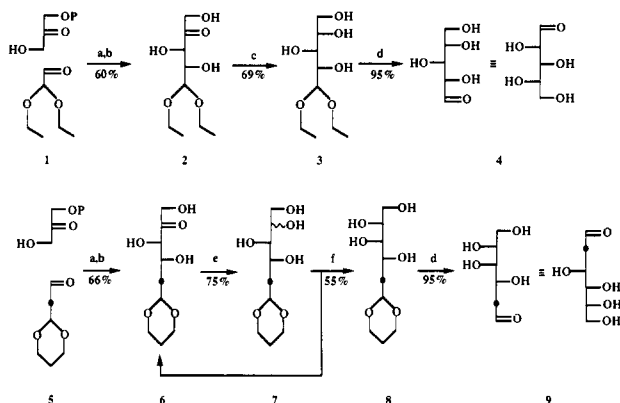


**Scheme II.** Synthesis of L-Xylose (**4**) and 2-Deoxy-D-arabino-hexose (**9**)<sup>a</sup>

<sup>a</sup> (a) RAMA (EC 4.1.2.13); (b) AP (EC 3.1.3.2); (c) IDH (EC 1.1.1.14, from *Candida utilis*)/NADH/FDH (EC 1.2.1.2)/formate; (d) aqueous HCl/THF; (e) NaHB(OAc)<sub>3</sub>/HOAc; (f) IDH (EC 1.1.1.14 from sheep liver)/NAD<sup>+</sup>/GluDH (EC 1.4.1.3)/KG/NH<sub>4</sub><sup>+</sup>.

to recycle NADH (0.017 mmol).<sup>12</sup> Hydrolysis of the acetal with aqueous HCl (0.5 M)/THF (1:1) yielded **4** (95%), which was indistinguishable by <sup>13</sup>C and <sup>1</sup>H NMR (500 MHz) spectroscopy from the commercially available enantiomer D-xylose.

To generate the opposite (D) stereochemistry on reduction of the ketone required an additional step (Scheme II). Ketone **6** was obtained in 66% yield by RAMA-catalyzed (250 units) reaction of 1,3-dioxane-2-acetaldehyde (**5**)<sup>13</sup> (3.8 mmol) and DHAP<sup>14</sup> (3.5 mmol) followed by dephosphorylation with AP (200 units). Compound **6** (2 mmol) was reduced with NaHB(OAc)<sub>3</sub> (5 mmol)<sup>15</sup> in acetic acid. This reduction yielded a mixture of the desired (5*R*) and undesired (5*S*) diastereomers in a 2:1 ratio (NMR analysis) and 75% yield. The 5*S* diastereomer was removed by treating the mixture of diastereomers **7** (0.9 mmol) with IDH (13 units)<sup>8</sup> and NAD<sup>+</sup> (0.005 mmol),<sup>16</sup> using an L-glutamic dehydrogenase (GluDH, 48 units)/2-ketoglutarate (KG, 0.3 mmol), ammonium sulfate (0.3 mmol) cofactor recycling system.<sup>12</sup> The product of oxidation, **6** (15%), could, in principle, have been recycled to increase the yield of **8**, but was, instead, discarded. Compound **8** was isolated in 55% yield (from **7**). Deprotection of the aldehyde **8** with aqueous 1.0 M HCl/THF (1:1) yielded 2-deoxy-D-arabino-hexose (**9**, 95%), which was indistinguishable from authentic material by <sup>13</sup>C and <sup>1</sup>H NMR (500 MHz) spectroscopy.

These two procedures demonstrate that RAMA accepts the half-protected aldehydes **1** and **5** as substrates and illustrate the application of this observation in syntheses of aldoses. These syntheses also show the value of IDH, or of NaHB(OAc)<sub>3</sub> in combination with IDH, in generating alcohols of either stereochemistry from the ketones derived from DHAP.

We are now addressing the most important remaining limitation of aldolase-catalyzed synthesis—the restriction of the D-threo stereochemistry for the vicinal diol—by exploring aldolases having stereochemical preferences different from RAMA.<sup>6</sup>

**Supplementary Material Available:** Experimental details for the synthesis of compounds **2–9** (5 pages). Ordering information is given on any current masthead page.

