yield (L2, 74%; L3, 64%; see the Supporting Information, SI). The model ligands L4 and L5 were generated using similar procedures (see the SI).

The new ligands (L2 and L3) were characterized using  ${}^{1}\text{H}$  and  ${}^{13}\text{C}$  NMR and IR spectroscopies, HR-ESI-MS, and elemental analysis (see the SI). It is well established that 1,1'-diarylferrocenes adopt a folded/stacked syn conformation in both solution and the solid state (Figures 1 and 2).<sup>31</sup> We

previously showed, using <sup>1</sup>H NMR spectral and X-ray diffraction evidence, along with DFT calculations, that L1 adopts the syn conformation, in both solution and the solid state, because of favorable  $\pi$ - $\pi$  interactions<sup>32</sup> between the bipy "arms".<sup>26</sup> The <sup>1</sup>H NMR spectra (Figures 3 and S9) indicate



**Figure 3.** Partially stacked <sup>1</sup>H NMR spectra (400 MHz, CD<sub>3</sub>CN, 298 K) showing 5-ethynyl-2,2'-bipyridine (top), L2 (middle), and S2 (bottom). Upfield shifts are observed for all of the proton signals, indicating that L2 predominantly forms a  $\pi$ - $\pi$ -stacked syn conformation in solution.

that, like L1, both of the new ligands L2 and L3 prefer a syn  $\pi$ - $\pi$ -stacked conformation in solution. The proton signals associated with the bipy  $(H_{c-i})$  and pytri  $(H_{l-o})$  arms of L2 and L3 were shifted upfield relative to those of the model compounds 5-ethynyl-2,2'-bipyridine and S2, indicating that the diarmed ferrocene ligands adopt a stacked (syn) conformation in solution.

**Cu(I)** Assemblies. Since the pioneering self-assembly work of Lehn and co-workers<sup>33</sup> with Cu(I) ions and bis(bipy) ligands, it has been well established that combining Cu(I) ions with flexible or bent bis-bidentate N–N ligands results in the formation of double-stranded metallohelicates,<sup>34</sup> while more rigid ligand assemblies form [4 + 4] grid complexes.<sup>35</sup> Inspired by those assemblies and with the knowledge that other ferrocene-linked bis-bidentate ligands had generated double-stranded metallohelicates with Cu(I) ions,<sup>20,21</sup> we initially examined the complexation of L1–L3 with [Cu(CH<sub>3</sub>CN)<sub>4</sub>]-(PF<sub>6</sub>).

The addition of an acetone solution of  $[Cu(CH_3CN)_4](PF_6)$ (1 equiv) to one of the ligands (L1, L2, or L3, 1 equiv) suspended in acetone at room temperature resulted in the immediate formation of deep-red (L1 and L2) or dark-orange (L3) solutions, indicative of complex formation.<sup>25,26,36,37</sup> The solutions of Cu(I) complexes were analyzed using HR-ESI-MS (performed under pseudo-cold-spray conditions) and, surprisingly, only featured ions corresponding to  $[CuL]^+$  and  $[CuL]^{2+}$ , which presumably result from the fragmentation of larger discrete or polymeric systems (see the SI). <sup>1</sup>H NMR analysis of the Cu(I) complexes in a range of common deuterated solvents of varying polarity and coordination ability resulted in very broad spectra in each case. To rule out paramagnetic broadening due to the presence of a small amount of Cu(II) (from oxidation) in the samples, the spectra were reacquired in the presence of 2 equiv of L-sodium ascorbate (a common Cu reducing agent). Essentially identical broad spectra were obtained, ruling out oxidation of the Cu ions as the cause and suggesting that the broadening is related to either a fluxional process or the presence of coordination polymers in solution (or both).

Fortunately, X-ray analysis of the Cu(I) complex of L3 was able to be performed on single crystals spawned from the slow diffusion of diethyl ether into an acetone solution. The structure obtained revealed that in the solid state the complex exists as a 1D coordination polymer,  $[Cu_n(L3)_n](PF_6)_n$  (Figure 4), which is consistent with the broad <sup>1</sup>H NMR spectra



**Figure 4.** Solid-state structure of  $[Cu_n(L3)_n](PF_6)_n$ . Selected bond lengths (Å): Cu1-N9 = 2.075(9), Cu1-N10 = 1.975(1), Cu1-N15 = 1.984(9), Cu1-N16 = 2.080(8), Cu2-N1 = 2.038(1), Cu2-N2 = 2.025(9), Cu2-N7 = 1.999(1), Cu2-N8 = 2.080(1). Color scheme: C, gray; N, purple; Fe, orange red; Cu, copper. H atoms and PF<sub>6</sub><sup>-</sup> counterions were omitted for clarity.

observed above. The coordination polymer crystallized in the monoclinic  $P2_1/c$  space group, and the asymmetric unit contains two ligands and two Cu(I) ions and two hexafluorophosphate anions. The Cu(I) ion was coordinated to two pytri units in a tetrahedral fashion ( $\tau_4 = 0.68$ ).<sup>38</sup> The Cu–N bond lengths range from 1.984(1) to 2.085(1) Å, similar to those observed for the related [Cu(Bnpytri)<sub>2</sub>](PF<sub>6</sub>) [where Bnpytri = 1-benzyl-4-(2-pyridyl)-1,2,3-triazole].<sup>39</sup> The L3 ligands maintain the syn  $\pi$ - $\pi$ -stacked conformation upon complexation, and the Fc units adopted the expected eclipsed conformation. Torsion angles  $(\tau)^{15}$  between the two pytri units of the 1,1'-disubstituted ferrocene L3, the angle between the two substituents of each cp ring, and the centroid of the cp rings, in the two crystallographically independent Fc units were  $\tau = 6.45^{\circ}$  and 14.61°. Disappointingly, X-ray-quality crystals of the Cu(I) complexes formed from L1 or L2 were not obtained. However, given that each complex displays similar solution data, it seems likely that all of the Cu(I) complexes are coordination polymers (i.e.,  $[Cu_n(L)_n](PF_6)_n)$ . While [2 + 2]double-stranded metallohelicates were obtained previously when related 1,1'-disubstituted ferrocene bis-bidentate ligands were reacted with Cu(I) ions, the formation of Cu(I) coordination polymers has been observed with more rigid bis-bidentate N-N ligands.<sup>40</sup> In order for L1–L3 to form [2 + 2] double-stranded metallohelicates with the Cu(I) ion, the ligands would need to rotate into the anti (open) conformer. Thus, we presume that coordination polymers are observed here because of the relative stability of the syn ( $\pi$ - $\pi$ -stacked) conformation of the ligands.

**Ag(I)** Assemblies. Ag(I) ions are commonly used for the generation of metallosupramolecular architectures.<sup>41</sup> However,

unlike Cu(I), the Ag(I)  $d^{10}$  ion adopts a wider variety of coordination modes and geometries. With bidentate N–N ligands, Ag(I) ions often form four-coordinate complexes; both tetrahedral<sup>41</sup> and square-planar<sup>42</sup> coordination geometries have been observed. The plasticity of the Ag(I) coordination sphere may result in the formation of different metallosupramolecular architectures with the ferrocene ligands L1–L3. Therefore, we examined the complexation of the ferrocene ligands with Ag(I) ions.

The addition of solid AgPF<sub>6</sub> (1 equiv) to a solution [2:1 (v/ v)  $CDCl_3/CD_3NO_2$  of one of the ligands (L1, L2, or L3, 1) equiv) at room temperature was monitored using <sup>1</sup>H NMR spectroscopy (400 MHz, 298 K). Unlike the Cu(I) complexes, the addition of Ag(I) ions to the ligands resulted in sharp welldefined <sup>1</sup>H NMR spectra. All of the proton resonances were shifted relative to the respective free ligands, with downfield shifts of the triazole and  $\alpha$ -pyridyl proton signals indicative of coordination of the Ag(I) ions to the bidentate ligand units (see Figures S16-S18). <sup>1</sup>H DOSY NMR experiments [500 MHz, 298 K, 2:1 (v/v) CDCl<sub>3</sub>/CD<sub>3</sub>NO<sub>2</sub>] were used to elucidate the structure of the Ag(I) complexes based on the diffusion rates. The diffusion coefficients  $(D; \times 10^{-10} \text{ m}^2 \text{ s}^{-1})$  of each of the ligands (L1, L2, or L3) and the corresponding Ag(I) complexes are presented in Table S1. For L1 and L2, the diffusion coefficients of the Ag(I) complexes (D = 6.40 and  $5.84 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) were only slightly lower than those of the corresponding ligands (D = 6.60 and  $6.26 \times 10^{-10}$  m<sup>2</sup> s<sup>-1</sup>), indicating that the relative sizes of the ligands and complexes are quite similar, consistent with the formation of  $\begin{bmatrix} 1 + 1 \end{bmatrix}$ metallomacrocyclic structures. Conversely, a larger difference in the diffusion coefficients of L3 ( $D = 5.55 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) and the corresponding Ag(I) complex ( $D = 4.72 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) was observed, suggesting the formation of a [2 + 2]metallomacrocyclic structure in this case (Figure S44). The HR-ESI-MS spectra (performed under pseudo-cold-spray conditions) of the complexes formed with L1-L3 each showed ions consistent with the  $[Ag(L)]^+$  formulation. While this was consistent with the expectation for the L1 and L2 complexes, it suggests that the Ag(I) [2 + 2] metallomacrocycle of L3 is fragmenting under the conditions of the experiment (Figures S14, S16, and S19).

