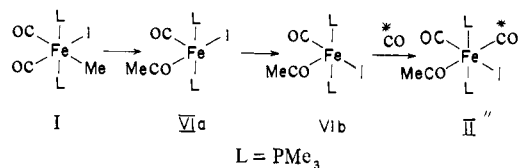


Scheme III



than vi or vii, resulting in enrichment in the site trans to the acetyl group. While a species such as V appears to rationalize the pattern of labeling observed for the cyano system, however, it does not explain the simultaneous formation of II' and II'' in the iodo system in methylene chloride. The intermediacy of V also does not rationalize the introduction of label into I', and thus involvement of a trigonal-pyramidal species such as V must be rejected for the iodo system. Similar conclusions have been reached for the isoelectronic manganese system<sup>5</sup>, and have been justified theoretically.<sup>24</sup>

A mechanism different from that of Scheme I may well apply for carbonylation of both I in the nonpolar solvent *n*-hexane at low temperatures and of the cyano analogue in methylene chloride at room temperature.<sup>9,11</sup> Labeling at the acetyl carbonyl site does not appear to occur in either case in the initial stages of the reactions, and anion dissociation must therefore not occur prior to combination of the methyl and carbonyl ligands within the inner coordination spheres.<sup>25</sup> These reactions presumably proceed as in Scheme III, much as suggested by Cardaci<sup>11</sup> except that we favor square-pyramidal intermediates in order to be consistent with our findings presented above. The hypothesized rapid isomerization of VIa to VIb would be reasonable in view of the high trans influence of the acetyl group.<sup>18</sup> We note also that the isoelectronic rhodium compound RhCl<sub>2</sub>(MeCO)(PPh<sub>3</sub>)<sub>2</sub> has an analogous structure.<sup>27</sup>

(24) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

(25) Iodide would be a relatively poor leaving group in the hydrocarbon solvent, and cyanide generally coordinates relatively strongly to transition-metal ions and thus would be a very poor leaving group.<sup>26</sup>

(26) No obviously relevant equilibrium data are known to us, but stability constants for formation of cyano complexes of transition metals are generally larger than those of halo complexes. See: Martell, A. E.; Sillen, L. G. "Stability Constants"; 25, Chemical Society: London, 1964, 1971; Special Publications No. 17 and 25.

(27) Egglestone, D. L.; Lock, C. J. L.; Turner, G.; Baird, M. C. *J. Chem. Soc., Dalton Trans.* **1977**, 1576.

Our results and interpretations appear to be largely consistent with the results of Mawby et al. for the chemistry of the analogous ruthenium system with dimethylphenylphosphine.<sup>21</sup> Although detailed comparisons are clearly not justified, it seems likely that trigonal-bipyramidal intermediates need not be postulated here either.

**Restricted Rotation of the Acetyl Group in III.** While carrying out the low-temperature NMR experiments discussed above, we noted variations of the line width of the resonance of the terminal carbonyl group of III. We therefore carried out with enriched III a more extensive variable-temperature NMR experiment, in which the well-resolved (at room temperature) triplet at 213.4 ppm ( $J(\text{P}-\text{C}) = 24.5$  Hz) was found to broaden at lower temperatures and finally split at about 225 K into two well-resolved triplets at 214.8 ppm ( $J(\text{P}-\text{C}) = 23$  Hz) and 210.7 ppm ( $J(\text{P}-\text{C}) = 26$  Hz). These results are clearly to be interpreted in terms of restricted rotation of the acetyl group about the iron-carbon bond, and as the two terminal carbonyl groups become non-equivalent at low temperature, the low-energy structure undoubtedly has the plane of the acetyl group lying in the FeI(CO)<sub>2</sub> plane. The coalescence temperature was found to be about 260 K, giving  $\Delta G^\ddagger = 11.6 \pm 1.0$  kcal/mol<sup>28</sup> for eclipsing of the acyl group with the trimethylphosphines. This is considerably higher than barriers to rotation about the metal-acyl bonds of compounds of the type CFH<sub>2</sub>COC<sub>2</sub>(CO)<sub>3</sub>PPh<sub>3</sub><sup>29</sup> and CpFe(CO)(PPh<sub>3</sub>)(COMe)<sub>3</sub><sup>30</sup> in which the barriers to acyl rotation are sufficiently low that different rotamers can be detected by IR but not by NMR spectroscopy. Somewhat higher barriers have been reported for rotation of aryl groups in the compounds  $\eta^5\text{-C}_5\text{Me}_5\text{RhX(aryl)-PMe}_3$ , but here the  $\eta^5\text{-C}_5\text{Me}_5$  ligand undoubtedly contributes significantly to the barrier.<sup>31</sup>

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**Registry No.** I, 33542-07-3; II, 78306-61-3; III, 33542-06-2; Fe(CO)<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>, 25921-55-5; CO, 630-08-0; <sup>13</sup>CO, 1641-69-6; tri-carbonyl(benzylideneacetone)iron, 53861-80-6; methyl iodide, 74-88-4.

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## Binucleating Tetrapyrrole Macrocycles

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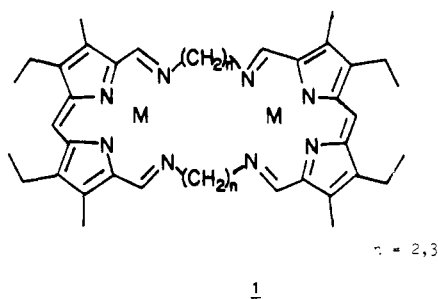
**Abstract:** Tetrapyrrolic bimetallic macrocyclic complexes have been synthesized in which the two metal ions are incorporated within one macrocyclic ring. The ligand, 4,16,20,32-tetraethyl-5,15,21,31-tetramethyl-8,12,24,28,33,34,35,36-octazapentacyclo[28.2.1.1<sup>3,6</sup>.1<sup>14,17</sup>.1<sup>19,22</sup>]hexatriaconta-1,3,5,7,12,14(35),15,17,19,21,23,28,30(33),31-tetradecane (bi-dptmd), can be obtained by Schiff base condensation of the precursor 5,5'-diformyl-dipyrromethane with trimethylenediamine. Related ligands can be synthesized by varying the diamine. Lead(II), zinc(II), and copper(II) complexes have been isolated. Copper(II) complexes with BF<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, N<sub>3</sub><sup>-</sup>, and NCS<sup>-</sup> as anions were investigated. Electrochemical studies using cyclic voltammetric techniques indicate a ligand-centered irreversible two-electron oxidation wave and two one-electron processes associated with the bicopper center. Crystals of Cu<sub>2</sub>(bi-dptmd)(N<sub>3</sub>)<sub>2</sub> are monoclinic, space group P2<sub>1</sub>/n, with  $a = 18.508$  (5) Å,  $b = 12.311$  (3) Å, and  $c = 20.185$  (6) Å,  $\beta = 112.65^\circ$ , and  $Z = 4$ . Refinement resulted in  $R = 0.068$  and  $R_w = 0.076$ . The coordination sphere of each copper ion is distorted trigonal bipyramidal and consists of four ligand nitrogen atoms and a nitrogen from the azide. The ligand has folded so that the two dipyrromethane portions are facing each other, providing a hydrophobic walled-in cavity.

The quest for catalytic systems capable of activating species such as molecular oxygen and nitrogen has led to biomimetic models because of the ease with which certain biomolecules can

accomplish these feats. For example, the porphyrins and porphyrin-related ligands exhibit diverse chemistry, which includes oxygenase and oxidase activity as well as the complex reactions

overseen by chlorophyll and vitamin B<sub>12</sub>.<sup>1</sup> Likewise, bimetallic systems such as certain cuproproteins play a major role in oxygen transport and oxidase activity.<sup>2</sup> Thus, both porphyrins and potentially binucleating ligands are being avidly investigated in a number of laboratories. In the macrocyclic realm, for example, the binuclear selection is extensive, including the relatively rigid side-by-side macrocycles like those first reported by Robson,<sup>3</sup> flexible macrocyclic inclusion complexes such as those of Lehn,<sup>4</sup> and the cofacial diporphyrins reported in 1977 by Collman<sup>5</sup> and Chang.<sup>6</sup>

With an eye to the importance of the porphyrins and their relatives in biological systems as well as the extensive role of metal-metal interactions in many biochemical reactions, we strove to design a hybrid porphyrin-like bimetallic system. Unlike the cofacial diporphyrins, however, this ligand would allow incorporation of the two metals within one ring system. In this manner, a less-hindered approach of substrate molecules was envisioned, while potentially maintaining at least some aspects of the tetrapyrrolic ring system. Hence, a novel macrocyclic ligand **1** was synthesized by a template-assisted Schiff base reaction of diamines with a 5,5'-diformyldipyrromethane.<sup>7</sup>