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(14) DHAP was synthesized by a literature procedure: Effenberger, F.; Straub, A. *Tetrahedron Lett.* **1987**, *28*, 1641. We added DHAP rather than generating it in situ in order to minimize reaction time.<sup>6</sup> Longer reaction times led to deactivation of RAMA in the presence of aldehyde **5**.

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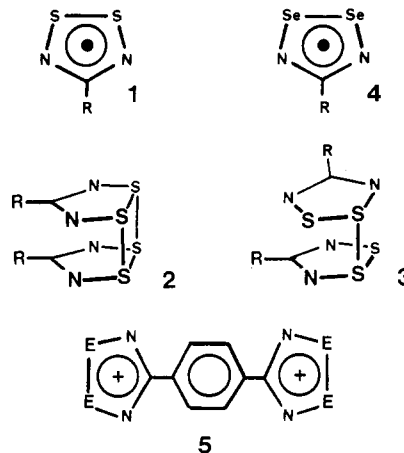
## 1,2,3,5-Diselenadiazolyls as Building Blocks for Molecular Metals. Preparation and Structures of [PhCN<sub>2</sub>Se<sub>2</sub>]<sup>+</sup>PF<sub>6</sub><sup>−</sup> and [PhCN<sub>2</sub>Se<sub>2</sub>]<sub>2</sub>

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The search for neutral, low-dimensional conducting materials<sup>2</sup> has kindled interest in the preparation and study of heterocyclic thiazyl radicals;<sup>3,4</sup> recent attention has been focused on 1,2,3,5-dithiadiazolyls.<sup>1,5</sup> These planar seven- $\pi$ -electron radicals are known to associate in the solid state in one of two modes, i.e., **2** (R = Ph)<sup>5e</sup> and **3** (R = CF<sub>3</sub>,<sup>5d</sup> NMe<sub>2</sub>,<sup>5a</sup> Me<sup>6</sup>). To date, however, there is no evidence of the desired packing mode, i.e., vertical stacks of uniformly spaced radicals.<sup>7</sup> In order to test the effect on interdimer interactions of the replacement of sulfur by selenium, we have prepared and structurally characterized the hitherto unknown 1,2,3,5-diselenadiazolyl **4** (R = Ph).



1,2,3,5-Dithiadiazolium salts are accessible by a variety of routes.<sup>3,4,8</sup> We have found, however, that the reaction of the

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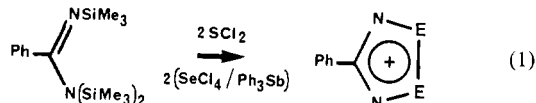
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persilylated benzamidine  $\text{PhC}(\text{NSiMe}_3)\text{N}(\text{SiMe}_3)_2$ <sup>9</sup> with excess  $\text{SeCl}_2$  in acetonitrile provides an improved (yield 70%) method for  $\text{R} = \text{Ph}$  (eq 1). This same approach also allows access to the corresponding 4-phenyl-1,2,3,5-diselenadiazolium ring system, although more careful control of stoichiometry is needed. Preparation of  $[\text{PhCN}_2\text{Se}_2]^+\text{Cl}^-$  requires the use of an equimolar mixture of  $\text{SeCl}_4$  and  $\text{Ph}_3\text{Sb}$ , i.e.,  $\text{SeCl}_2$  generated in situ. The product (yield 90%) can be readily converted by metathesis with  $\text{NOPF}_6$  into the corresponding  $\text{PF}_6^-$  salt.<sup>10,11</sup> The structure of this latter salt (as its  $\text{PhCN}$  solvate) has been confirmed by X-ray crystallography.<sup>12</sup>