X-ray-quality single crystals of the Ag(I) complex of L3 were obtained by the vapor diffusion of diethyl ether into a CHCl<sub>3</sub>/  $CH_3NO_2$  (2:1, v/v) solution of the complex. The complex crystallized in the monoclinic  $P2_1/c$  space group, and the asymmetric unit contains one ligand, one Ag(I) ion, and one hexafluorophosphate anion (see the SI). The structure data confirmed the formation of the expected  $\begin{bmatrix} 2 + 2 \end{bmatrix}$  metallomacrocycle  $[Ag_2(L3)_2](PF_6)_2$  (Figure 5). The Ag(I) ions are coordinated to two pytri units in a square-planar fashion ( $\tau_4$  = 0.083).<sup>38</sup> The Ag-N bond lengths range from 2.207(3) to 2.623(3) Å with two short and two longer bond distances. Similar, square-planar coordination modes of Ag(I) pytri complexes<sup>43,44</sup> have been observed, but tetrahedral complexes, such as  $[Ag(Bnpytri)_2](SbF_6)_1^{45}$  have also been identified. The formation of the square-planar geometry is presumably stabilized by the presence of  $\pi - \pi$  (3.665 and 3.989 Å), Ag-Ag (3.935 Å), and hydrogen-bonding [N2-H28-C28 3.599 Å (N---H) and 4.269(5) Å (N---HC); N7-H13-C13 3.324 Å (N---H) and 4.028(5) Å (N---HC)] interactions. The L3 ligands maintain the syn  $\pi$ - $\pi$ -stacked conformation upon complexation, and the Fc units adopt the expected eclipsed



**Figure 5.** Solid-state structure of  $[Ag_2(L3)_2](PF_6)_2$ . Selected bond lengths (Å): Ag1–N3 = 2.207(3), Ag1–N4 = 2.623(3), Ag1–N5 = 2.560(3), Ag1–N6 = 2.214(3). Selected bond angles (deg): N3–Ag1–N4 = 69.83(1), N4–Ag1–N6 = 106.21(1), N6–Ag1–N5 = 69.76(1), N5–Ag1–N3 = 114.35(1). Color scheme: *C*, gray; N, purple; Fe, orange; Ag, white. PF<sub>6</sub><sup>-</sup> counterions and H atoms were omitted for clarity.

conformation. The torsion angle ( $\tau$ ) between the two pytri units of the 1,1'-disubstituted ferrocene L3 is 0.59°.

Unfortunately, X-ray-quality crystals of the Ag(I) complexes formed from L1 or L2 were not obtained. However, given that each complex displays solution phase data similar to those of the corresponding Pd(II) complexes (vide infra), it seems likely that the Ag(I) complexes of L1 and L2 are the smaller entropically favored [1 + 1] metallomacrocycles. The Ag(I) ions in the [1 + 1] metallomacrocycles presumably display a distorted tetrahedral coordination geometry because this geometry would reduce unfavorable steric clashes between the  $\alpha$ -pyridyl protons of the bipy and pytri units.<sup>46</sup> Similar [1 + 1] Ag(I) metallomacrocycles have been generated using ferrocene-containing bis-bidentate Schiff-base ligands.<sup>23</sup>

**Pd(II)** Assemblies. Having observed the square-planar coordination geometry of the Ag(I) ions in the  $[Ag_2(L3)_2]$ - $(PF_6)_2$  complex, we next examined complexation of the ferrocene ligands with Pd(II) ions. Pd(II)-based self-assembled architectures<sup>47</sup> have been extensively studied, but they most commonly feature a single cis-protecting N–N chelating ligand.<sup>24</sup> It is unusual for bis-bidentate N–N ligands to be used with Pd(II) ions to generate self-assembled architectures,<sup>48</sup> although we have recently shown that bis(pytri) complexes of Pd and Pt can be used to generate metallomacrocycles.<sup>43</sup>

The addition of  $[Pd(CH_3CN)_4](BF_4)_2$  (either 0.5 or 1 equiv) to an acetonitrile solution of one of the ligands (L1-L3, 1 equiv) resulted in the instant formation of either red or deeppurple solutions, indicative of complex formation.<sup>27,37</sup> Interestingly, the behavior of the bis(bipy) ligand L1 differed from that of the pytri-containing ligands L2 and L3. The addition of  $[Pd(CH_3CN)_4](BF_4)_2$  (0.5 equiv) to an acetonitrile solution of L1 (1 equiv) resulted in a broad undefined <sup>1</sup>H NMR spectrum (Figure S31). In contrast, the addition of 1 equiv of  $[Pd(CH_3CN)_4](BF_4)_2$  to an acetonitrile solution of L1 (1 equiv) resulted in a clear sharp <sup>1</sup>H NMR spectrum consistent with complex formation (Figure S31). The HR-ESI-MS spectrum of the 1:1 Pd(II)/L1 mixture displayed two peaks at m/z 324.014 and 667.0146, consistent with the  $[Pd(L1)]^{2+}$ and  $[Pd(L1)(H_2O)(H^-)]^+$  ions,<sup>49</sup> respectively, suggesting the formation of complex with a 1:1 M/L stoichiometry (Figure S21). The <sup>1</sup>H DOSY NMR experiment [500 MHz, 298 K, 2:1 (v/v) CDCl<sub>3</sub>:CDNO<sub>2</sub>] on the 1:1 L1/Pd mixture indicated that all proton resonances of the complexes had the same

diffusion coefficient ( $D = 5.92 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ ), suggesting the clean formation of a single species. The diffusion coefficient of the 1:1 L1/Pd complex was very similar to those observed for the Ag(I) complexes of L1 or L2 (D = 6.40 and  $5.84 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ , respectively), providing further support for the [Pd(L1)](BF<sub>4</sub>)<sub>2</sub> formulation. The 1:1 M/L stoichiometry was confirmed unequivocally using X-ray diffraction analysis. Darkpurple single crystals of [Pd(L1)](BF<sub>4</sub>)<sub>2</sub> were obtained from the slow diffusion of diethyl ether into an acetonitrile solution of the Pd complex (Figure 6 and the SI). The complex



**Figure 6.** Solid-state structure of  $[Pd(L1)]^{2+}$ . Selected bond lengths (Å): Pd1–N1 = 2.065(2), Pd1–N2 = 2.032(2), Pd1–N3 = 2.019(2), Pd1–N4 = 2.070(2). Selected atom distances (Å): H10–H25 = 2.139, H1–H34 = 1.789 . Color scheme: C, gray; H, white; N, purple; Fe, orange red; Pd, dark cyan. BF<sub>4</sub><sup>-</sup> counterions and the remaining H atoms were omitted for clarity.

crystallizes in the  $P\overline{1}$  space group, with two metallocycles and four BF<sub>4</sub><sup>-</sup> counterions present in the unit cell. While the Fc unit of L1 still adopts an essentially eclipsed conformation, the bipy "arms" of the ligands are no longer stacked and have  $\tau = 46.61^{\circ}$ . Each bipy "arm" is coordinated to the Pd(II) ion in a pseudosquare-planar fashion ( $\tau_4 = 0.16$ ). The Pd–N bond lengths range from 2.019(2) to 2.070(3) Å, similar to those of other Pd(bipy) complexes.<sup>27,37,48</sup> The flexibility of the alkyne linkers, which are bent away from the normal linear geometry (angles of 170.20° and 167.13°, respectively), enables the two bipy "arms" to bind to the Pd ion in a distorted square-planar arrangement. This arrangement also reduces the steric clash between the  $\alpha$ -pyridyl protons of the adjacent bipy units (Figure 6).<sup>46,48</sup>

When either L2 or L3 were combined with 0.5 equiv of  $[Pd(CH_3CN)_4](BF_4)_2$  in acetonitrile, red solutions were obtained. Conversely, when 1 equiv of  $[Pd(CH_3CN)_4](BF_4)_2$ was added to one of the ligands (either L2 or L3, 1 equiv) in acetonitrile, deep-purple solutions were obtained. <sup>1</sup>H NMR spectra confirmed that the complexes that were formed with 0.5 equiv of Pd(II) were different from those obtained with 1 equiv of the metal ion (Figure 7 and the SI). The <sup>1</sup>H NMR spectrum of the 0.5:1 mixture of Pd(II) and L3 clearly indicated the clean formation of a single complex (Figure S28). However, two sets of pytri resonances were observed: one set shifted downfield from the positions in the "free" L3, and the other set shifted upfield. This suggested the formation of a  $[Pd(L3)_2]^{2+}$ -type complex, where two pytri units are coordinated to a Pd(II) ion in a head-to-tail fashion and the other pytri units are not complexed but are involved in strong  $\pi$ - $\pi$ -stacking interactions with the planar  $[Pd(pytri)_2]^{2+}$  motif.<sup>50</sup> The <sup>1</sup>H NMR spectrum



Figure 7. Partially stacked <sup>1</sup>H NMR spectra (400 MHz, CD<sub>3</sub>CN, 298 K) of (a)  $[Pd(L2)_2](BF_4)_4$ , (b) L2, and (c)  $[Pd(L2)](BF_4)_4$ .

of the 0.5:1 mixture of Pd(II) and L2 was similar to that observed with L3: downfield shifts of the pytri proton resonances were observed, indicative of Pd complexation with the pytri pockets, while upfield shifts for the proton resonances associated with the bipy units were consistent with a  $\pi - \pi$ interaction. However, unlike the  $[Pd(L3)_2]^{2+}$  complex, the <sup>1</sup>H NMR spectrum of the 0.5:1 mixture of Pd(II) and L2 contained two species, the  $[Pd(L2)_2]^{2+}$  complex (80-90%) and a second species that had a broad uninterpretable spectrum (10-20%) that we presume is a coordination polymer/ oligomer (Figure 7). The HR-ESI-MS data for both mixtures only displayed intense peaks consistent with  $[Pd(L)_2]^{2+}$  ions, confirming formation of the 1:2 M/L complexes (Figures S25 and S30). The vapor diffusion of diethyl ether into an acetonitrile solution containing a 0.5:1 mixture of [Pd- $(CH_3CN)_4$  (BF<sub>4</sub>)<sub>2</sub> and L2 resulted in deep-purple crystals of  $[Pd(L2)_2](BF_4)_2$  (Figure 8 and the SI). The complex



**Figure 8.** Solid-state structure of  $[Pd(L2)_2]^{2+}$ . Selected bond lengths (Å) and angles (deg): Pd1–N3 = 2.076(2), Pd1–N4 = 2.022(2); N3–Pd1–N4 = 79.58. Color scheme: *C*, gray; H, white; N, purple; Fe, orange red; Pd, dark cyan. BF<sub>4</sub><sup>-</sup> counterions and the remaining H atoms were omitted for clarity.

crystallizes in the triclinic  $P\overline{1}$  space group, with two L2 coordinated in a head-to-tail fashion to a single square-planar Pd(II) ion. The Pd–N bond lengths (Figure 8) are similar to those observed for other  $[Pd(pytri)_2]^{2+}$  complexes,<sup>43,50</sup> and the Fc units adopt the eclipsed conformation with the bipy and pytri arms in the syn arrangement ( $\tau = 5.52^{\circ}$ ). This results in a bipy– $[Pd(pytri)_2]^{2+}$ –bipy triple stack that is stabilized by  $\pi-\pi$  interactions [centroid–centroid distances of 3.692 Å (py–tri) and 3.481 Å (py–py)].