## Experimental Section

**Physical Measurements.** Infrared spectra were recorded from 4000 to 600 cm<sup>-1</sup> on an IBM IR-32. Electronic spectral data were obtained on a Hewlett-Packard Model 8450A diode array spectrophotometer from 800 to 230 nm. NMR spectra were recorded on a Varian XL-300 spectrometer, using TMS as an internal standard. EPR measurements were made on a Varian E-line Century Series spectrometer with a Varian E102 microwave bridge at X-band frequency. Solution conductivities were determined by using an Industrial Instruments, Inc., Model RC-216B2 conductivity bridge. Mass spectra were run by Dr. Charles Judson of the Mass Spectrometer Laboratory, University of Kansas, using a Ribermag R10-10 spectrometer. Elemental analyses for carbon, hydrogen, and nitrogen were performed at the Microanalytical Laboratory, University of Kansas, by Dr. Tho Nguyen, and at MicAnal-Organic Microanalysis, Tucson, AZ. Electrochemical measurements were obtained on a PAR 173 potentiostat/galvanostat equipped with a PAR 179 digital coulometer and a PAR 175 universal programmer. A three-electrode glass cell was used with a glassy carbon working electrode, a platinum wire counterelectrode, and saturated calomel as reference electrode. Data were collected at room temperature, and no correction was made for junction potentials. Controlled potential electrolyses were performed at a rotating platinum-mesh working electrode using the same instrumentation.

**Synthesis.** All the chemicals used were reagent grade. The abbreviations used for the ligands derive from their component parts, i.e., bi for two, dp for dipyrromethane, tmd for 1,3-propanediamine (trimethylenediamine), and en for ethylenediamine.

**4,16,20,32-Tetraethyl-5,15,21,31-tetramethyl-8,12,24,28,33,34,35,36-octaazapentacyclo[28.2.1.1<sup>3,6</sup>.1<sup>14,17</sup>.1<sup>19,22</sup>]hexatriaconta-**

**Table I.** Crystallographic Data for Cu<sub>2</sub>(bi-dptmd)(N<sub>3</sub>)<sub>2</sub>

compound	Cu <sub>2</sub> C <sub>40</sub> H <sub>50</sub> N <sub>14</sub> <sup>1</sup> /2CH <sub>3</sub> OH
fw	869.64
a, Å	18.508 (5)
b, Å	12.311 (3)
c, Å	20.185 (6)
β, deg	112.65 (3)
V, Å <sup>3</sup>	4244 (2)
ρ <sub>calcd</sub> , g cm <sup>-3</sup>	1.361
ρ <sub>obsd</sub> (flotation), g cm <sup>-3</sup>	1.36 (1)
Z	4
space group	P2 <sub>1</sub> /n
cryst dimens, mm	0.40 × 0.40 × 0.15
temp, °C	25
radiatn	Mo Kα
diffractometer	Syntex P <sub>2</sub>
μ, cm <sup>-1</sup>	10.93
2θ range, deg	4.0–45.0
no. indep. reflcns	5586
no. with I > 3σ(I)	4418
final R	0.068
final R <sub>w</sub>	0.076

**3,5,7,12,14,16,19,21,23,28,30,32-dodecaene (bi-dptmd-6H).** To a suspension of 3,3'-diethyl-5,5'-diformyl-4,4'-dimethyldipyrromethane<sup>8</sup> (100 mg, 0.350 mmol) in 90 mL of methanol, Ba(ClO<sub>4</sub>)<sub>2</sub> (118 mg, 0.350 mmol) and 1,3-propanediamine (29.2 μL, 0.350 mmol) were added, and the mixture was refluxed with stirring for 24 h. The fluffy white product, which begins to separate after 1 h, was collected by filtration, washed with methanol, and dried in vacuo: yield 97 mg (81%); mp 200 °C dec; MS, m/e 648 (M + 6); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.05 (12 H, t, CH<sub>2</sub>CH<sub>3</sub>), 1.80 (4H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.10 (12 H, s, CH<sub>3</sub>), 2.39 (8 H, q, CH<sub>2</sub>CH<sub>3</sub>), 3.50 (8 H, t, CH<sub>2</sub>N=), 3.80 (4 H, s, CH<sub>2</sub>), 8.03 (4 H, s, CH=N); <sup>13</sup>C NMR δ 150.29, 129.20, 125.71, 124.29, 122.51, 59.40, 33.68, 22.07, 17.40, 16.43, 8.82. The free ligand can also be obtained in an analogous fashion from Sr<sup>2+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> salts.

**M<sub>2</sub>(bi-dptmd)(X)<sub>2</sub> (M = Pb, Zn; X = SCN, Cl, respectively).** Finely divided MX<sub>2</sub> (0.9 mmol) was added to a suspension of 3,3'-diethyl-5,5'-diformyl-4,4'-dimethyldipyrromethane<sup>8</sup> (252 mg, 0.883 mmol) in 90 mL of methanol. To this mixture, 1,3-propanediamine (74.3 μL, 0.883 mmol) was added. The solution was refluxed for 8 h for the ZnCl<sub>2</sub> reaction, at which time the product had precipitated. The Pb(SCN)<sub>2</sub> reaction was refluxed for 24 h, followed by filtration while hot, and the product precipitated after standing at room temperature overnight. The microcrystalline products were filtered, washed with cold methanol and ether, and dried at 50 °C in vacuo: yield Pb<sub>2</sub>(bi-dptmd)(SCN)<sub>2</sub> 93 mg (18%); MS, m/e 1058 (M - 2SCN); <sup>1</sup>H NMR (Me<sub>2</sub>SO-d<sub>6</sub>) 1.12 (12 H, t, CH<sub>2</sub>CH<sub>3</sub>), 2.19 (16 H, b, CH<sub>3</sub> + CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.75 (8 H, q, CH<sub>2</sub>CH<sub>3</sub>), 3.76 (8 H, t, CH<sub>2</sub>N=), 7.36 (2 H, s, CH), 8.87 (4 H, s, CH=N-). Yield Zn<sub>2</sub>(bi-dptmd)(Cl)<sub>2</sub> 343 mg (80%); MS, m/e 774 (M - 2Cl). Sparging solubilities prevented the acquisition of NMR data.

**Cu<sub>2</sub>(bi-dptmd)(X)<sub>2</sub> (X = Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, or BF<sub>4</sub><sup>-</sup>).** These complexes can be obtained from direct reaction with the free ligand or metathesis with either the lead or zinc complex. The best yields are obtained from the metathesis reactions. Zn<sub>2</sub>(bi-dptmd)(Cl)<sub>2</sub> (72.9 mg, 0.083 mmol) was stirred under reflux in 30 mL of methanol. Cu(X)<sub>2</sub> (0.318 mmol) was added and the mixture refluxed for 4 h. AgClO<sub>4</sub> or AgBF<sub>4</sub> (0.160 mmol) was added at this point to the ClO<sub>4</sub><sup>-</sup> or BF<sub>4</sub><sup>-</sup> solution, respectively, and refluxing was continued an additional 1 h, followed by filtration to remove the AgCl. The filtrate was cooled, and the dark-blue crystalline product was separated by filtration and dried in vacuo: yield >60%; MS, m/e 769 (M - 2X).

**Cu<sub>2</sub>(bi-dptmd)(X)<sub>2</sub> (X = N<sub>3</sub>, SCN).** Cu<sub>2</sub>(bi-dptmd)(ClO<sub>4</sub>)<sub>2</sub> (66.4 mg, 0.069 mmol) was dissolved in 25 mL of methanol. The solution was stirred, and NaX<sub>2</sub> (0.277 mmol) was added. The solution was then brought to reflux slowly and refluxed for 2 h. Upon cooling of the solution, the brown microcrystalline product was separated by filtration and dried in vacuo: yield 60–80%; MS, m/e 769 (M - 2X). The azido complex was recrystallized by slow evaporation of a methanol solution to obtain crystals suitable for X-ray analysis.

**Zn<sub>2</sub>(bi-dpen)(Cl)<sub>2</sub>.** ZnCl<sub>2</sub> (57.5 mg, 0.428 mmol), 3,3'-diethyl-5,5'-diformyl-4,4'-dimethyldipyrromethane<sup>8</sup> (121.2 mg, 0.423 mmol) and ethylenediamine (28.2 μL, 0.423 mmol) were refluxed with stirring in 80 mL of methanol for 24 h. The brownish-pink product was separated by filtration and dried in vacuo: yield 141 mg (75%); MS, m/e unavailable due to decomposition.