Cyclic voltammetry of  $[\text{PhCN}_2\text{E}_2]^+\text{PF}_6^-$  ( $\text{E} = \text{S}, \text{Se}$ )<sup>13</sup> in acetonitrile with 0.1 M  $\text{Bu}_4\text{N}^+\text{PF}_6^-$  supporting electrolyte shows single reversible one-electron-reduction waves at 0.68 V ( $\text{E} = \text{S}$ ) and 0.61 V ( $\text{E} = \text{Se}$ ), reference  $\text{Ag}/\text{AgCl}$ ; in accord with simple electronegativity arguments, the heavier chalcogen-containing cation is slightly harder to reduce. Like  $[\text{PhCN}_2\text{S}_2]^+\text{Cl}^-$ ,  $[\text{PhCN}_2\text{Se}_2]^+\text{Cl}^-$  can be reduced chemically by  $\text{Ph}_3\text{Sb}$  to yield the radical dimer  $[\text{PhCN}_2\text{Se}_2]_2$  as black microcrystalline needles, dec 178 °C (yield 87%). This material dissociates (partially) in  $\text{CH}_2\text{Cl}_2$  to the diselenadiazolyl radical **4** ( $\text{R} = \text{Ph}$ ), which exhibits a broad unresolved ESR signal (at 295 K) with  $g = 2.0394$ .<sup>14</sup>

The radical dimer  $[\text{PhCN}_2\text{Se}_2]_2$  can be sublimed at 100 °C/0.1 Torr to afford small blocks suitable for X-ray crystallography.<sup>15</sup> An ORTEP drawing of a single dimer unit is shown in Figure 1. The two  $\text{CN}_2\text{Se}_2$  rings are eclipsed, as in the corresponding sulfur dimer,<sup>5e</sup> with a dihedral angle between the rings of 5.5°. Comparison of the mean structural parameters within the two  $[\text{PhCN}_2\text{Se}_2]$  rings with those observed in the  $[\text{PhCN}_2\text{Se}_2]^+$  cation reveals a substantial lengthening of the Se-Se bond upon reduction (from 2.260 (5) Å in the cation to 2.341 (5) Å in the radical dimer); a smaller increase in the mean Se-N distance (from 1.76 to 1.78 Å) is also observed.<sup>16</sup> Collectively the trends reflect the phase properties of the  $a_2$  orbital which accommodates the extra electron in the radical.<sup>5a</sup> Crystals of  $[\text{PhCN}_2\text{Se}_2]_2$  are orthorhombic, space group  $Pbca$ , with the dimer units stacked along the  $c$  axis with the herringbone arrangement shown in Figure 2; the two distinct mean  $\text{CN}_2\text{Se}_2$  planes lie at angles of 44.1° and 47.7° with this axis. Within the dimers, the two rings are connected by two unequal Se...Se contacts (3.160 (2) and 3.347 (2) Å). The average of these two values is longer than the interannular contacts in  $[\text{SeN}_2\text{Se}_2]_2^{2+}2\text{AsF}_6^-$  and  $[\text{SN}_2\text{Se}_2]_2^{2+}2\text{X}^-$  (range = 3.12–3.18 Å,  $\text{X}^- = \text{AsF}_6^-, \text{SbF}_6^-$ )<sup>16,17</sup> and also longer than the

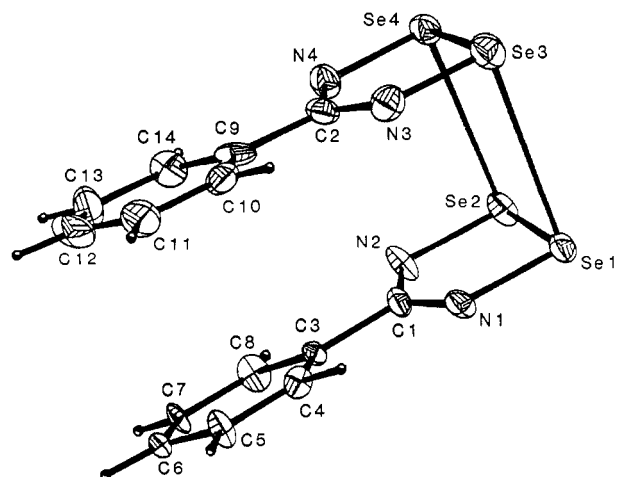


Figure 1. ORTEP drawing of a single dimer unit in  $[\text{PhCN}_2\text{Se}_2]_2$ , showing atom numbering scheme.