The <sup>1</sup>H NMR spectra (400 MHz, CD<sub>3</sub>CN, 298 K) of 1:1 mixtures of Pd(II) ions and one of the ligands (either L2 or L3) were completely different from those observed at the 0.5:1 ratio (Figures 7 and S33). When L2 was combined with 1 equiv of  $[Pd(CH_3CN)_4](BF_4)_2$ , all of the proton resonances of the ligand were shifted downfield, clearly indicative of complexation. The DOSY experiment confirmed that all of the proton signals had the same diffusion coefficient ( $D = 5.55 \times 10^{-10} \text{ cm}^2$  $s^{-1}$ ), suggesting the clean formation of a single species. Additionally, the diffusion coefficient observed for the 1:1 L2/Pd(II) mixture was very similar to those of the [Pd(L1)]- $(BF_4)_{2}$ ,  $[Ag(L1)](PF_6)$ , and  $[Ag(L2)](PF_6)$  complexes, suggesting a  $[Pd(L2)](BF_4)_2$  formulation. Consistently, the HR-ESI-MS spectrum displayed a dominant signal at m/z361.0565 (2+ peak), confirming the presence of the  $[Pd(L2)]^{2+}$ ion in solution (Figure S23). We were unable to generate Xray-quality crystals of the  $[Pd(L2)](BF_4)_2$  complex, but presumably a combination of entropic and enthalpic (steric repulsion between the  $\alpha$ -pyridyl protons of the adjacent bipy and pytri units) factors led to formation of the [1 + 1] Pd(II) metallomacrocycle.

The <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>3</sub>CN, 298 K) of a 1:1 mixture of  $[Pd(CH_3CN)_4](BF_4)_2$  and L3 was completely different from that of  $[Pd(L3)_2](BF_4)_2$ , indicating that two different Pd(II) complexes were obtained from the different molar ratios. All of the proton signals of the ligand were shifted downfield relative to the free L3 in the spectrum of the 1:1 mixture (Figure 9). However, like the <sup>1</sup>H NMR spectrum of the



**Figure 9.** Partially stacked <sup>1</sup>H NMR spectra (400 MHz, CD<sub>3</sub>CN, 298 K) of (a) L3 and (b)  $[Pd_2(L3)_2](BF_4)_4$ . Blue dotted lines indicate peaks corresponding to the major species observed in the solid state, and red dotted lines indicate the minor, less symmetric species.

 $[Pd(L3)_2](BF_4)_2$  complex, two sets of pytri resonances were observed (in a 4:3 ratio), with both sets shifted downfield from the free ligand, suggesting that both were coordinated to Pd(II) ions. The NMR spectrum could be interpreted in two ways: (1) either a mixture of [1 + 1] and [2 + 2] Pd(II) metallomacrocycles had formed or (2) a mixture of isomeric/rotameric complexes was obtained. A DOSY experiment [500 MHz, 298 K, 2:1 (v/v) CDCl<sub>3</sub>/CD<sub>3</sub>NO<sub>2</sub>] revealed that all of the signals in the <sup>1</sup>H NMR spectrum were diffusing at the same rate (D = $4.24 \times 10^{-10}$  cm<sup>2</sup> s<sup>-1</sup>), indicating that the two species had the same molecular weight and thereby ruling out a mixture of [1 +1] and [2 + 2] metallomacrocycles. The diffusion coefficient was similar to that observed for the  $[Ag_2(L3)_2](PF_6)_2$  complex

 $(D = 4.72 \times 10^{-10} \text{ m}^2 \text{ s}^{-1})$ , suggesting that the solution contained an isomeric mixture of  $[Pd_2(L3)_2](BF_4)_2$  metallomacrocycles. The HR-ESI-MS data were also consistent with that postulate, with three peaks observed at m/z 398.6106, 537.8092, and 560.4782, which correspond to [Pd<sub>2</sub>(L3)<sub>2</sub>]<sup>4+</sup>,  $[Pd_2(L3)_2(H^-)(H_2O)]^{3+}$ , and  $[Pd_2(L3)_2(BF_4)]^{3+}$ , respectively.<sup>49</sup> Closer inspection of the <sup>1</sup>H NMR spectrum provided further insight into the structures of the two  $\begin{bmatrix} 2 + 2 \end{bmatrix}$ metallomacrocycles. One set of proton resonances could be readily assigned to a highly symmetric system (e.g., the ferrocene protons were observed as two triplets at 4.78 and 4.64 ppm), which was analogous to the  $[Ag_2(L3)_2](PF_6)_2$ compound (this was confirmed via X-ray diffraction vide infra). The second series of peaks displayed four signals due to the Fc units (4.91, 4.79, 4.72, and 4.50 ppm), suggesting that the cp rings of the second metallomacrocycle adopted a staggered conformation, lowering the symmetry of the system. Additionally, the peak corresponding to the protons of the triazole-bound methylene (which is a triplet in the symmetric species) splits into two overlapping pairs of triplets in the second species. Finally, the three aromatic signals of the pyridine moieties are deshielded relative to the other isomer, indicative of a reduced  $\pi - \pi$  interaction. The collected <sup>1</sup>H NMR data are consistent with the formation of two isomeric [2 + 2]metallomacrocycles, one where the Fc units are staggered and the second displaying eclipsed Fc units.

DFT [B3LYP/6-31G(d), CH<sub>3</sub>CN solvent field] calculations of the staggered and eclipsed [2 + 2] metallomacrocycles were carried out to determine the relative energies (Figures 10 and S64).<sup>51</sup> The calculation indicated that the staggered conformer



**Figure 10.** DFT calculations [B3LYP/6-31G(d), CH<sub>3</sub>CN solvent field] of the (a) eclipsed and (b) staggered conformers of the  $[Pd_2(L3)_2](BF_4)_4$  complex. The hexyl chains were truncated to methyl groups for computation expediency.

was 2.93 kJ mol<sup>-1</sup> lower in energy than the eclipsed conformer. However, the small energy different suggests that both conformers would be present in solution, consistent with the observed <sup>1</sup>H NMR data.

X-ray-quality purple crystals of  $[Pd_2(L3)_2](BF_4)_4$  were obtained by the vapor diffusion of diethyl ether into a concentrated acetonitrile solution of the complex. The macrocycle crystallizes in the monoclinic  $P2_1/n$  space group, with one Pd(II) ion, one ligand, and two tetrafluoroborate counterions in the asymmetric unit (see the SI). Only the eclipsed conformer of the [2 + 2] metallomacrocycle  $[Pd_2(L3)_2](BF_4)_4$  was observed in the solid state (Figure 11).



**Figure 11.** Solid-state structure of  $[Pd_2(L3)_2](BF_4)_2$ . Selected bond lengths (Å): Pd1–N1 = 2.074(3), Pd1–N2 = 1.996(3), Pd1–N5 = 2.048(3), Pd1–N6 = 2.014(3). Selected bond angles (deg): N1– Pd1–N2 = 80.0(1), N2–Pd1–N5 = 98.2(1), N5–Pd1–N6 = 79.7(1), N6–Pd1–N1 = 102.0(1). Color scheme: C, gray; N, purple; Fe, orange; Pd, dark cyan.  $BF_4^-$  counterions and H atoms were omitted for clarity.

The Pd(II) ions are coordinated to two pytri units in the expected "head-to-tail" fashion with a square-planar coordination geometry ( $\tau_4 = 0.02$ ).<sup>38</sup> The Pd–N bond lengths range from 1.996(3) to 2.074(3) Å, similar to those observed in  $[Pd(L3)_2](BF_4)_2$  and related complexes. The Fc units of the metallocycle are eclipsed ( $\tau = 12.72^\circ$ ), and the pytri "arms" exhibit  $\pi$ - $\pi$  interactions [centroid–centroid distances of 3.519 Å (tri–tri) and 3.789 Å (py–py)]. Additionally, the two Pd(II) ions are aligned with a Pd–Pd distance of 3.625(6) Å.

The purple single crystals of  $[Pd_2(L3)_2](BF_4)_4$  were dissolved in CD<sub>3</sub>CN, and the <sup>1</sup>H NMR spectrum was immediately collected (see the SI). One set of signals consistent with the presence of the eclipsed conformer observed in the crystal structure was apparent by the number of signals and the corresponding integrations. However, a second, smaller, set of signals consistent with the staggered conformation of  $[Pd_2(L3)_2](BF_4)_4$  was also observed. Subsequent reacquisition of the <sup>1</sup>H NMR spectrum over time (CH<sub>3</sub>CN, 298 K) showed the system equilibration, finally settling after approximately 40 h at a 4:3 ratio of the staggered and eclipsed conformations (Figure S33).