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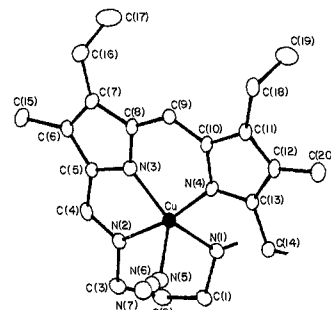
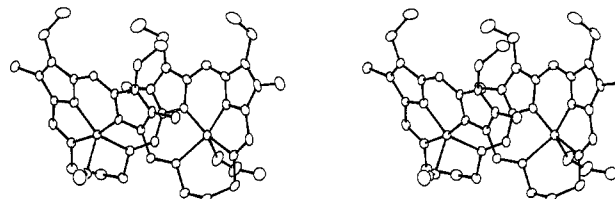
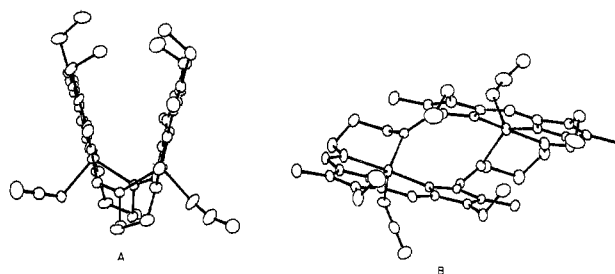
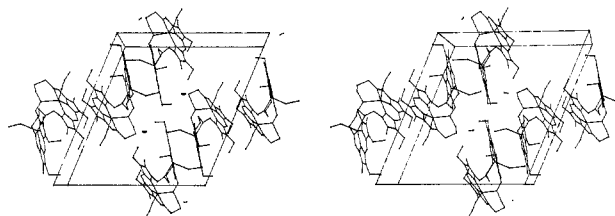
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**Table II.** Fractional Coordinates for  $\text{Cu}_2(\text{bi-dptmd})(\text{N}_3)_2$ 

atom	x	y	z
Cu <sub>A</sub>	0.718 29 (4)	0.210 02 (5)	0.848 15 (3)
Cu <sub>B</sub>	0.695 26 (4)	0.464 18 (6)	1.056 75 (4)
N <sub>A</sub> (1)	0.702 5 (3)	0.167 3 (4)	0.942 6 (2)
N <sub>A</sub> (2)	0.700 4 (3)	0.051 4 (4)	0.818 1 (3)
N <sub>A</sub> (3)	0.656 7 (3)	0.225 1 (4)	0.747 7 (2)
N <sub>A</sub> (4)	0.723 1 (3)	0.371 7 (4)	0.857 8 (2)
N <sub>A</sub> (5)	0.841 6 (3)	0.182 2 (5)	0.891 7 (3)
N <sub>A</sub> (6)	0.885 0 (3)	0.246 2 (5)	0.884 7 (3)
N <sub>A</sub> (7)	0.927 6 (4)	0.310 6 (6)	0.877 6 (5)
C <sub>A</sub> (1)	0.749 5 (4)	0.072 3 (5)	0.979 0 (3)
C <sub>A</sub> (2)	0.717 3 (4)	-0.029 8 (5)	0.934 5 (4)
C <sub>A</sub> (3)	0.734 0 (4)	-0.039 4 (5)	0.866 5 (4)
C <sub>A</sub> (4)	0.660 2 (4)	0.037 6 (5)	0.750 6 (3)
C <sub>A</sub> (5)	0.633 5 (3)	0.134 0 (5)	0.709 1 (3)
C <sub>A</sub> (6)	0.587 6 (3)	0.159 5 (5)	0.636 5 (3)
C <sub>A</sub> (7)	0.583 4 (4)	0.271 2 (5)	0.632 2 (3)
C <sub>A</sub> (8)	0.626 9 (3)	0.311 3 (4)	0.703 4 (3)
C <sub>A</sub> (9)	0.642 2 (4)	0.415 5 (4)	0.732 0 (3)
C <sub>A</sub> (10)	0.684 2 (3)	0.444 7 (4)	0.802 3 (3)
C <sub>A</sub> (11)	0.696 8 (4)	0.553 9 (4)	0.830 3 (3)
C <sub>A</sub> (12)	0.740 9 (4)	0.545 0 (4)	0.902 5 (3)
C <sub>A</sub> (13)	0.755 4 (3)	0.432 8 (4)	0.916 4 (3)
C <sub>A</sub> (14)	0.806 9 (3)	0.385 3 (4)	0.985 2 (3)
C <sub>A</sub> (15)	0.551 0 (4)	0.078 0 (6)	0.576 2 (3)
C <sub>A</sub> (16)	0.542 5 (5)	0.340 1 (6)	0.567 2 (4)
C <sub>A</sub> (17)	0.476 1 (6)	0.398 (1)	0.566 8 (5)
C <sub>A</sub> (18)	0.667 1 (4)	0.655 6 (5)	0.788 9 (3)
C <sub>A</sub> (19)	0.597 7 (5)	0.704 5 (6)	0.801 0 (5)
C <sub>A</sub> (20)	0.771 3 (4)	0.637 8 (5)	0.954 0 (3)
N <sub>B</sub> (1)	0.798 4 (3)	0.405 4 (4)	1.043 8 (2)
N <sub>B</sub> (2)	0.769 6 (3)	0.556 4 (4)	1.138 6 (2)
N <sub>B</sub> (3)	0.640 3 (3)	0.599 9 (4)	1.036 6 (3)
N <sub>B</sub> (4)	0.612 3 (3)	0.403 5 (4)	0.968 4 (2)
N <sub>B</sub> (5)	0.690 4 (5)	0.335 4 (6)	1.123 3 (3)
N <sub>B</sub> (6)	0.694 0 (5)	0.324 1 (7)	1.176 5 (3)
N <sub>B</sub> (7)	0.683 (1)	0.341 (1)	1.232 6 (9)
N <sub>B</sub> (7')	0.643 (2)	0.297 (3)	1.208 (2)
N <sub>B</sub> (7'')	0.762 (2)	0.297 (3)	1.237 (2)
C <sub>B</sub> (1)	0.860 7 (4)	0.369 5 (5)	1.111 8 (3)
C <sub>B</sub> (2)	0.896 8 (4)	0.467 6 (6)	1.158 6 (3)
C <sub>B</sub> (3)	0.844 1 (4)	0.519 5 (6)	1.192 9 (3)
C <sub>B</sub> (4)	0.747 3 (4)	0.655 9 (5)	1.137 9 (4)
C <sub>B</sub> (5)	0.673 5 (4)	0.683 0 (5)	1.080 1 (3)
C <sub>B</sub> (6)	0.625 7 (4)	0.776 2 (5)	1.058 7 (4)
C <sub>B</sub> (7)	0.560 0 (4)	0.747 6 (5)	0.999 8 (4)
C <sub>B</sub> (8)	0.570 2 (3)	0.635 0 (5)	0.985 8 (3)
C <sub>B</sub> (9)	0.525 6 (4)	0.564 5 (5)	0.932 7 (3)
C <sub>B</sub> (10)	0.545 2 (3)	0.459 0 (5)	0.923 1 (3)
C <sub>B</sub> (11)	0.500 8 (4)	0.387 1 (5)	0.865 3 (3)
C <sub>B</sub> (12)	0.542 5 (4)	0.292 2 (5)	0.875 2 (3)
C <sub>B</sub> (13)	0.609 5 (3)	0.306 2 (4)	0.938 8 (3)
C <sub>B</sub> (14)	0.667 0 (3)	0.222 1 (5)	0.974 6 (3)
C <sub>B</sub> (15)	0.644 7 (5)	0.887 6 (6)	1.094 3 (5)
C <sub>B</sub> (16)	0.490 3 (4)	0.815 8 (6)	0.958 5 (4)
C <sub>B</sub> (17)	0.492 1 (6)	0.868 6 (9)	0.893 3 (6)
C <sub>B</sub> (18)	0.422 3 (4)	0.411 8 (7)	0.806 9 (4)
C <sub>B</sub> (19)	0.429 1 (7)	0.433 (1)	0.737 5 (6)
C <sub>B</sub> (20)	0.519 1 (4)	0.191 7 (6)	0.830 5 (4)
O <sub>Me</sub>	0.583 2 (8)	0.229 (1)	0.384 (1)
C <sub>Me</sub>	0.603 (1)	0.326 (1)	0.382 (1)

$\text{Cu}_2(\text{bi-dpen})(\text{ClO}_4)_2$ ,  $\text{Zn}_2(\text{bi-dpen})(\text{Cl})_2$  (50.9 mg, 0.057 mmol) and  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (85 mg, 0.228 mmol) were refluxed with stirring in 30 mL of methanol for 4 h. The unreacted  $\text{Zn}_2(\text{bi-dpen})(\text{Cl})_2$  was filtered and the filtrate was reduced to half its original volume. The blue microcrystalline product precipitated, was filtered, and dried in vacuo at 50 °C: yield 29 mg (54%); MS,  $m/e$  741 ( $\text{M}-2\text{ClO}_4$ ).