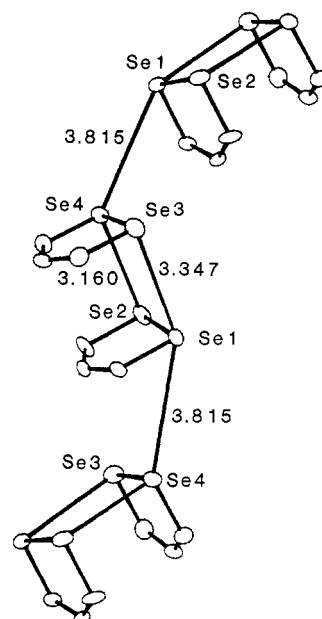


Figure 2. Stacking of  $(\text{CN}_2\text{Se}_2)_2$  units along  $c$  axis.

corresponding S...S distances in  $[\text{PhCN}_2\text{S}_2]_2$  (mean = 3.105 Å).<sup>5e</sup> The dimer units are separated by secondary interactions  $\text{Se1} \cdots \text{Se4} = 3.815$  Å and  $\text{Se2} \cdots \text{Se3} = 4.075$  Å.<sup>18</sup>

The crystal packing of the  $[\text{PhCN}_2\text{Se}_2]_2$  dimer units can be viewed as arising from a severe Peierls distortion<sup>19</sup> of the idealized perpendicular packing arrangement. Alleviation of this situation, to produce a more uniform, nonlocalized stack, may be possible by suitable modification of the exocyclic ligand or by the design of polyfunctional radicals. Toward the latter end, we have prepared, starting from the bifunctional amidine  $(\text{Me}_3\text{Si})_2\text{N}-(\text{Me}_3\text{SiN})\text{CC}_6\text{H}_4\text{C}(\text{NSiMe}_3)\text{N}(\text{SiMe}_3)_2$ <sup>9</sup> and using the synthetic procedure outlined above for  $[\text{PhCN}_2\text{E}_2]^+$ , salts of the 1,4-phenylene-substituted dication  $[(\text{E}_2\text{N}_2\text{C})\text{C}_6\text{H}_4(\text{CN}_2\text{E}_2)]^{2+}$  ( $\text{E} = \text{S}, \text{Se}$ ) **5**.<sup>20</sup> Cyclic voltammetry on these materials (as their  $\text{SbF}_6^-$  salts) reveals single, broad reduction waves<sup>21</sup> in the same region

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(10)  $[\text{PhCN}_2\text{Se}_2]^+\text{Cl}^-$  forms fibrous red-orange needles (from  $\text{CH}_3\text{CN}$ ), dec > 180 °C. Treatment of this salt with  $\text{NOPF}_6$  affords the  $\text{PF}_6^-$  derivative, which crystallizes from benzonitrile as  $[\text{PhCN}_2\text{Se}_2]^+\text{PF}_6^- \cdot \text{PhCN}$  (yield 80%), mp 125–130 °C.

(11) Satisfactory elemental analyses were obtained for this and all other new compounds reported here.

(12) Selected bond lengths (angstroms) and angles (degrees) within the cation:  $\text{Se1-Se2}$ , 2.260 (5);  $\text{Se1-N1}$ , 1.74 (2);  $\text{Se2-N2}$ , 1.78 (2);  $\text{N1-C1}$ , 1.38 (3);  $\text{N2-C1}$ , 1.33 (3);  $\text{C1-C2}$ , 1.45 (3);  $\text{Se2-Se1-N1}$ , 91.3 (6);  $\text{Se1-Se2-N2}$ , 93.0 (8);  $\text{Se1-N1-C1}$ , 117 (2);  $\text{Se2-N2-C1}$ , 115 (2);  $\text{N1-C1-N2}$ , 124 (3). The  $\text{Se}_2\text{N}_2\text{C}$  plane is twisted 12.6° from the plane of the phenyl group.

(13)  $[\text{PhCN}_2\text{S}_2]^+\text{PF}_6^-$  was also prepared by metathesis of the chloride salt with  $\text{NOPF}_6$ .