**Electrochemistry.** The electrochemistry of the 3 ligands (L1–L3) and 11 complexes in a dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>)/ nitromethane solution (2:1, v/v) was investigated with CV and differential pulse voltammetry (DPV) using Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte. The results are presented in Table 1 and Figures 12 and S51–S55. All ligands and complexes exhibited the predicted reversible  $Fc^{+/0}$  redox couple. In the ligands L1– L3,  $E^{\circ}$  for this is observed between 0.78 and 0.79 V; i.e., exchanging one or two bipy arms with pytri has little effect on the ferrocenyl/ferrocenium potential. As expected, coordination

Table 1. Formal Electrode Potentials  $(E^{\circ})$  Exhibited by L1–L3 and the Corresponding Cu(I), Ag(I), and Pd(II) Complexes

		$E^{\circ} (V)^{a}$	
species	Fc <sup>+/0</sup>	Cu <sup>II/I</sup>	Pd <sup>I/II</sup>
L1	0.79		
L2	0.78		
L3	0.78		
$[\operatorname{Cu}_n(\mathbf{L1})_n]^{n+1}$	0.88	$0.58^{b}_{,b} - 0.01^{c}_{,c}$	
$[\operatorname{Cu}_n(\mathbf{L2})_n]^{n+1}$	0.88	$0.48,^{b} 0.14^{c}$	
$[\operatorname{Cu}_n(\mathbf{L3})_n]^{n+1}$	0.88	$0.56^{b}_{,b} 0.68^{b}_{,b} 0.18^{c}_{,c} 0.50^{c}_{,c}$	
$[Pd(L2)_2]^{2+}$	0.80, 0.87		$-0.28^{c,d}$
$[Pd(L3)_2]^{2+}$	0.83, 0.89		$-0.34^{c,d}$
$[Pd(L1)]^{2+}$	0.91		$-0.09^{c,d}$
$[Pd(L2)]^{2+}$	0.91		$-0.20^{c,d}$
$[Pd_2(L3)_2]^{4+}$	0.95		-0.27, 0.02
$[Ag(L1)]^+$	0.85 <sup>e</sup>		
$[Ag(L2)]^+$	0.83 <sup>e</sup>		
$[Ag_2(L3)_2]^{2+}$	0.83 <sup>e</sup>		

<sup>*a*</sup>CV at 100 mV s<sup>-1</sup>;  $E^{\circ} = (E_{pc} + E_{pa})/2$ ; 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>/ nitromethane (2:1, v/v); [Fc\*]<sup>+/0</sup> = 0.00 V.<sup>55</sup> <sup>*b*</sup>E<sub>pa</sub>. <sup>*c*</sup>E<sub>pc</sub>. <sup>*d*</sup>Irreversible reduction. <sup>*e*</sup>[FcH]<sup>+/0</sup> = 0.53 V.<sup>56</sup>



Figure 12. Overlayed cyclic voltammograms of 1 mM solutions of L3 and  $[Pd_2(L3)_2](BF_4)_4$  recorded at a glassy carbon electrode in  $CH_2Cl_2/nitromethane$  (2:1, v/v) containing 0.1 M NBu<sub>4</sub>PF<sub>6</sub>.

of the ligands with copper, palladium, and silver salts shifts the ferrocenyl oxidation to the anodic potential. The current response for the Fc<sup>+/0</sup> couple is consistent with the number of ferrocenyl groups in the molecular formula; thus, the Pd(II) 2:2 M/L macrocycle  $[Pd_2(L3)_2]^{4+}$  shows twice the peak current of ligand L3 and simpler  $[Pd(L1)]^{2+}$  and  $[Pd(L2)]^{2+}$  systems. The electrochemistry of the Cu coordination polymers with ligands L1 and L2 is complex. Oxidation of the Cu occurs before the Fc, as observed in similar systems.<sup>20,25,26,37,52</sup> There is significant separation between the anodic and cathodic peaks, consistent with a change of the coordination environment between the Cu(I) and Cu(II) states and the likelihood of nitromethane solvent coordination.<sup>53</sup>  $[Cu_n(L3)_n]^{n+}$  displays even more complex behavior, presumably associated with the weaker binding ability of the pytri ligands versus the bipy units.

The 0.5:1 Pd(II) complexes  $[Pd(L2)_2]^{2+}$  and  $[Pd(L3)_2]^{2+}$  showed two poorly resolved ferrocenyl oxidations (ca. 0.80 and 0.87 V for L2 and 0.83 and 0.89 V for L3; Table 1 and Figure S54), suggesting lability of the metal center or stepwise

oxidation. Predictably, the observed oxidation potentials lie between those of the uncomplexed ligands and the 1:1 species. In the case of the 1:1 Pd(II) complexes  $[Pd(L1)]^{2+}$  and  $[Pd(L2)]^{2+}$ , an irreversible Pd-based reduction process occurs with  $E_{pc}$  observed at -0.09 and -0.20 V, respectively. Similar reductions have been observed previously by the authors for other Pd(II) pytri complexes<sup>54</sup> and also for the model compounds  $[Pd(L4)_2]^{2+}$  and  $[Pd(L5)_2]^{2+}$  (Figure S55) and the 0.5:1 Pd(II) complexes  $[Pd(L2)_2]^{2+}$  and  $[Pd(L3)_2]^{2+}$ . In the case of the 2:2 macrocyclic Pd(II) complex of  $[Pd_2(L3)_2]^{2+}$ , two resolved quasi-reversible one-electron redox couples are observed at -0.27 and 0.02 V (Figure 12), assigned to the sequential reduction of the two Pd metals. The forward and reverse currents for the Pd redox couples are maintained in multicycle experiments.

# CONCLUSION

Three bis-bidentate 1,1'-disubstituted ferrocene ligands, functionalized with either bipy or pytri chelating units, were synthesized. The free ligands were found to adopt a syn  $\pi - \pi$ stacked conformation in solution. The coordination chemistry of these redox-active, conformational flexible, ligands was examined with the (usually) four-coordinate, diamagnetic metal ions Cu(I), Ag(I), and Pd(II). The resulting complexes were characterized using a range of techniques including <sup>1</sup>H and DOSY NMR spectroscopies, HR-ESI-MS, DFT calculations, and, where possible, X-ray crystallography. The Cu(I) complexes of the 1,1'-disubstituted ferrocene ligands were found to be coordination polymers, while the Ag(I) and Pd(II) complexes formed discrete [1 + 1] or [2 + 2] metallomacrocyclic architectures depending on the ligand architecture. Additionally, the electrochemical properties of these redox-active metallosupramolecular assemblies were examined using CV and DPV. All of the complexes displayed reversible ferrocene-based redox processes, while  $[Pd_2(L3)_2](BF_4)_4$ showed unusual quasi-reversible Pd reductions.

The results suggest that, despite the conformational flexibility of the 1,1'-disubstituted ferrocenes, these ligands can be used to assemble discrete, redox-active, metallosupramolecular assemblies. In the majority of examples herein, the ferrocene ligands remain in the syn  $\pi$ - $\pi$ -stacked conformation upon complex formation. Thus, a careful ligand design may be required in order to favor the anti conformers and allow the formation of metallocages and helicates rather than macrocycles and coordination polymers. Polyferrocene macrocycles<sup>57</sup> are generating considerable interest because of their interesting redox/electronic properties. The ligands reported here and related systems could be exploited to generate polyferrocene macrocycles via self-assembly. Efforts in these directions are underway.

#### EXPERIMENTAL SECTION

**General Procedures.** Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. Solvents were laboratory-reagent-grade with the following exceptions: dry tetrahydrofuran and diethyl ether were obtained by passing the solvents through an activated alumina column on a PureSolv solvent purification system (Innovative Technologies, Inc., Amesbury, MA). Reactions performed under microwave irradiation were carried out in a Discover CEM focused microwave synthesis system. Petrol refers to the fraction of petroleum ether boiling in the range 40–60 °C. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on either a 400 MHz Varian 400 MR or a Varian 500 MHz VNMRS spectrometer. Unless otherwise stated, all NMR spectra were obtained from isolated samples. Chemical shifts are reported in parts per million and referenced to residual solvent peaks (CDCl<sub>3</sub>, <sup>1</sup>H  $\delta$  7.26 ppm, <sup>13</sup>C  $\delta$ 77.16 ppm; CD<sup>3</sup>CN, <sup>1</sup>H  $\delta$  1.94, <sup>13</sup>C  $\delta$  1.32 and 118.26 ppm; CD<sub>3</sub>NO<sub>2</sub>, <sup>1</sup>H  $\delta$  4.30 ppm; n.b. the NMR spectra recorded in a mixture of CDCl<sub>3</sub> and CD<sub>3</sub>NO<sub>2</sub> were referenced to the nitromethane residual solvent peak). Coupling constants (J) are reported in hertz (Hz). Standard abbreviations indicating the multiplicity used are as follows: m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet, quin =quintet, dd = double doublet, dt = double triplet, td = triple doublet. Other abbreviations include DMF = dimethylformamide, DMSO = dimethyl sulfoxide, MeOH = methanol, TEA = trimethylamine, THF = tetrahydrofuran, TMEDA = tetramethylethylenediamine, and RT = room temperature. IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer with an attached ALPHA-P measurement module. Microanalyses were performed at the Campbell Microanalytical Laboratory at the University of Otago. HR-ESI-MS were collected on a Bruker micro-TOF-Q spectrometer (pseudo-cold-spray conditions refer to the collection of mass spectra with the temperature of the ion source at 40 °C, as opposed to the standard 180 °C). UV-vis absorption spectra were acquired with a PerkinElmer Lambda-950 spectrophotometer. Experimental information for intermediates and model compounds can be found in the SI.

**Safety Note!** While no problems were encountered during the course of this work, azide compounds are potentially explosive, and appropriate precautions should be taken when working with them.