**X-ray Data.** Crystal data information is given in Table I. Preliminary measurements indicated monoclinic symmetry with systematic absences,  $0k0$ ,  $k = 2n + 1$ , and  $h0l$ ,  $h + l = 2n + 1$ , indicative of the space group  $P2_1/n$ , a nonstandard setting of  $P2_1/c$ . Unit cell parameters were derived from a least-squares fit of 15 reflections with  $2\theta > 20.0^\circ$ . Three standard reflections, chosen and monitored every 100 reflections, showed a maximum correction factor of 1.10, which was subsequently applied to the data. The data were collected on a Syntex P2<sub>1</sub> diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). Lorentz and polarization factors were applied to obtain structure factors, and an

**Figure 1.** Numbering scheme for  $\text{Cu}_2(\text{bi-dptmd})(\text{N}_3)_2$ .**Figure 2.** Stereoview of  $\text{Cu}_2(\text{bi-dptmd})(\text{N}_3)_2$ .**Figure 3.** (A) Perspective view of  $\text{Cu}_2(\text{bi-dptmd})(\text{N}_3)_2$  showing the hydrophobic walls provided by the dipyrromethenes. (B) View Looking "down" into the walled cavity.**Figure 4.** Packing diagram for  $\text{Cu}_2(\text{bi-dptmd})(\text{N}_3)_2$  as viewed down the  $b$  axis,  $a$  axis horizontal.

absorption correction was applied by using an empirical method.<sup>9</sup>

**Solution and Refinement.** The positions of the copper atoms were determined from a Patterson map, and a subsequent Fourier synthesis based on copper phasing revealed the remaining non-hydrogen atoms.<sup>10</sup> Refinement was performed by using block-diagonal least-squares techniques, for which the scale factor and overall thermal factor were put in one block, while the positional and thermal parameters of each atom were put in individual blocks ( $9 \times 9$ ) for non-hydrogen atoms, ( $1 \times 1$ ) for hydrogen atoms, and ( $4 \times 4$ ) for  $\text{N}_B(7)$ ,  $\text{N}_B(7')$ , and  $\text{N}_B(7'')$ .

Initial refinement and Fourier maps indicated the presence of two disordered species: a partial methanol of crystallization and one of the coordinated azides. The disorder about the methanol was manifested by residual electron density in that region after refinement and a short C—O distance. Since this was not the major region of interest, and no straightforward model could be found to account for the disorder, the original positions were maintained. For one of the azides, large temperature factors were noted for all three nitrogens, especially the terminal one. Several models were examined in order to describe this disorder, the best of which was to assign three positions to the terminal nitrogen,

(9) The programs were written in the DNA system by Dr. Fusao Takusagawa. All calculations were performed on a Honeywell 66/6000 computer at the University of Kansas.

(10) Atomic scattering factors were taken from: Cromer, D. T.; Weber, J. T., "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2A, 2.2B, and 2.3.1.

Table III. Interatomic Distances for Cu<sub>2</sub>(bi-dptmd)(N<sub>3</sub>)<sub>2</sub>

atoms	distances, Å	atoms	distances, Å
Cu <sub>A</sub> -Cu <sub>B</sub>	5.393 (2)	Cu <sub>B</sub> -N <sub>B</sub> (1)	2.150 (5)
Cu <sub>A</sub> -N <sub>A</sub> (1)	2.103 (5)	Cu <sub>B</sub> -N <sub>B</sub> (2)	2.039 (5)
Cu <sub>A</sub> -N <sub>A</sub> (2)	2.034 (5)	Cu <sub>B</sub> -N <sub>B</sub> (3)	1.917 (5)
Cu <sub>A</sub> -N <sub>A</sub> (3)	1.914 (4)	Cu <sub>B</sub> -N <sub>B</sub> (4)	1.997 (4)
Cu <sub>A</sub> -N <sub>A</sub> (4)	1.999 (4)	Cu <sub>B</sub> -N <sub>B</sub> (5)	2.103 (7)
Cu <sub>A</sub> -N <sub>A</sub> (5)	2.134 (5)	N <sub>B</sub> (1)-C <sub>B</sub> (1)	1.479 (6)
N <sub>A</sub> (1)-C <sub>A</sub> (1)	1.474 (7)	N <sub>B</sub> (1)-C <sub>A</sub> (14)	1.277 (8)
N <sub>A</sub> (1)-C <sub>B</sub> (14)	1.277 (9)	N <sub>B</sub> (2)-C <sub>B</sub> (3)	1.465 (8)
N <sub>A</sub> (2)-C <sub>A</sub> (3)	1.457 (7)	N <sub>B</sub> (2)-C <sub>B</sub> (4)	1.292 (9)
N <sub>A</sub> (2)-C <sub>B</sub> (4)	1.287 (7)	N <sub>B</sub> (3)-C <sub>B</sub> (5)	1.334 (7)
N <sub>A</sub> (3)-C <sub>A</sub> (5)	1.338 (7)	N <sub>B</sub> (3)-C <sub>B</sub> (8)	1.377 (7)
N <sub>A</sub> (3)-C <sub>A</sub> (8)	1.360 (7)	N <sub>B</sub> (4)-C <sub>B</sub> (10)	1.404 (7)
N <sub>A</sub> (4)-C <sub>A</sub> (10)	1.400 (6)	N <sub>B</sub> (4)-C <sub>B</sub> (13)	1.330 (7)
N <sub>A</sub> (4)-C <sub>A</sub> (13)	1.333 (6)	N <sub>B</sub> (5)-N <sub>B</sub> (6)	1.058 (10)
N <sub>A</sub> (5)-N <sub>A</sub> (6)	1.172 (8)	N <sub>B</sub> (6)-N <sub>B</sub> (7)	1.241 (22)
N <sub>A</sub> (6)-N <sub>A</sub> (7)	1.164 (11)	N <sub>B</sub> (6)-N <sub>B</sub> (7')	1.363 (43)
C <sub>A</sub> (1)-C <sub>A</sub> (2)	1.526 (8)	N <sub>B</sub> (6)-N <sub>B</sub> (7'')	1.415 (34)
C <sub>A</sub> (2)-C <sub>A</sub> (3)	1.524 (12)	C <sub>B</sub> (1)-C <sub>B</sub> (2)	1.520 (9)
C <sub>A</sub> (4)-C <sub>A</sub> (5)	1.426 (8)	C <sub>B</sub> (2)-C <sub>B</sub> (3)	1.536 (12)
C <sub>A</sub> (5)-C <sub>A</sub> (6)	1.418 (7)	C <sub>B</sub> (4)-C <sub>B</sub> (5)	1.452 (8)
C <sub>A</sub> (6)-C <sub>A</sub> (7)	1.378 (9)	C <sub>B</sub> (5)-C <sub>B</sub> (6)	1.411 (9)
C <sub>A</sub> (6)-C <sub>A</sub> (15)	1.521 (9)	C <sub>B</sub> (6)-C <sub>B</sub> (7)	1.380 (8)
C <sub>A</sub> (7)-C <sub>A</sub> (8)	1.437 (7)	C <sub>B</sub> (6)-C <sub>B</sub> (15)	1.524 (10)
C <sub>A</sub> (7)-C <sub>A</sub> (16)	1.500 (9)	C <sub>B</sub> (7)-C <sub>B</sub> (8)	1.442 (8)
C <sub>A</sub> (8)-C <sub>A</sub> (9)	1.391 (8)	C <sub>B</sub> (7)-C <sub>B</sub> (16)	1.495 (9)
C <sub>A</sub> (9)-C <sub>A</sub> (10)	1.377 (7)	C <sub>B</sub> (8)-C <sub>B</sub> (9)	1.379 (8)
C <sub>A</sub> (10)-C <sub>A</sub> (11)	1.442 (7)	C <sub>B</sub> (9)-C <sub>B</sub> (10)	1.382 (9)
C <sub>A</sub> (11)-C <sub>A</sub> (12)	1.373 (7)	C <sub>B</sub> (10)-C <sub>B</sub> (11)	1.442 (8)
C <sub>A</sub> (11)-C <sub>A</sub> (18)	1.488 (8)	C <sub>B</sub> (11)-C <sub>B</sub> (12)	1.371 (9)
C <sub>A</sub> (12)-C <sub>A</sub> (13)	1.414 (7)	C <sub>B</sub> (11)-C <sub>B</sub> (18)	1.509 (8)
C <sub>A</sub> (12)-C <sub>A</sub> (20)	1.501 (8)	C <sub>B</sub> (12)-C <sub>B</sub> (13)	1.410 (7)
C <sub>A</sub> (13)-C <sub>A</sub> (14)	1.468 (7)	C <sub>B</sub> (12)-C <sub>B</sub> (20)	1.493 (9)
C <sub>A</sub> (16)-C <sub>A</sub> (17)	1.414 (15)	C <sub>B</sub> (13)-C <sub>B</sub> (14)	1.462 (7)
C <sub>A</sub> (18)-C <sub>A</sub> (19)	1.521 (13)	C <sub>B</sub> (16)-C <sub>B</sub> (17)	1.481 (16)
		C <sub>B</sub> (18)-C <sub>B</sub> (19)	1.477 (16)
		O <sub>Me</sub> -C <sub>Me</sub>	1.260 (23)