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(15) Selected bond lengths (angstroms) and angles (degrees) in the radical dimer:  $\text{Se1-Se2}$ , 2.338 (2);  $\text{Se1-N1}$ , 1.806 (12);  $\text{Se2-N2}$ , 1.792 (12);  $\text{Se3-Se4}$ , 2.343 (3);  $\text{Se3-N3}$ , 1.759 (14);  $\text{Se4-N4}$ , 1.778 (12);  $\text{Se1-Se3}$ , 3.347 (2);  $\text{Se2-Se4}$ , 3.160 (2);  $\text{C1-N1}$ , 1.29 (2);  $\text{C1-N2}$ , 1.33 (2);  $\text{C1-C3}$ , 1.53 (2);  $\text{C2-N3}$ , 1.32 (2);  $\text{C2-N4}$ , 1.35 (2);  $\text{C2-C9}$ , 1.51 (2);  $\text{Se1-Se1-N1}$ , 89.5 (4);  $\text{Se1-Se2-N2}$ , 91.1 (4);  $\text{Se4-Se3-N3}$ , 90.6 (5);  $\text{Se3-Se4-N4}$ , 91.1 (4);  $\text{Se1-N1-C1}$ , 117 (1);  $\text{Se2-N2-C1}$ , 115 (1);  $\text{Se3-N3-C2}$ , 117 (1);  $\text{Se4-N4-C2}$ , 115 (1);  $\text{N1-C1-N2}$ , 128 (1);  $\text{N3-C2-N4}$ , 127 (2).

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as found for the monofunctional salts, i.e., the two heterocyclic rings are noninteracting. Characterization of the neutral species obtained by reduction of these dications is in progress.

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada, the National Science Foundation (EPSCOR program), and the State of Arkansas for financial support.

**Supplementary Material Available:** Tables of crystallographic data (S1), atomic coordinates (S2 and S3), bond lengths and angles (S4 and S5), and anisotropic thermal parameters (S6 and S7) for  $[\text{PhCN}_2\text{Se}_2]^+\text{PF}_6^-\cdot\text{PhCN}$  and  $[\text{PhCN}_2\text{Se}_2]_2$  (11 pages); tables of observed and calculated structure factors (S8 and S9) for  $[\text{PhCN}_2\text{Se}_2]^+\text{PF}_6^-\cdot\text{PhCN}$  and  $[\text{PhCN}_2\text{Se}_2]_2$  (24 pages). Ordering information is given on any current masthead page.

### (Template)<sup>2</sup> Synthesis of a Dinucleating Macrocyclic Ligand and Crystal Structure of Its Dicopper(II) Imidazolate Complex

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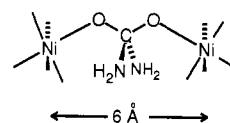
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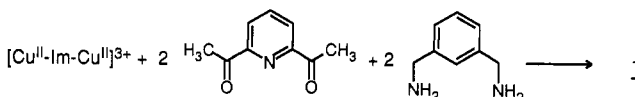
Mimicry of metalloprotein active sites lends insight toward structure-function relationships in biological systems as well as the development of abiotic catalysts. Reaction centers containing two or more transition-metal ions are of particular interest in studying the cooperative effects of redox-active or Lewis acid sites.<sup>2</sup> In these systems, synthetic macrocyclic ligands offer a convenient means of preorganization of ligands for controlling both metal ion and auxiliary ligand or substrate binding.<sup>3</sup> Dinuclear complexes as mimics of the nickel-containing enzyme urease would aid in deciphering the features that give rise to a 10<sup>14</sup> rate acceleration in urea hydrolysis.<sup>4</sup> Here we report the design, synthesis, and characterization of dicopper(II) and dinickel(II) macrocyclic complexes as a first step toward this goal.

Recent magnetic measurements by Wilcox<sup>5</sup> indicate that urease has a dinuclear Ni<sup>II</sup> center with weak antiferromagnetic coupling between the two distorted O<sub>h</sub> sites due to a bridging ligand and also suggest coordination of bridging substrates. A proposed

mechanism involves binding of both urea and H<sub>2</sub>O between the metal ions, leading to a carbon tetrahedral intermediate with a three-atom bridge (O-C-O) spanning the metal centers.<sup>6</sup> One arrangement of the relevant players would place the nickel ions at an internuclear separation of nearly 6 Å.<sup>7</sup>