Synthesis of L2. 1-(5-yl-Ethynyl-2,2'-bipyridine)-1'-iodoferrocene (438 mg, 0.89 mmol), 5-ethynyl-2-(1-hexyl-1H-1,2,3-triazol-4-yl)pyridine (250 mg, 0.98 mmol), CuI (17.0 mg, 0.090 mmol),  $[Pd(CH_3CN)_2Cl_2]$  (13.9 mg, 0.05 mmol), and  $[PH(^tBu)_3](BF_4)$ (31.1 mg, 0.110 mmol) were combined in degassed (argon) diisopropylamine (7 mL) and stirred under microwave irradiation (200 W) at 100 °C for 2 h. The crude reaction mixture was taken up in CHCl<sub>3</sub> (50 mL) and added to ethylenediaminetetraacetic acid (EDTA)/NH<sub>4</sub>OH(aq) (0.1 M, 50 mL). The organic layer was separated and the aqueous phase extracted with  $CHCl_3$  (5 × 50 mL). The combined organic layers were washed with brine (50 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel, gradient CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and then 9:1 CHCl<sub>3</sub>/CH<sub>3</sub>CN) to give the desired product as an orange solid upon the removal of solvent. Yield: 407 mg, 74%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  8.53 (d, J = 4.0 Hz, 1H, H<sub>i</sub>), 8.45 (dd, J = 2.2 and 0.8 Hz, 1H, H<sub>c</sub>), 8.34 (dd, J = 2.2 and 0.9 Hz, 1H, H<sub>l</sub>), 8.18-8.10 (m, 2H, H<sub>e</sub> and H<sub>f</sub>), 7.88 (s, 1H, H<sub>o</sub>), 7.77 (dd, J = 8.2 and 0.9 Hz, 1H,  $H_n$ ), 7.75–7.71 (m, 1H,  $H_g$ ), 7.66 (dd, J = 8.2 and 2.2 Hz, 1H,  $H_d$ ), 7.61 (dd, J = 8.2 and 2.2 Hz, 1H,  $H_m$ ), 7.30 (ddd, J = 7.5, 4.7, and 1.2 Hz, 1H, H<sub>b</sub>), 4.64-4.59 (m, 4H, H<sub>b</sub> and H<sub>k</sub>), 4.46-4.41 (m, 4H,  $H_a$  and  $H_j$ ), 4.27 (t, J = 7.3 Hz, 2H,  $H_p$ ), 1.86 (quin, J = 7.1 Hz, 2H,  $H_{g}$ , 1.36–1.26 (m, 6H,  $H_{r-t}$ ), 0.89 (t, J = 6.8 Hz, 3H,  $H_{u}$ ). <sup>13</sup>C NMR  $(126 \text{ MHz}, \text{CDCl}_3)$ :  $\delta$  155.6, 154.1, 151.6, 151.4, 149.2, 148.5, 148.0, 138.9, 136.9, 123.7, 122.0, 121.4, 120.9, 120.3, 119.8, 119.5, 91.5, 90.8, 84.3, 84.2, 74.6, 73.1, 73.1, 71.2, 71.1, 67.1, 67.0, 50.6, 31.3, 30.3, 26.3, 22.5, 14.1. IR (ATR, cm<sup>-1</sup>): v 2951, 2920, 2854, 2206, 1587, 1433, 1030, 793. HR-ESI-MS (MeOH). Found: *m*/*z* 617.2145 ([M + H]<sup>+</sup>). Calcd for C<sub>37</sub>H<sub>33</sub>N<sub>6</sub>Fe: m/z 617.2111. UV–vis [CHCl<sub>3</sub>;  $\lambda_{max}$ , nm ( $\varepsilon$ , L  $mol^{-1} cm^{-1}$ ]: 443 (1500), 380 (6000). Anal. Calcd for  $C_{37}H_{33}N_6Fe$ : C, 72.08; H, 5.23; N, 13.63. Found: C, 72.03; H, 5.45; N, 13.77.

Synthesis of L3. 1,1'-Diiodoferrocene (782 mg, 1.79 mmol), 5bromo-2-(1-hexyl-1H-1,2,3-triazol-4-yl)pyridine (954 mg, 3.75 mmol), CuI (34 mg, 0.179 mmol), [Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub>] (23 mg, 0.089 mmol), and [PH('Bu)<sub>3</sub>](BF<sub>4</sub>) (52 mg, 0.179 mmol) were combined in degassed (argon) diisopropylamine (15 mL) and stirred under microwave irradiation (200 W) at 100 °C for 2 h. The crude reaction mixture was taken up in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and added to EDTA/ NH<sub>4</sub>OH(aq) (0.1 M, 100 mL). The organic layer was separated and the aqueous phase extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 × 50 mL). The combined organic layers were washed with brine (80 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel, gradient CH<sub>2</sub>Cl<sub>2</sub>, and then 9:1 CH<sub>2</sub>Cl<sub>2</sub>/acetone) to give an orange solid upon the removal of solvent. The product was further purified by precipitation from CH<sub>2</sub>Cl<sub>2</sub> with petroleum ether and collected via filtration. Yield: 792 mg, 64%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 8.43 (d, *J* = 1.6 Hz, 2H, H<sub>c</sub>), 8.05 (s, 2H, H<sub>f</sub>), 7.73 (dd, *J* = 8.2 and 0.7 Hz, 1H, H<sub>e</sub>), 7.62 (dd, *J* = 8.2 and 2.1 Hz, 2H, H<sub>d</sub>), 4.61 (t, *J* = 1.9 Hz, 4H, H<sub>h</sub>), 4.44 (t, *J* = 1.9 Hz, 4H, H<sub>a</sub>), 4.36 (t, *J* = 7.2 Hz, 4H, H<sub>g</sub>), 1.93 (quin, signal obscured by residual acetonitrile solvent peak, H<sub>h</sub>), 1.35–1.29 (m, 12H, H<sub>i-k</sub>), 0.90 (t, *J* = 6.7 Hz, 6H, H<sub>l</sub>). <sup>13</sup>C NMR (126 MHz, CHCl<sub>3</sub>): δ 151.6, 148.4, 147.9, 138.8, 122.2, 119.8, 119.5, 90.7, 84.3, 73.1, 71.0, 67.3, 50.7, 31.3, 30.3, 26.3, 22.6, 14.1. IR (ATR, cm<sup>-1</sup>): ν 3092, 2922, 2855, 2209, 1593, 1437, 1377, 844. HR-ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>). Found: *m/z* 713.2795 ([M + Na]<sup>+</sup>). Calcd for C<sub>40</sub>H<sub>42</sub>FeN<sub>8</sub>Na: *m/z* 713.2775. UV–vis [CHCl<sub>3</sub>;  $\lambda_{max}$ , nm ( $\varepsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>)]: 449 (1500), 381 (5500). Anal. Calcd for C<sub>40</sub>H<sub>42</sub>N<sub>8</sub>Fe·0.3hexane: C, 70.07; H, 6.50; N, 15.64. Found: C, 70.09; H, 6.63; N, 15.79.

Synthesis of  $[Cu(L1)]_{n}(PF_{6})_{n}$ .  $[Cu(CH_{3}CN)_{4}](PF_{6})$  (27.5 mg, 0.074 mmol) was dissolved in ~1 mL of CHCl<sub>3</sub>/nitromethane (2:1, v/v) and added to a solution of L1 (40 mg, 0.074 mmol) in 4 mL of CHCl<sub>3</sub>/nitromethane (2:1, v/v), and the mixture was stirred for 1 h. The solution was filtered through Celite and precipitated via the addition of diethyl ether. The dark-red precipitate was collected by filtration and rinsed with diethyl ether  $(2 \times 5 \text{ mL})$ , before being dried in vacuo. Yield: 50 mg, 90%. <sup>1</sup>H NMR spectra (400 MHz) of the material in any of acetone-d<sub>6</sub>, CD<sub>3</sub>CN, CD<sub>3</sub>NO<sub>2</sub>, or a 2:1 mixture of CDCl<sub>3</sub>/CD<sub>3</sub>NO<sub>2</sub> yielded very broad spectra despite sharp solvent signals. IR (ATR, cm<sup>-1</sup>): v 2206, 1593, 1475, 1439, 1169, 1027, 828, 789, 556. HR-ESI-MS (acetone). Found: m/z 302.5346. Calcd for C34H22FeN4Cu2+: m/z 302.5239. Found: m/z 640.0162. Calcd for  $C_{34}^{+}H_{22}^{-}$ FeN<sub>4</sub>Cu·H<sub>2</sub>O·(H<sup>-</sup>)<sup>+</sup>: m/z 640.0617. UV–vis [acetone;  $\lambda_{max}$ nm ( $\varepsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>)]: 464 (4300), 432 (4200). Anal. Calcd for C34H22N4FeCuPF6 0.9CHCl3: C, 48.83; H, 2.96; N, 6.53. Found: C, 48.98; H, 2.75; N, 6.72.

Synthesis of  $[Cu(L2)]_n(PF_6)_n$ .  $[Cu(CH_3CN)_4]PF_6$  (24.2 mg, 0.065 mmol) was dissolved in ~1 mL of CHCl<sub>3</sub>/nitromethane (2:1, v/v) and added to a solution of L2 (40 mg, 0.074 mmol) in 4 mL of  $CHCl_3$ /nitromethane (2:1, v/v), and the mixture was stirred for 1 h. The solution was filtered through Celite and precipitated via the addition of diethyl ether. The dark-red precipitate was collected by filtration and rinsed with diethyl ether (2  $\times$  5 mL), before being dried in vacuo. Yield: 41 mg, 77%. <sup>1</sup>H NMR spectra (400 MHz) of the material in any of acetone- $d_{61}$  CD<sub>3</sub>CN<sub>1</sub> CD<sub>3</sub>NO<sub>2</sub>, or a 2:1 mixture of CDCl<sub>3</sub>/CD<sub>3</sub>NO<sub>2</sub> yielded very broad spectra despite sharp solvent signals. IR (ATR, cm<sup>-1</sup>): v 2953, 2931, 2861, 2207, 1594, 1476, 1439, 1030, 832, 556. HR-ESI-MS (acetone). Found: m/z 339.5842. Calcd for C<sub>37</sub>H<sub>32</sub>FeN<sub>6</sub>Cu<sup>2+</sup>: *m/z* 339.5661. Found: *m/z* 679.1472. Calcd for  $C_{37}H_{32}FeN_6Cu^+$ : m/z 679.1328. UV-vis [acetone;  $\lambda_{max}$  nm ( $\varepsilon$ , L  $mol^{-1} cm^{-1}$ ]: 446 (5400). Anal. Calcd for  $C_{37}H_{32}N_6FeCuPF_6 H_2O$ . 0.5CHCl3: C, 49.89; H, 3.85; N, 9.31. Found: C, 49.74; H, 3.93; N, 9.41.