i.e., N<sub>B</sub>(7), N<sub>B</sub>(7'), and N<sub>B</sub>(7''), and to allow the two remaining nitrogens to vibrate anisotropically while the N(7)'s were kept isotropic. Hamilton's R-value test after subsequent refinement indicated that the disordered model gave significantly better fit to the data than an ordered model (99.5% confidence level).<sup>11</sup> Final refinements, in which hydrogen atom positions were included (except for the methanol molecule) and their isotropic thermal parameters refined, resulted in convergence at  $R = 0.068$  and  $R_w = 0.076$ . The highest peak found in a difference Fourier map at this point was 0.67 e/Å<sup>3</sup>. Atom numbering is shown in Figure 1, stereoscopic and perspective views in Figures 2 and 3, and a packing diagram in Figure 4. Final positional parameters, bond lengths, and bond angles of interest are provided in Tables II, III, and IV, respectively.

## Results and Discussion

**Synthesis.** Elemental analyses for the complexes agreed well with calculated values. Both lead(II) and zinc(II) could be utilized as templates in ligand synthesis, the latter with shorter reaction times and higher yields. When other metal salts with relatively weak coordination tendencies were used, e.g., barium(II), strontium(II), calcium(II), and magnesium(II), the uncomplexed free ligand was isolated for the 1,3-diaminopropane reactions. <sup>1</sup>H and <sup>13</sup>C NMR data indicated the product to be the dihydro-bis(dipyrromethane) form of **1**. Either direct reaction of the metal salts with the free ligand or metathesis with either the lead(II) or zinc(II) complex is a viable avenue to a variety of metal complexes. The ethylenediamine-derived ligand, bi-dpen, was not readily isolable in its free-base form, possibly due to a more strained structure induced by the shorter diamine.

**Physical Properties.** Several conformers are possible, which are the result of the orientation of the imine, i.e., whether pointed "into" or "out of" the macrocyclic cavity. As will be seen, the crystal structure of Cu<sub>2</sub>(bi-dptmd)(N<sub>3</sub>)<sub>2</sub> revealed an "in-out" structure for the coordinated ligand.

The N<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> anions are coordinated according to solution conductivity measurements, which showed these complexes to be