In order to construct a mimic of the urease active site, we sought a semirigid macrocyclic framework that would allow coordination of two Ni<sup>II</sup> ions in a nearly octahedral geometry with a three-atom separation for a bridging substrate (or intermediate). In this strategy, the N-C-N portion of imidazolate served as a mimic of the desired O-C-O spacer. The well-known propensity for formation of  $\mu$ -bridged imidazolate complexes of Cu<sup>II</sup><sup>9</sup> (and more rarely Ni<sup>II</sup>)<sup>10</sup> led us to postulate the use of the Cu-Im-Cu (or Ni-Im-Ni) moiety in the template synthesis of the macrocyclic complex  $[\text{LCu}_2(\mu\text{-Im})](\text{CF}_3\text{SO}_3)_3\cdot\text{H}_2\text{O}$  (**1**). To our knowledge, this is the first use of a simple dinuclear metal unit as a template for macrocyclization. We have termed this reaction a (template)<sup>2</sup> synthesis to reflect the role of imidazolate in first defining the metal-metal distance, which subsequently results in organization and condensation of the Schiff base macrocycle around the secondary template,<sup>11</sup> according to the following reaction:



The synthetic procedure consisted of addition of equimolar amounts of  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$  and imidazole in  $\text{CH}_3\text{OH}$  to an equimolar solution of 2,6-diacetylpyridine and *m*-xylylenediamine in  $\text{CH}_3\text{OH}$ . After 12 h at room temperature, a green precipitate was isolated in 82% yield and characterized.<sup>12</sup> Recrystallization from propylene carbonate and THF yielded crystals suitable for X-ray crystallographic analysis. Substituting nickel in place of copper led to the formation of a yellow solid, proposed to be an analogous complex,  $[\text{LNi}_2(\mu\text{-Im})](\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ .<sup>13</sup> The usual method of synthesis of dinucleating Schiff base macrocycles entails the use of a single large metal ion template such as  $\text{Pb}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ , or  $\text{Ag}^+$ ,<sup>14</sup> which, in our system, failed to give soluble non-polymeric products; the rigidity of the *m*-xylyl groups is, in fact, likely to prevent templation around a single metal ion. Furthermore, it is important to note that  $\text{Cu}^{2+}$  or  $\text{Ni}^{2+}$  ions in the absence of imidazole were ineffective toward macrocyclization.<sup>15</sup>

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(11) The precise sequence of template formation cannot be well-defined; however, it is certain that two  $\text{Cu}^{2+}$  and one Im<sup>-</sup> are required in the cavity before final ring closure may occur.

(12)  $[\text{LCu}_2(\mu\text{-Im})](\text{CF}_3\text{SO}_3)_3\cdot\text{H}_2\text{O}$  (82% yield): IR (KBr pellet)  $\nu$  1631 (m, C=N), 1596 (m, phenyl), 1476 (m, pyridine), 3460 (s, OH), 1278 (s,  $(\text{SO}_3)_3$  ionic  $\text{CF}_3\text{SO}_3^-$ ), 1248 (s,  $(\text{SO}_3)_3$  bound  $\text{CF}_3\text{SO}_3^-$ )  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{40}\text{H}_{39}\text{N}_9\text{O}_9\text{S}_3\text{F}_9\text{Cu}_2$ : C, 40.50; H, 3.31; N, 9.45; Cu, 10.71. Found: C, 40.10; H, 3.39; N, 9.15; Cu, 10.46.

(13) The compound analyzed correctly for the formula  $[\text{LNi}_2(\mu\text{-Im})](\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ . Anal. Calcd for  $\text{C}_{37}\text{H}_{47}\text{N}_{11}\text{O}_{14}\text{Ni}_2$ : C, 45.27; H, 4.87; N, 15.88. Found: C, 45.01; H, 4.80; N, 15.61.

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(15) Extensive attempts made in the absence of imidazole gave reproducibly poor yields. Specifically, extraction of copper from the reaction mixture with EDTA as described below<sup>19</sup> yielded mainly unidentified polymeric species; analysis by <sup>1</sup>H NMR of the organic material taken up in  $\text{CH}_2\text{Cl}_2$  indicated that the macrocycle was formed in less than 5% yield, and the diacetylpyridine could be recovered in 15% yield.

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(7) Alternatively, Buchanan et al.<sup>8</sup> have proposed substrate bridging between two apical positions in a  $\text{Ni}_2$  model complex with a Ni-Ni separation of 3.42 Å.

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