Synthesis of  $[Cu(L3)]_n(PF_6)_n$ .  $[Cu(CH_3CN)_4]PF_6$  (27.0 mg, 0.072 mmol) was dissolved in ~1 mL of CHCl<sub>3</sub>/nitromethane (2:1, v/v) and added to a solution of L3 (50 mg, 0.072 mmol) in 4 mL of  $CHCl_3$ /nitromethane (2:1, v/v), and the mixture was stirred for 1 h. The solution was filtered through Celite and precipitated via the addition of diethyl ether. The bright-orange precipitate was collected by filtration and rinsed with diethyl ether  $(2 \times 5 \text{ mL})$ , before being dried in vacuo. Yield: 52 mg, 80%. <sup>1</sup>H NMR spectra (400 MHz) of the material in any of acetone- $d_{6}$ , CD<sub>3</sub>CN, CD<sub>3</sub>NO<sub>2</sub>, or a 2:1 mixture of CDCl<sub>3</sub>/CD<sub>3</sub>NO<sub>2</sub> yielded very broad spectra despite sharp solvent signals. IR (ATR, cm<sup>-1</sup>): v 2954, 2929, 2859, 2210, 1577, 1433, 1231, 1100, 1030, 839, 824, 556. HR-ESI-MS (acetone). Found: m/z 376.6247. Calcd for  $C_{40}H_{42}FeN_8Cu^{2+}$ : m/z 376.6083. Found: m/z753.2268. Calcd for  $C_{40}H_{42}FeN_8Cu^+$ : 753.2172. UV-vis [acetone;  $\lambda_{max}$ , nm ( $\varepsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>)]: 480 (2800), 409 (4800). Anal. Calcd for C40H42N8FeCuPF6·2H2O: C, 51.37; H, 4.96; N, 11.98. Found: C, 51.15; H, 4.93; N, 12.05.

Synthesis of  $[Ag(L1)](PF_6)$ . AgPF<sub>6</sub> (5.66 mg, 0.0180 mmol) was dissolved in ~1 mL of nitromethane and added to a stirring solution of L1 (10 mg, 0.018 mmol) in CHCl<sub>3</sub>/nitromethane (6 mL, 2:1, v/v). The resulting mixture was stirred for 30 min before being filtered through Celite and precipitated via the addition of diethyl ether. The

orange precipitate was collected by vacuum filtration, rinsed with diethyl ether (2 × 5 mL), and dried in vacuo. Yield: 10 mg, 68%. <sup>1</sup>H NMR [400 MHz, 2:1 (v/v) CDCl<sub>3</sub>/CD<sub>3</sub>NO<sub>2</sub>]:  $\delta$  8.90 (d, J = 4.8 Hz, 2H, H<sub>i</sub>), 8.37 (d, J = 2.0 Hz, 2H, H<sub>c</sub>), 8.29 (d, J = 8.0 Hz, 2H, H<sub>e</sub>), 8.22 (d, J = 8.3 Hz, 2H, H<sub>f</sub>), 8.19–8.11 (m, 4H, H<sub>d</sub> and H<sub>g</sub>), 7.70 (dd, J = 7.5, 5.0 Hz, 2H, H<sub>h</sub>), 4.64 (t, J = 1.8 Hz, 4H, H<sub>b</sub>), 4.48 (d, J = 1.8 Hz, 4H, H<sub>a</sub>). <sup>13</sup>C NMR (complex insufficiently soluble for the collection of adequate <sup>13</sup>C NMR spectra). IR (ATR, cm<sup>-1</sup>):  $\nu$  2211, 1590, 1473, 1434, 1168, 1029, 828, 556. HR-ESI-MS (acetone). Found: m/z 324.5287 ([M – (PF<sub>6</sub>)<sup>-</sup> – e<sup>-</sup>]<sup>2+</sup>). Calcd for C<sub>34</sub>H<sub>22</sub>N<sub>4</sub>FeAg<sup>2+</sup>: m/z 324.5117. Found: m/z 649.0320 [M – (PF<sub>6</sub>)<sup>-</sup>]<sup>+</sup>). Calcd for C<sub>34</sub>H<sub>22</sub>N<sub>4</sub>FeAg<sup>2+</sup>: m/z 649.0329. UV–vis [acetone;  $\lambda_{max}$  nm ( $\varepsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>)]: 495 (2700), 400 (5900). Anal. Calcd for C<sub>34</sub>H<sub>22</sub>N<sub>4</sub>FeAgPF<sub>6</sub>·CHCl<sub>3</sub>: C, 47.94; H, 2.63; N, 6.46. Found: C, 47.91; H, 2.67; N, 6.23.

Synthesis of [Ag(L2)](PF<sub>6</sub>). AgPF<sub>6</sub> (16.4 mg, 0.0650 mmol) was dissolved in  $\sim$ 1 mL of nitromethane and added to a stirring solution of L2 (40 mg, 0.065 mmol) in CHCl<sub>3</sub>/nitromethane (10 mL, 2:1, v/v). The resulting mixture was stirred for 30 min before being filtered through Celite and precipitated via the addition of diethyl ether. The orange precipitate was collected by vacuum filtration, rinsed with diethyl ether (2  $\times$  5 mL), and dried in vacuo. Yield: 51 mg, 90%. <sup>1</sup>H NMR [400 MHz, 2:1 (v/v) CDCl<sub>3</sub>/CD<sub>3</sub>NO<sub>2</sub>]:  $\delta$  8.75 (d, J = 5.1 Hz, 1H, H<sub>i</sub>), 8.72 (s, 1H, H<sub>c</sub>), 8.37 (d, J = 2.0 Hz, 1H, H<sub>i</sub>), 8.31 (s, 1H,  $H_0$ ), 8.16 (d, J = 8.0 Hz, 1H,  $H_f$ ), 8.11 (dd, J = 7.6 and 1.7 Hz, 1H,  $H_{g}$ ), 8.07 (d, J = 8.0 Hz, 1H,  $H_{e}$ ), 7.99 (dd, J = 8.4 and 2.1 Hz, 1H,  $H_{d}^{\circ}$ ), 7.89 (dd, J = 8.2 and 2.1 Hz, 1H, H<sub>m</sub>), 7.67-7.63 (m, 1H, H<sub>h</sub>), 7.61 (d, J = 8.2 Hz, 1H, H<sub>n</sub>), 4.63 (dt, J = 4.2 and 1.9 Hz, 4H, H<sub>b</sub> and  $H_k$ ), 4.51–4.43 (m, 6H,  $H_a$ ,  $H_j$  and  $H_p$ ), 2.04 (quin, J = 6.8 Hz, 2H,  $H_q$ ), 1.49–1.24 (m, 6H,  $H_r$ ,  $H_{sr}$  and  $H_t$ ), 0.90 (t, J = 6.9 Hz, 3H,  $H_u$ ). <sup>13</sup>C NMR (complex insufficiently soluble for the collection of adequate <sup>13</sup>C NMR spectra). IR (ATR, cm<sup>-1</sup>): ν 2930, 2860, 2208, 1592, 1471, 1433, 1028, 825, 556. HR-ESI-MS (acetone). Found: m/z 361.5676  $([M - (PF_6)^- - e^-]^{2+})$ . Calcd for  $C_{37}H_{32}N_6FeAg^{2+}$ : m/z 361.5539. Found: m/z 723.1197 ([M - (PF<sub>6</sub>)<sup>-</sup>]<sup>+</sup>). Calcd for (C<sub>37</sub>H<sub>32</sub>N<sub>6</sub>FeAg<sup>+</sup>: m/z 723.1083. UV-vis [acetone;  $\lambda_{max}$ , nm ( $\varepsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>)]: 473 (3100), 397 (6200). Anal. Calcd for  $C_{37}H_{32}N_6PF_6FeAg:$  C, 51.12; H, 3.71; N, 9.67. Found: C, 51.04; H, 3.87; N, 9.94.

Synthesis of [Ag<sub>2</sub>(L3)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>. AgPF<sub>6</sub> (14.6 mg, 0.0580 mmol) was dissolved in ~1 mL of nitromethane and added to a stirring solution of L3 (40 mg, 0.058 mmol) in CHCl<sub>3</sub>/nitromethane (10 mL, 2:1, v/v). The resulting mixture was stirred for 30 min before being filtered through Celite and precipitated via the addition of diethyl ether. The orange precipitate was collected by vacuum filtration, rinsed with diethyl ether  $(2 \times 5 \text{ mL})$ , and dried in vacuo. Yield: 46 mg, 84%. <sup>1</sup>H NMR [400 MHz, 2:1 (v/v) CDCl<sub>3</sub>/CD<sub>3</sub>NO<sub>2</sub>]:  $\delta$  8.55 (d, J = 2.0 Hz, 4H, H<sub>c</sub>), 8.35 (s, 4H, H<sub>f</sub>), 7.87 (dd, J = 8.2 and 2.0 Hz, 4H, H<sub>d</sub>), 7.60  $(d, J = 8.2 \text{ Hz}, 4\text{H}, \text{H}_{a}), 4.61 (t, J = 1.9 \text{ Hz}, 8\text{H}, \text{H}_{b}), 4.52 (t, J = 7.3$ Hz, 8H, H<sub>a</sub>), 4.45 (t, J = 1.9 Hz, 8H, H<sub>g</sub>), 2.03 (quin, J = 7.3 Hz, 8H), 1.45–1.26 (m, 24H, H<sub>i</sub>, H<sub>i</sub>, and H<sub>k</sub>), 0.88 (t, J = 6.9 Hz, 12H, H<sub>l</sub>). <sup>13</sup>C NMR [101 MHz, 2:1 (v/v) CDCl<sub>3</sub>/CD<sub>3</sub>NO<sub>2</sub>]:  $\delta$  152.4, 144.3, 144.0, 139.5, 123.1, 121.8, 121.1, 92.6, 83.0, 73.2, 70.4, 66.9, 51.3, 30.8, 29.7, 25.8, 22.1, 13.5. IR (ATR, cm<sup>-1</sup>): ν 2952, 2929, 2870, 2208, 1435, 1225, 835, 556. HR-ESI-MS (acetone). Found: m/z 398.6097 ([M - $(PF_6)^- - e^-]^{2+}$ ). Calcd for  $C_{40}H_{42}N_8FeAg^{2+}$ : m/z 398.5961. Found: m/z 797.2044 ([M - (PF<sub>6</sub>)<sup>-</sup>]<sup>+</sup>). Calcd for (C<sub>40</sub>H<sub>42</sub>N<sub>8</sub>FeAg<sup>+</sup>: m/z797.1297. UV–vis [acetone;  $\lambda_{max}$  nm ( $\varepsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>)]: 467 (5000), 390 (11700). Anal. Calcd for  $C_{80}H_{84}N_{16}P_2F_{12}Fe_2Ag_2{:}$  C, 50.92; H, 4.49; N, 11.88. Found: C, 50.74; H, 4.50; N, 11.96.