Table IV. Bond Angles in Cu<sub>2</sub>(bi-dptmd)(N<sub>3</sub>)<sub>2</sub>

atoms	angle, deg	atoms	angle, deg
N <sub>A</sub> (1)-Cu <sub>A</sub> -N <sub>A</sub> (2)	88.1 (2)	N <sub>A</sub> (1)-C <sub>A</sub> (1)-C <sub>A</sub> (2)	109.7 (4)
N <sub>A</sub> (1)-Cu <sub>A</sub> -N <sub>A</sub> (3)	138.6 (2)	C <sub>A</sub> (1)-C <sub>A</sub> (2)-C <sub>A</sub> (3)	115.2 (6)
N <sub>A</sub> (1)-Cu <sub>A</sub> -N <sub>A</sub> (4)	100.2 (2)	N <sub>A</sub> (2)-C <sub>A</sub> (3)-C <sub>A</sub> (2)	111.2 (6)
N <sub>A</sub> (1)-Cu <sub>A</sub> -N <sub>A</sub> (5)	95.0 (2)	N <sub>A</sub> (2)-C <sub>A</sub> (4)-C <sub>A</sub> (5)	116.1 (5)
N <sub>A</sub> (2)-Cu <sub>A</sub> -N <sub>A</sub> (3)	79.3 (2)	N <sub>A</sub> (3)-C <sub>A</sub> (5)-C <sub>A</sub> (4)	113.2 (4)
N <sub>A</sub> (2)-Cu <sub>A</sub> -N <sub>A</sub> (4)	168.9 (2)	N <sub>A</sub> (3)-C <sub>A</sub> (5)-C <sub>A</sub> (6)	110.3 (5)
N <sub>A</sub> (2)-Cu <sub>A</sub> -N <sub>A</sub> (5)	89.7 (2)	C <sub>A</sub> (4)-C <sub>A</sub> (5)-C <sub>A</sub> (6)	136.5 (5)
N <sub>A</sub> (3)-Cu <sub>A</sub> -N <sub>A</sub> (4)	89.6 (2)	C <sub>A</sub> (5)-C <sub>A</sub> (6)-C <sub>A</sub> (7)	106.4 (5)
N <sub>A</sub> (3)-Cu <sub>A</sub> -N <sub>A</sub> (5)	123.9 (2)	C <sub>A</sub> (5)-C <sub>A</sub> (6)-C <sub>A</sub> (15)	125.9 (5)
N <sub>A</sub> (4)-Cu <sub>A</sub> -N <sub>A</sub> (5)	96.8 (2)	C <sub>A</sub> (7)-C <sub>A</sub> (6)-C <sub>A</sub> (15)	127.7 (5)
N <sub>B</sub> (1)-Cu <sub>B</sub> -N <sub>B</sub> (2)	86.1 (2)	C <sub>A</sub> (6)-C <sub>A</sub> (7)-C <sub>A</sub> (8)	106.5 (5)
N <sub>B</sub> (1)-Cu <sub>B</sub> -N <sub>B</sub> (3)	133.7 (2)	C <sub>A</sub> (6)-C <sub>A</sub> (7)-C <sub>A</sub> (16)	128.0 (5)
N <sub>B</sub> (1)-Cu <sub>B</sub> -N <sub>B</sub> (4)	100.3 (2)	C <sub>A</sub> (8)-C <sub>A</sub> (7)-C <sub>A</sub> (16)	125.5 (6)
N <sub>B</sub> (1)-Cu <sub>B</sub> -N <sub>B</sub> (5)	94.7 (3)	N <sub>A</sub> (3)-C <sub>A</sub> (8)-C <sub>A</sub> (7)	108.6 (5)
N <sub>B</sub> (2)-Cu <sub>B</sub> -N <sub>B</sub> (3)	79.8 (2)	N <sub>A</sub> (3)-C <sub>A</sub> (8)-C <sub>A</sub> (9)	118.7 (4)
N <sub>B</sub> (2)-Cu <sub>B</sub> -N <sub>B</sub> (4)	168.1 (2)	C <sub>A</sub> (7)-C <sub>A</sub> (8)-C <sub>A</sub> (9)	137.7 (5)
N <sub>B</sub> (2)-Cu <sub>B</sub> -N <sub>B</sub> (5)	94.8 (2)	C <sub>A</sub> (8)-C <sub>B</sub> (9)-C <sub>A</sub> (10)	127.8 (5)
N <sub>B</sub> (3)-Cu <sub>B</sub> -N <sub>B</sub> (4)	88.5 (2)	N <sub>A</sub> (4)-C <sub>A</sub> (10)-C <sub>A</sub> (9)	124.7 (5)
N <sub>B</sub> (3)-Cu <sub>B</sub> -N <sub>B</sub> (5)	130.0 (3)	N <sub>A</sub> (4)-C <sub>A</sub> (10)-C <sub>A</sub> (11)	109.2 (4)
N <sub>B</sub> (4)-Cu <sub>B</sub> -N <sub>B</sub> (5)	94.7 (2)	C <sub>A</sub> (9)-C <sub>A</sub> (10)-C <sub>A</sub> (11)	126.0 (5)
C <sub>A</sub> (1)-N <sub>A</sub> (1)-C <sub>B</sub> (14)	119.1 (5)	C <sub>A</sub> (10)-C <sub>A</sub> (11)-C <sub>A</sub> (12)	106.4 (4)
C <sub>A</sub> (3)-N <sub>A</sub> (2)-C <sub>A</sub> (4)	122.2 (5)	C <sub>A</sub> (10)-C <sub>A</sub> (11)-C <sub>A</sub> (18)	126.6 (5)
C <sub>A</sub> (5)-N <sub>A</sub> (3)-C <sub>A</sub> (8)	108.2 (4)	C <sub>A</sub> (12)-C <sub>A</sub> (11)-C <sub>A</sub> (18)	127.1 (5)
C <sub>A</sub> (10)-N <sub>A</sub> (4)-C <sub>A</sub> (13)	105.3 (4)	C <sub>A</sub> (11)-C <sub>A</sub> (12)-C <sub>A</sub> (13)	106.2 (5)
N <sub>A</sub> (5)-N <sub>A</sub> (6)-N <sub>A</sub> (7)	179.4 (7)	C <sub>A</sub> (11)-C <sub>A</sub> (12)-C <sub>A</sub> (20)	125.8 (5)
C <sub>A</sub> (13)-C <sub>A</sub> (14)-C <sub>A</sub> (20)	127.8 (5)	C <sub>B</sub> (6)-C <sub>B</sub> (7)-C <sub>B</sub> (8)	106.0 (5)
N <sub>A</sub> (4)-C <sub>A</sub> (13)-C <sub>A</sub> (12)	112.9 (4)	C <sub>B</sub> (6)-C <sub>B</sub> (7)-C <sub>B</sub> (16)	128.5 (6)
N <sub>A</sub> (4)-C <sub>A</sub> (13)-C <sub>A</sub> (14)	121.3 (5)	C <sub>B</sub> (8)-C <sub>B</sub> (7)-C <sub>B</sub> (16)	125.5 (5)
C <sub>A</sub> (12)-C <sub>A</sub> (13)-C <sub>A</sub> (14)	125.5 (4)	N <sub>B</sub> (3)-C <sub>B</sub> (8)-C <sub>B</sub> (7)	108.2 (5)
C <sub>A</sub> (13)-C <sub>A</sub> (14)-N <sub>B</sub> (1)	122.2 (5)	N <sub>B</sub> (3)-C <sub>B</sub> (8)-C <sub>B</sub> (9)	119.5 (5)
C <sub>A</sub> (7)-C <sub>A</sub> (16)-C <sub>A</sub> (17)	115.7 (8)	C <sub>B</sub> (7)-C <sub>B</sub> (8)-C <sub>B</sub> (9)	132.3 (5)
C <sub>A</sub> (11)-C <sub>A</sub> (18)-C <sub>A</sub> (19)	113.3 (7)	C <sub>B</sub> (8)-C <sub>B</sub> (9)-C <sub>B</sub> (10)	126.2 (5)
C <sub>A</sub> (14)-N <sub>B</sub> (1)-C <sub>B</sub> (1)	118.2 (5)	N <sub>B</sub> (4)-C <sub>B</sub> (10)-C <sub>B</sub> (9)	125.4 (5)
C <sub>B</sub> (3)-N <sub>B</sub> (2)-C <sub>B</sub> (4)	120.5 (5)	N <sub>B</sub> (4)-C <sub>B</sub> (10)-C <sub>B</sub> (11)	108.3 (5)
C <sub>B</sub> (5)-N <sub>B</sub> (3)-C <sub>B</sub> (8)	108.2 (5)	C <sub>B</sub> (9)-C <sub>B</sub> (10)-C <sub>B</sub> (11)	126.3 (5)
C <sub>B</sub> (10)-N <sub>B</sub> (4)-C <sub>B</sub> (13)	105.9 (4)	C <sub>B</sub> (10)-C <sub>B</sub> (11)-C <sub>B</sub> (12)	107.0 (5)
N <sub>B</sub> (5)-N <sub>B</sub> (6)-N <sub>B</sub> (7)	159.3 (12)	C <sub>B</sub> (10)-C <sub>B</sub> (11)-C <sub>B</sub> (18)	125.9 (6)
N <sub>B</sub> (5)-N <sub>B</sub> (6)-N <sub>B</sub> (7')	135.9 (14)	C <sub>B</sub> (12)-C <sub>B</sub> (11)-C <sub>B</sub> (18)	127.1 (6)
N <sub>B</sub> (5)-N <sub>B</sub> (6)-N <sub>B</sub> (7'')	126.4 (22)	C <sub>B</sub> (11)-C <sub>B</sub> (12)-C <sub>B</sub> (13)	106.0 (5)
N <sub>B</sub> (1)-C <sub>B</sub> (1)-C <sub>B</sub> (2)	109.8 (5)	C <sub>B</sub> (11)-C <sub>B</sub> (12)-C <sub>B</sub> (20)	127.0 (5)
C <sub>B</sub> (1)-C <sub>B</sub> (2)-C <sub>B</sub> (3)	114.0 (6)	C <sub>B</sub> (13)-C <sub>B</sub> (12)-C <sub>B</sub> (20)	126.8 (5)
N <sub>B</sub> (2)-C <sub>B</sub> (3)-C <sub>B</sub> (2)	111.7 (5)	N <sub>B</sub> (4)-C <sub>B</sub> (13)-C <sub>B</sub> (12)	112.8 (5)
N <sub>B</sub> (2)-C <sub>B</sub> (4)-C <sub>B</sub> (5)	115.2 (5)	N <sub>B</sub> (4)-C <sub>B</sub> (13)-C <sub>B</sub> (14)	121.4 (4)
N <sub>B</sub> (3)-C <sub>B</sub> (5)-C <sub>B</sub> (4)	113.9 (5)	C <sub>B</sub> (12)-C <sub>B</sub> (13)-C <sub>B</sub> (14)	125.5 (5)
N <sub>B</sub> (3)-C <sub>B</sub> (5)-C <sub>B</sub> (6)	110.3 (5)	N <sub>A</sub> (1)-C <sub>B</sub> (14)-C <sub>B</sub> (13)	122.9 (5)
C <sub>B</sub> (4)-C <sub>B</sub> (5)-C <sub>B</sub> (6)	135.8 (6)	C <sub>B</sub> (7)-C <sub>B</sub> (16)-C <sub>B</sub> (17)	115.6 (8)
C <sub>B</sub> (5)-C <sub>B</sub> (6)-C <sub>B</sub> (7)	107.3 (5)	C <sub>B</sub> (11)-C <sub>B</sub> (18)-C <sub>B</sub> (19)	111.5 (8)
C <sub>B</sub> (5)-C <sub>B</sub> (6)-C <sub>B</sub> (15)	125.7 (5)		
C <sub>B</sub> (7)-C <sub>B</sub> (6)-C <sub>B</sub> (15)	127.0 (6)		

nonelectrolytes. Unfortunately, solubility difficulties prevented measurements for the NCS<sup>-</sup> salt of copper(II), although it is also anticipated to be coordinated on the basis of similarities with the aforementioned anions in the other physical properties.

EPR measurements were made at room temperature for ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, N<sub>3</sub><sup>-</sup>, and NCS<sup>-</sup> salts of Cu<sub>2</sub>(bi-dptmd)<sup>2+</sup>. Both solution (CH<sub>2</sub>Cl<sub>2</sub>) and microcrystalline samples showed the presence of a signal centered at  $g = 2.18-2.21$ . Further magnetic measurements are currently in progress.

Infrared spectral data indicate that more than one conformer is present in these complexes. While the general trends in the infrared spectra from 4000 to 600 cm<sup>-1</sup> are very similar, certain features are distinctly different, especially for the C=N stretch (Table V). All the complexes with Cl<sup>-</sup> as the anion exhibit a C=N stretch at 1651-1653 cm<sup>-1</sup>, which may be indicative of uncoordinated imine as observed in other Schiff base complexes.<sup>12</sup> Because of the propensity of Cl<sup>-</sup> to bridge two metals and the particular tendency of zinc(II) to form tetrahedral, four-coordinate complexes, tetrahedral or pseudotetrahedral (for the copper(II) ion) coordination, with the imine nitrogens not coordinated, is a