Synthesis of  $[Pd(L1)](BF_4)_2$ .  $[Pd(CH_3CN)_4](BF_4)_2$  (32.8 mg, 0.074 mmol) was dissolved in ~1 mL of acetonitrile and added to a suspension of L1 (40.0 mg, 0.074 mmol) in 5 mL of acetonitrile, and the mixture was stirred at RT for 1 h, giving a deep-purple solution. The solution was filtered through Celite before precipitation via the addition of diethyl ether. The dark-purple powder was isolated by vacuum filtration, rinsed with diethyl ether (3 × 5 mL), and air-dried. Yield: 43 mg, 79%. <sup>1</sup>H NMR [400 MHz, 2:1 (v/v) CDCl<sub>3</sub>/CD<sub>3</sub>NO<sub>2</sub>]:  $\delta$  8.75 (d, *J* = 5.8 Hz, 2H, H<sub>i</sub>), 8.61 (s, 2H, H<sub>c</sub>), 8.49–8.40 (m, 4H, H<sub>g</sub> and H<sub>d</sub>), 8.37 (d, *J* = 8.4 Hz, 2H, H<sub>e</sub> or H<sub>f</sub>), 8.32 (d, *J* = 8.4 Hz, 2H, H<sub>h</sub>).

<sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN): δ 157.7, 155.5, 154.8, 152.0, 144.1, 142.0, 129.0, 126.5, 125.8, 125.0, 100.5, 82.2, 76.4, 72.5, 65.6. IR (ATR, cm<sup>-1</sup>): ν 2201, 2188, 1012, 813, 786, 518. HR-ESI-MS (acetonitrile). Found: *m*/*z* 324.0140 ([M - 2(BF<sub>4</sub>)<sup>-</sup>]<sup>2+</sup>). Calcd for C<sub>34</sub>H<sub>22</sub>FeN<sub>4</sub>Pd<sup>2+</sup>: *m*/*z* 324.0109. Found: *m*/*z* 667.0146 ([M - 2(BF<sub>4</sub>)<sup>-</sup>·H<sub>2</sub>O·H<sup>-</sup>]<sup>+</sup>). Calcd for C<sub>34</sub>H<sub>22</sub>FeN<sub>4</sub>Pd·H<sub>2</sub>O·(H<sup>-</sup>)<sup>+</sup>: *m*/*z* 667.0407. UV–vis [acetone; λ<sub>max</sub> nm (ε, L mol<sup>-1</sup> cm<sup>-1</sup>)]: 512 (5000). Anal. Calcd for C<sub>34</sub>H<sub>22</sub>FeN<sub>4</sub>PdB<sub>2</sub>F<sub>8</sub>·H<sub>2</sub>O: C, 48.59; H, 2.88; N, 6.67. Found: C, 48.48; H, 2.73; N, 6.96.

Synthesis of [Pd(L2)](BF<sub>4</sub>)<sub>2</sub>. [Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> (28.8 mg, 0.0650 mmol) was dissolved in ~1 mL of acetonitrile and added to a suspension of L2 (40.0 mg, 0.0650 mmol) in 5 mL of acetonitrile, and the mixture was stirred at RT for 1 h, giving a deep-purple solution. The solution was filtered through Celite before precipitation via the addition of diethyl ether. The dark-purple powder was isolated by vacuum filtration, rinsed with diethyl ether  $(3 \times 5 \text{ mL})$ , and airdried. Yield: 45 mg, 86%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 9.41 (dd, J = 5.8 and 1.3 Hz, 1H, H<sub>i</sub>), 8.78 (s, 1H, H<sub>o</sub>), 8.71 (s, 2H, H<sub>c</sub>, H<sub>l</sub>), 8.48–8.39 (m, 2H, H<sub>a</sub> and H<sub>e</sub> or H<sub>f</sub>), 8.35 (d, J = 1.2 Hz, 2H, H<sub>d</sub> and  $H_e$  or  $H_f$ ), 8.30 (dd, J = 8.3 and 1.5 Hz, 1H,  $H_m$ ), 8.12 (d, J = 8.3 Hz, 1H, H<sub>n</sub>), 7.89 (ddd, J = 7.5, 5.8, and 1.8 Hz, 1H, H<sub>h</sub>), 4.74–4.68 (m, 6H, H<sub>b</sub>, H<sub>k</sub>, and H<sub>p</sub>), 4.62 (t, J = 1.9 Hz, 2H, H<sub>a</sub> or H<sub>i</sub>), 4.60 (t, J = 1.9Hz, 2H, H<sub>a</sub> or H<sub>i</sub>), 2.12–2.07 (m, 2H, H<sub>a</sub>), 1.48–1.31 (m, 6H, H<sub>r</sub>, H<sub>s</sub>) and  $H_t$ ), 0.93 (t, J = 7.0 Hz, 3H,  $H_u$ ). <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN): δ 157.4, 155.6, 155.5, 154.8, 153.2, 149.0, 146.3, 144.1, 141.8, 141.8, 129.2, 127.4, 126.7, 125.8, 125.1, 125.1, 123.6, 100.9, 99.3, 82.3, 82.1, 76.3, 76.3, 72.4, 72.3, 65.7, 65.5, 54.6, 31.7, 30.2, 26.4, 23.1, 14.2. IR (ATR, cm<sup>-1</sup>): v 2929, 2859, 2201, 1593, 1478, 1443, 1250, 1047, 1025, 847, 520. HR-ESI-MS (acetonitrile). Found: m/z 361.0565 ([M  $-2(BF_4)^{-}]^{2+}$ ). Calcd for  $C_{37}H_{32}FeN_6Pd^{2+}$ : m/z 361.0531. Found: m/zz 741.1004 ([M - 2(BF<sub>4</sub>)<sup>-</sup>·H<sub>2</sub>O·H<sup>-</sup>]<sup>+</sup>). Calcd for  $C_{37}H_{32}FeN_6Pd$ · H<sub>2</sub>O·(H<sup>-</sup>)<sup>+</sup>: m/z 741.1251. UV-vis [acetone;  $\lambda_{max}$  nm ( $\varepsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>)]: 511 (4200). Anal. Calcd for C<sub>37</sub>H<sub>32</sub>FeN<sub>6</sub>Pd: C, 49.57; H, 3.60; N, 9.37. Found: C, 49.30; H, 3.83; N, 9.62.

Synthesis of  $[Pd(L2)_2](BF_4)_2$ .  $[Pd(CH_3CN)_4](BF_4)_2$  (30.0 mg, 0.0490 mmol) was dissolved in ~1 mL of acetonitrile and added to a suspension of L2 (10.8 mg, 0.0245 mmol) in acetonitrile, and the mixture was stirred at RT overnight, giving a deep-red solution. The solution was filtered through Celite and crystallized via the slow diffusion of diethyl ether into an acetonitrile solution. The dark-red/ purple crystals were isolated by filtration, rinsed with diethyl ether (2  $\times$  5 mL), and air-dried before being dried in vacuo. Yield: 30 mg, 84%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN; n.b. because of the presence of multiple broad signals throughout the spectrum, integration of many of the sharp signals listed are inferred logically):  $\delta$  8.69 (s, 1H, H<sub>o</sub>), 8.29 (dd, J = 8.2 and 1.7 Hz, 1H, H<sub>n</sub>), 8.16 (d, J = 1.7 Hz, 1H, H<sub>l</sub>), 8.13 (d, J =5.2 Hz, 1H, H<sub>i</sub>), 8.05 (d, J = 8.2 Hz, 1H, H<sub>m</sub>), 7.97 (d, J = 2.1 Hz, 1H,  $H_c$ ), 7.88 (d, J = 8.3 Hz, 1H,  $H_e$ ), 7.82 (d, J = 7.9 Hz, 1H,  $H_f$ ), 7.42 (td, J = 7.7 and 1.9 Hz, 1H, H<sub>g</sub>), 7.22 (dd, J = 8.2 and 2.2 Hz, 1H, H<sub>d</sub>), 7.17 (dd, J = 7.0 and 4.6 Hz, 1H, H<sub>h</sub>), 4.80 (t, J = 1.8 Hz, 2H, H<sub>k</sub>),  $4.72-4.65 \text{ (m, 4H, H}_{b} \text{ and H}_{p}), 4.60 \text{ (t, } J = 1.9 \text{ Hz}, 2\text{H}, \text{H}_{a} \text{ or H}_{j}), 4.51 \text{ Hz}$  $(t, J = 1.9 \text{ Hz}, 2\text{H}, \text{H}_{a} \text{ or } \text{H}_{j})$ , 2.27–2.19 (m, 2H, H<sub>q</sub>), 1.69–1.45 (m, 6H,  $H_{r-t}$ ), 1.01 (t, J = 7.2 Hz, 3H,  $H_{u}$ ). <sup>13</sup>C NMR: the broadness of the <sup>1</sup>H NMR spectrum precluded the collection of a <sup>13</sup>C NMR spectrum. IR (ATR, cm<sup>-1</sup>):  $\nu$  3112, 2929, 2855, 2206, 1586, 1434, 1031, 800. HR-ESI-MS (acetonitrile). Found: m/z 669.1686 ( $[M - 2(BF_4)^{-}]^{2+}$ ). Calcd for  $C_{74}H_{64}Fe_2N_{12}Pd^{2+}$ : m/z 669.1563. UV–vis [acetone;  $\lambda_{max}$ , nm ( $\epsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>)]: 541 (shoulder, 3800). Anal. Calcd for C<sub>74</sub>H<sub>68</sub>N<sub>12</sub>B<sub>2</sub>F<sub>12</sub>Fe<sub>2</sub>Pd·CH<sub>3</sub>CN·0.2CHCl<sub>3</sub>: C, 57.85; H, 4.54; N, 11.51. Found: C, 57.51, H, 4.25; N, 11.52.

Synthesis of  $[Pd_2(L3)_2](BF_4)_4$ .  $[Pd(CH_3CN)_4](BF_4)_2$  (16.1 mg, 0.0360 mmol) was dissolved in ~1 mL of acetonitrile and added to a suspension of L3 (25.0 mg, 0.0360 mmol), and the mixture was stirred at RT for 1 h, giving a deep-purple solution. The solution was filtered through Celite before precipitation via the addition of diethyl ether. The dark-purple powder was isolated by vacuum filtration, rinsed with diethyl ether (3 × 5 mL), and air-dried. Yield: 29 mg, 82%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, after equilibrium was established, n.b. all assignments containing a prime have integration of approximately  $^{3}/_{4}$  that of the major species):  $\delta$  9.09 (d, J = 1.5 Hz, 4H, H<sub>c</sub>'), 8.93 (d, J

 $= 1.5 \text{ Hz}, 4\text{H}, \text{H}_{c}$ , 8.77 (s, 4H, H<sub>f</sub>), 8.76 (s, 4H, H<sub>f</sub>), 8.54 (dd, J = 8.3and 1.8 Hz, 4H, H<sub>d'</sub>), 8.08 (dd, J = 8.3 and 1.8 Hz, 4H, H<sub>d</sub>), 8.04 (dd, J = 8.2 and 0.6 Hz, 4H, H<sub>e</sub>'), 7.92 (dd, J = 8.3 and 0.6 Hz, 4H, H<sub>a</sub>), 4.91  $(dd, J = 2.5 and 1.3 Hz, 4H, H_{b'} or H_{b1'}), 4.83-4.77 (m, 12H, H_{b} and$  $H_{b'}$  or  $H_{b1'}$ ), 4.75 (t, J = 7.2 Hz, 8H,  $H_g$ ), 4.72–4.70 (m, 4H,  $H_{a'}$  or  $H_{a1'}$ ), 4.64 (t, J = 1.9 Hz, 8H,  $H_a$ ), 4.61 and 4.35 (dt, J = 10.4 and 7.0 Hz, 2H,  $H_{g'}$ ), 4.50 (td, J = 2.6 and 1.3 Hz, 4H,  $H_{a'}$  or  $H_{a1'}$ ), 4.57 and 4.31 (dt, J = 10.4 and 7.0 Hz, 2H,  $H_{g'}$ ), 2.10–1.97 (m, 16H,  $H_{h}$  and  $H_{h'}$ ), 1.51–1.25 (m, 48H,  $H_{ij}$ ,  $H_{ij}$ ,  $H_{kj}$ ,  $H_{i'}$ ,  $H_{i'}$ , and  $H_{k'}$ ), 0.90–0.84 (m, 24H, H<sub>1</sub> and H<sub>1</sub>). <sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN): δ 153.4, 153.4, 148.6, 148.1, 145.3, 144.8, 144.6, 128.6, 128.5, 125.6, 125.4, 124.6, 124.3, 99.7, 97.4, 82.7, 81.7, 74.4, 74.2, 74.0, 73.0, 72.9, 72.7, 72.6, 67.1, 65.2, 55.4, 55.2, 31.7, 30.2, 26.4, 23.2, 14.2. IR (ATR, cm<sup>-1</sup>):  $\nu$ 2928, 2870, 2200, 1591, 1433, 1035, 828. HR-ESI-MS (acetonitrile). Found: m/z 884.2098 ([M - 2(BF<sub>4</sub>)<sup>-</sup>]<sup>2+</sup>). Calcd for  $C_{80}H_{84}N_{16}B_2F_8Fe_2Pd_2^{2+}$ : m/z 884.1942. Found: m/z 560.4782 ([M  $- 3(BF_4)^{-1}^{3+}$ . Calcd for  $(C_{80}H_{84}N_{16}BF_4Fe_2Pd_2^{3+}: m/z 560.4617.$ Found: m/z 398.6106 ([M - 4(BF<sub>4</sub>)<sup>-</sup>]<sup>4+</sup>). Calcd for  $C_{80}H_{84}N_{16}Fe_2Pd_2^{4+}$ : m/z 398.5954. UV-vis [acetone;  $\lambda_{max}$ , nm ( $\epsilon$ , L  $mol^{-1} cm^{-1}$ ]: 511 (7500). Anal. Calcd for  $C_{80}H_{84}N_{16}B_4F_{16}Fe_2Pd_2$ . H<sub>2</sub>O: C, 49.04; H, 4.42; N, 11.44. Found: C, 48.79 H, 4.33; N, 11.61.

Synthesis of  $[Pd(L3)_2](BF_4)_2$ .  $[Pd(CH_3CN)_4](BF_4)_2$  (37.4 mg, 0.084 mmol) was dissolved in ~1 mL of acetonitrile and added to a suspension of L3 (116 mg, 0.169 mmol) in acetonitrile, and the mixture was stirred at RT overnight, giving a deep-red solution. The solution was filtered through Celite and precipitated via the addition of diethyl ether. Isolation by filtration gave a dark-red/purple powder, which was rinsed with diethyl ether  $(2 \times 5 \text{ mL})$  and air-dried before being dried in vacuo. Yield: 118 mg, 84%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  8.75 (s, 2H, H<sub>r</sub>), 8.37 (d, J = 1.7 Hz, 2H, H<sub>o</sub>), 8.29 (dd, J= 8.2 and 1.8 Hz, 2H,  $H_p$ ), 8.06 (d, J = 8.2 Hz, 2H,  $H_q$ ), 7.97 (d, J = 1.7 Hz, 2H, H<sub>c</sub>), 7.76 (s, 2H, H<sub>f</sub>), 7.45 (d, J = 8.1 Hz, 2H, H<sub>d</sub>), 7.17  $(dd, J = 8.2 and 2.2 Hz, 2H, H_e), 4.79-4.72 (m, 8H, H_n and H_s), 4.65$  $(t, J = 1.9 \text{ Hz}, 4\text{H}, \text{H}_{b} \text{ or } \text{H}_{m}), 4.59 (t, J = 1.9 \text{ Hz}, 4\text{H}, \text{H}_{b} \text{ or } \text{H}_{m}), 4.50$  $(t, J = 1.9 \text{ Hz}, 4\text{H}, \text{H}_{a}), 4.14 (t, J = 7.6 \text{ Hz}, 4\text{H}, \text{H}_{g}), 2.29 (quin, J = 7.4)$ Hz, 4H, Ht,), 1.80-1.70 (m, 4H, Hh), 1.69-1.12 (m, 24H, Hi-k and  $H_{u-w}$ ), 0.99 (t, J = 7.2 Hz, 6H,  $H_x$ ), 0.78 (t, J = 6.9 Hz, 6H,  $H_1$ ). <sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN): δ 152.9, 152.9, 152.2, 148.2, 148.2, 145.0, 144.3, 139.3, 127.8, 127.7, 127.7, 124.6, 123.9, 123.5, 97.3, 91.0, 85.1, 82.8, 74.1, 73.6, 72.4, 71.8, 69.3, 66.8, 55.1, 51.2, 32.1, 31.7, 30.7, 30.0, 26.9, 26.8, 23.4, 23.2, 14.4, 14.2. IR (ATR, cm<sup>-1</sup>): ν 3116, 2926, 2858, 2207, 1591, 1456, 1027, 821. HR-ESI-MS (acetonitrile). Found: m/z 743.2543. Calcd for  $C_{80}H_{84}N_{16}Fe_2Pd^{2+}$ : m/z 743.2394. UV-vis [acetone;  $\lambda_{\text{max}}$ , nm ( $\varepsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>)]: 527 (shoulder, 4000). Anal. Calcd for  $C_{80}H_{84}N_{16}B_4F_{16}Fe_2Pd\cdot H_2O$ : C, 57.22; H, 5.16; N, 13.34. Found: C, 56.93; H, 5.30; N, 13.38.

*CV Experiments.* All CV experiments were performed in solutions at 20 °C [2:1 (v/v) CH<sub>2</sub>Cl<sub>2</sub>/nitromethane] with a concentration of 1 mM of the electroactive analyte and 0.1 M NBu<sub>4</sub>PF<sub>6</sub> as the supporting electrolyte. For the polymeric Cu(I) complexes, the concentration refers to the repeat unit. A three-electrode cell was used with Cypress Systems 1.4-mm-diameter glassy carbon working, Ag/AgCl reference, and platinum wire auxiliary electrodes. Voltammograms were recorded with the aid of a Powerlab/4sp computer-controlled potentiostat. The potentials for all complexes were referenced to the reversible formal potential (taken as  $E^{\circ} = 0.00$  V) of the [Fc\*]<sup>+/0</sup> redox couple of decamethylferrocene.<sup>55</sup> Under the same conditions,  $E^{\circ}$  measured for [FcH]<sup>+/0</sup> was 0.53 V. DPV studies were run as part of our normal procedure and support (are identical to)  $E^{\circ}$  values obtained using CV [where  $E^{\circ} = (E_{pc} + E_{pa})/2$ ]. All CV data are displayed in the SI.

*Crystallographic Information.* X-ray data were collected at 100 K on an Agilent Technologies Supernova system using Cu K $\alpha$  radiation with exposures over 1.0°, and data were treated using the *CrysAlisPro*<sup>58</sup> software. The structure was solved using *SHELXS* within the *X-Seed* package, <sup>59</sup> and weighted full-matrix refinement on  $F^2$  was carried out using *SHELXL-97*<sup>60</sup> running within the *WinGX* package, <sup>61</sup> All non-H atoms were refined anisotropically. H atoms attached to C atoms were placed in calculated positions and refined using a riding model.

Computational Methods. Computational modeling was carried at the B3LYP/6-31G(d) level with the LanL2DZ electron core potential

on the Pd centers in an acetonitrile solvent field, using *Gaussian* 09.<sup>62</sup> After an adjustment factor of 0.975 was applied, a MADS of less than 10 cm<sup>-1</sup> for the vibrational frequencies indicates a high level of agreement between the experimental and computational structures.

#### ASSOCIATED CONTENT

# **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02503.

Experimental section, <sup>1</sup>H, <sup>13</sup>C, and DOSY NMR spectral information, HR-ESI-MS, UV–vis, X-ray, and electrochemical data, DFT calculation details, and calculated structures (PDF)

DFT-calculated structures (XYZ)

DFT-calculated structures (XYZ)

#### Accession Codes

CCDC 1571461–1571468 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: jcrowley@chemistry.otago.ac.nz.

#### ORCID <sup>©</sup>

James D. Crowley: 0000-0002-3364-2267

#### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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# DEDICATION

The manuscript is dedicated to Professor Leonard (Len) Lindoy on the occasion of his 80th birthday.

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