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**Table V.** Infrared<sup>a</sup> and Electronic Spectral Data<sup>b</sup> for M<sub>2</sub>(bi-dptmd)<sup>2+</sup> and M<sub>2</sub>(bi-dpen)<sup>2+</sup> Complexes

complex	$\nu_{C=N}^c$	$\lambda_{max}, \text{cm}^{-1} (\log \epsilon)$
bi-dptmd·6H	1634 s	298 (4.30); 365 (sh)
Pb <sub>2</sub> (bi-dptmd)(SCN) <sub>2</sub>	~1635 (sh)	258 (sh); 306 (4.69); 440 (3.88); 568 (4.76); 594 (4.81)
Zn <sub>2</sub> (bi-dptmd)(Cl) <sub>2</sub> <sup>d</sup>	1651 vs	296 (4.56); 328 (sh); 372 (sh); 532 (4.45); 564 (4.43)
Cu <sub>2</sub> (bi-dptmd)(ClO <sub>4</sub> ) <sub>2</sub>	1636 w	204 (4.48); 316 (4.54); 478 (sh); 533 (sh); 622 (4.37); 680 (4.28)
Cu <sub>2</sub> (bi-dptmd)(BF <sub>4</sub> ) <sub>2</sub>	1637 w	238 (sh); 314 (4.55); 478 (sh); 533 (sh); 622 (4.38); 682 (4.29)
Cu <sub>2</sub> (bi-dptmd)(Cl) <sub>2</sub>	1653 m	236 (4.65); 308 (4.71); 367 (sh); 446 (sh); 563 (sh); 600 (4.54)
Cu <sub>2</sub> (bi-dptmd)(N <sub>3</sub> ) <sub>2</sub>	1636 m	240 (4.51); 308 (4.58); 450 (sh); 594 (4.48)
Cu <sub>2</sub> (bi-dptmd)(NCS) <sub>2</sub>	1637 w	240 (sh); 308 (4.58); 354 (sh); 446 (sh); 588 (4.49)
Zn <sub>2</sub> (bi-dpen)(Cl) <sub>2</sub> <sup>d,e</sup>	1653 vs	299; 317 (sh); 364 (sh); 572
Cu <sub>2</sub> (bi-dpen)(ClO <sub>4</sub> ) <sub>2</sub>	~1635 (sh)	238 (4.91); 326 (4.08); 476 (sh); 632 (4.62); 681 (sh)

<sup>a</sup>All spectra were recorded as KBr pellets. Frequencies are reported in cm<sup>-1</sup>. <sup>b</sup>Measured in CH<sub>2</sub>Cl<sub>2</sub> unless stated otherwise. <sup>c</sup>Key: vs, very strong; s, strong; m, medium; w, weak. <sup>d</sup>CH<sub>3</sub>CN. <sup>e</sup> $\epsilon$  not reported because of sparing solubility.

distinct possibility. The remaining complexes maintain a C=N stretch clearly in the region anticipated for coordinated C=N, i.e., between 1634 and 1637 cm<sup>-1</sup>, although in Pb<sub>2</sub>(bi-dptmd)(SCN)<sub>2</sub> and Cu<sub>2</sub>(bi-dpen)(ClO<sub>4</sub>)<sub>2</sub> only shoulders are observed. That the free ligand also displays a band in this region can be rationalized in terms of hydrogen binding of the pyrrole hydrogens with the imine nitrogens, effectively lowering the C=N bond order. The spectral characteristics of the dipyrromethene fragments are analogous to those observed for porphodimethenes (dihydroporphyrins).<sup>13</sup> A methene band is observed between 1590 and 1620 cm<sup>-1</sup>, and additional bands occur at 850, 1000, and 1220 cm<sup>-1</sup>.

The electronic spectra also indicate the presence of different structural forms and consist of several intense bands in the UV and visible regions, which are most probably related to  $\pi-\pi^*$  transitions or M  $\rightarrow$  L charge transfer as observed for dipyrromethene<sup>14,15</sup> and porphodimethene<sup>16</sup> complexes and porphyrins.<sup>17</sup> The copper(II) complexes show two distinct patterns in the electronic spectra depending on the coordination mode of the anion (Table V). In addition to two intense bands in the UV region, both the ClO<sub>4</sub><sup>-</sup> and BF<sub>4</sub><sup>-</sup> complexes have two strong absorptions separated by 60 nm in the 600–700-nm region in addition to two shoulders at higher energy, whereas the Cl<sup>-</sup>, N<sub>3</sub><sup>-</sup>, and NCS<sup>-</sup> salts exhibit a broad intense absorption around 600 nm. Thus, the complexes with coordinated anions are apparently isostructural in solution as are the ClO<sub>4</sub><sup>-</sup> and BF<sub>4</sub><sup>-</sup> complexes. The solution spectra of these latter two salts are also solvent-dependent, unlike those with coordinated anions. In coordinating solvents such as CH<sub>3</sub>CN, the spectra of the ClO<sub>4</sub><sup>-</sup> and BF<sub>4</sub><sup>-</sup> complexes more closely approach those of the other three copper(II) salts. The spectrum

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**Table VI.** Selected Least-Squares Planes and Atom Displacements for Cu<sub>2</sub>(bi-dptmd)(N<sub>3</sub>)<sub>2</sub>

atom	distance, Å	atom	distance, Å
A. Cu <sub>A</sub> -N <sub>A</sub> (1)-N <sub>A</sub> (3)-N <sub>A</sub> (5)			
0.006X + 0.980Y + 0.197Z = 5.558			
Cu <sub>A</sub>	0.132	N <sub>A</sub> (3)	-0.057
N <sub>A</sub> (1)	-0.042	N <sub>A</sub> (5)	-0.033
B. Cu <sub>B</sub> -N <sub>B</sub> (1)-N <sub>B</sub> (3)-N <sub>B</sub> (5)			
0.326X + 0.444Y + 0.834Z = 20.586			
Cu <sub>B</sub>	-0.104	N <sub>B</sub> (3)	0.044
N <sub>B</sub> (1)	0.030	N <sub>B</sub> (5)	0.029
C. Cu <sub>A</sub> -N <sub>A</sub> (2)-C <sub>A</sub> (4)-N <sub>A</sub> (3)-C <sub>A</sub> (5)-C <sub>A</sub> (6)-C <sub>A</sub> (7)-C <sub>A</sub> (8)-C <sub>A</sub> (9)-C <sub>A</sub> (10)-C <sub>A</sub> (11)-C <sub>A</sub> (12)-C <sub>A</sub> (13)-N <sub>A</sub> (4)			
0.981X + 0.032Y - 0.189Z = 3.650			
Cu <sub>A</sub>	0.018	C <sub>A</sub> (8)	0.013
N <sub>A</sub> (2)	-0.035	C <sub>A</sub> (9)	0.011
C <sub>A</sub> (4)	-0.017	C <sub>A</sub> (10)	0.004
N <sub>A</sub> (3)	0.026	C <sub>A</sub> (11)	-0.037
C <sub>A</sub> (5)	-0.002	C <sub>A</sub> (12)	-0.046
C <sub>A</sub> (6)	-0.014	C <sub>A</sub> (13)	0.018
C <sub>A</sub> (7)	0.001	N <sub>A</sub> (4)	0.061
D. Cu <sub>B</sub> -N <sub>B</sub> (2)-C <sub>B</sub> (4)-N <sub>B</sub> (3)-C <sub>B</sub> (5)-C <sub>B</sub> (6)-C <sub>B</sub> (7)-C <sub>B</sub> (8)-C <sub>B</sub> (9)-C <sub>B</sub> (10)-C <sub>B</sub> (11)-C <sub>B</sub> (12)-C <sub>B</sub> (13)-N <sub>B</sub> (4)			
-0.7678X - 0.306Y + 0.563Z = 5.681			
Cu <sub>B</sub>	0.082	C <sub>B</sub> (8)	0.048
N <sub>B</sub> (2)	0.026	C <sub>B</sub> (9)	0.073
C <sub>B</sub> (4)	-0.045	C <sub>B</sub> (10)	0.034
N <sub>B</sub> (3)	0.019	C <sub>B</sub> (11)	-0.016
C <sub>B</sub> (5)	-0.049	C <sub>B</sub> (12)	-0.087
C <sub>B</sub> (6)	-0.073	C <sub>B</sub> (13)	-0.046
C <sub>B</sub> (7)	-0.001	N <sub>B</sub> (4)	0.035

<sup>a</sup>The coordinate system used for the least-squares plane is  $X = ax + cz \cos \beta$ ,  $Y = by$ , and  $Z = cz \sin \beta$ , where  $x$ ,  $y$ , and  $z$  are fractional coordinates and  $a$ ,  $b$ ,  $c$ , and  $\beta$  are unit cell parameters.

of the lead(II) complex clearly resembles those of the Cl<sup>-</sup>, N<sub>3</sub><sup>-</sup>, and NCS<sup>-</sup> complexes. The zinc(II) complexes, on the other hand, show two intense bands in the 500–600-nm regions and are probably tetrahedral both in solution and solid state.

**Crystal Structure of Cu<sub>2</sub>(bi-dptmd)(N<sub>3</sub>)<sub>2</sub>.** The structure of the dicopper complex revealed a somewhat unanticipated overall geometry. Each copper(II) ion is coordinated to four ligand nitrogens and an azide, and the ligand is in the "in-out" geometry with respect to imine conformation. The coordination sphere of the metal ion consists of the two dipyrromethene nitrogens, an "in" imine nitrogen, and an "out" imine nitrogen of the same trimethylenediamine, the latter nitrogen being associated with the other dipyrromethene. A drawing of one-half of the molecule, along with the appropriate numbering scheme, is shown in Figure 1. Rather than a flattened macrocyclic geometry as depicted in 1, the ligand has twisted and folded so that the two dipyrromethenes are almost "facing" each other (Figures 2 and 3). Each half of the macrocycle is related by a pseudo 2-fold axis located midway between the two halves of the molecule in the plane bisecting the dipyrromethenes. The copper ions are separated by 5.393 (2) Å. As seen in Figure 3A, this geometry provides a hydrophobic wall-like environment, which is similar to Busch's lacunar vaulted macrobicycles minus the "lid".<sup>18</sup> The two dipyrromethenes are canted from each other (the dihedral angle between the two planes is 29.6°) and displaced so that the 3,3'-ethyl groups, which are pointed toward the opposing dipyrromethene, can be thought of as the interlocking jaws of a steel trap. The trimethylene bridge, then, forms the "hinge" and has assumed the chair conformation. The coordinated azides extend away from the molecule, and each forms one leg of a trigonal plane for each copper ion as discussed below. An overhead view of the molecule (Figure 3B) readily shows the substantial elliptical void, which can be envisioned as a potential site for substrate approach and interaction.

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**Table VII.** Electrochemical Data for  $\text{Cu}_2(\text{bi-dptmd})^{2+}$  Complexes<sup>a</sup>

complex	$E_{1/2}$ , V	$\Delta E_p$ , <sup>b</sup> mV	$i_p^c/i_p^a$	tot no. of electrons/molecule	scan rate, mV/s
$\text{Cu}_2(\text{bi-dptmd})(\text{ClO}_4)_2$	-0.18; -0.43	80; 80	1.02; 0.95	1.8	200
$\text{Cu}_2(\text{bi-dptmd})(\text{BF}_4)_2$	-0.18; -0.43	80; 80	1.03; 1.00	1.9	100
$\text{Cu}_2(\text{bi-dptmd})(\text{N}_3)_2$	-0.45	50	1.10	2.2	100
$\text{Cu}_2(\text{bi-dptmd})(\text{NCS})_2$	-0.40	70	1.08	1.7	100
$\text{Cu}_2(\text{bi-dptmd})(\text{Cl})_2$	-0.48	100	0.95	1.8	200

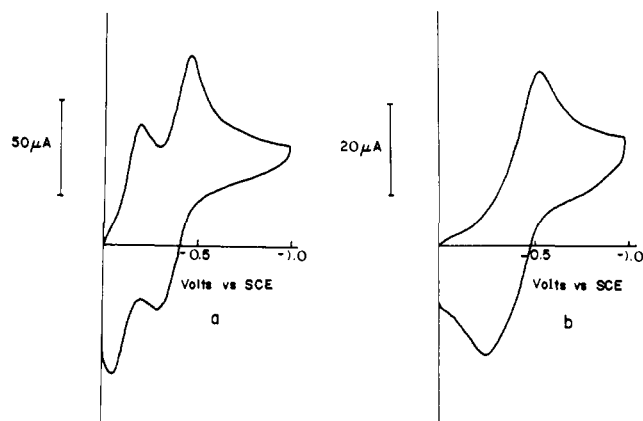
<sup>a</sup> $\text{CH}_2\text{Cl}_2$  solution; supporting electrolyte  $(\text{TBA})\text{ClO}_4$  (0.1 M). <sup>b</sup>Cyclic voltammetric peak-to-peak separation.

The coordination geometry about each copper(II) ion is a somewhat distorted trigonal bipyramid. The trigonal plane consists of N(1), N(3), and N(5) and is essentially planar (Table VI), although the copper ions are slightly elevated in the direction of N(4). The ideality of the trigonal bipyramidal structure is broken by the widely varying trigonal planar angles, which range from an average of  $95.0(2)^\circ$  for N(1)-Cu-N(5) to  $136.2(2)^\circ$  for N(1)-Cu-N(3). An examination of the immediate coordination sphere of the copper ion shows that the Cu-N distances also vary, ranging almost  $0.25 \text{ \AA}$ , from  $1.914(4) \text{ \AA}$  ( $\text{Cu}_A\text{-N}_A(3)$ ) to  $2.150(5) \text{ \AA}$  ( $\text{Cu}_B\text{-N}_B(1)$ ). For both halves of the molecule, the three shortest bonds are associated with the most rigid portions: Cu-N(2), Cu-N(3), and Cu-N(4). The less-restrained N(1) and N(5) exhibit relatively long bonds with the Cu(II) from  $2.10$  to  $2.15 \text{ \AA}$ .

The dipyrromethene fragments show extensive electron delocalization and, including the imines moieties, are planar (Table VI). For structural comparisons, each dipyrromethene can be thought of as possessing a pseudomirror plane. The N(3)-C(5) and N(4)-C(13) distances are the shortest, averaging  $1.334(7) \text{ \AA}$ . This finding is in agreement with structures of other dipyrromethene metal complexes, in which the shortest bonds have in general been found to emanate from the pyrrole nitrogens to the 5,5'-carbons.<sup>15,19,20</sup> In terms of general trend, however, electron delocalization is somewhat different from that described by Cotton for other dipyrromethene complexes<sup>19</sup> and is more like that seen generally in porphyrin structures, where the distances between the 4,4'- and 5,5'-carbons are commonly about  $1.44 \text{ \AA}$ .<sup>21</sup>

The overall structure itself is reminiscent of that of zinc with octaethyl formylbiliverdinate, in which a dimeric complex is formed with a helical orientation of each of two octapyrrolic biliverdinate ligands.<sup>22</sup> The Zn-Zn separation is only  $3.37 \text{ \AA}$  compared to the  $5.393(2) \text{ \AA}$  of the dicopper complex, but in both structures it would appear that an energetically favorable orientation is formed when the dipyrromethenes are face-to-face. Such stacking interactions are noted for the porphyrins<sup>23</sup> and highly conjugated systems in general and are also important factors contributing to the stability of the secondary structure of nucleic acids.<sup>24</sup>

In the bicopper complex, there is a "pseudostacking" throughout the crystal lattice (Figure 4). Parallel orientations are observed intermolecularly, but not intramolecularly, due to the canted nature of the dipyrromethenes within each molecule. Each molecule contains one dipyrromethene related by inversion to a parallel one on the adjacent molecule at a distance of  $3.575 \text{ \AA}$ . The other dipyrromethene is parallel but offset by one-half of the unit cell ( $6.16 \text{ \AA}$ ) to a dipyrromethene generated by the 2-fold screw axis, the distance between the two planes being  $3.014 \text{ \AA}$ . The net result is a rather uneven stepwise stacking arrangement throughout the crystal lattice. The bent orientation of the coordinated azides (Cu-N(5)-N(6) angle of  $121.1(4)$  and  $138.2$



**Figure 5.** Cyclic voltammograms: (a)  $7.2 \times 10^{-4} \text{ M}$   $\text{Cu}_2(\text{bi-dptmd})(\text{ClO}_4)_2$  in  $\text{CH}_2\text{Cl}_2$  at  $200 \text{ mV/s}$ ; (b)  $3.02 \times 10^{-4} \text{ M}$   $\text{Cu}_2(\text{bi-dptmd})(\text{N}_3)_2$  in  $\text{CH}_2\text{Cl}_2$  at  $100 \text{ mV/s}$ .

$(7)^\circ$  for A and B halves, respectively) can be seen to blend in readily with the packing scheme in the direction of the 3,3'-ethyl groups of the dipyrromethenes.

**Electrochemistry.** The cyclic voltammetric data for  $\text{Cu}_2(\text{bi-dptmd})(\text{X})_2$  are shown in Table VII. Each copper(II) ion undergoes a reversible one-electron reduction, but depending on the anion, this in the form of either two one-electron steps at different potentials or two one-electron steps at the same potential. Scanning to negative potentials (0.0 to  $-1.5 \text{ V}$  vs. SCE) for the  $\text{ClO}_4^-$  and  $\text{BF}_4^-$  salts clearly shows two one-electron processes (Figure 5a), which occur at  $-0.18$  and  $-0.43 \text{ V}$  vs. SCE and are separated by  $250 \text{ mV}$ . On the other hand, the  $\text{N}_3^-$ ,  $\text{NCS}^-$ , and  $\text{Cl}^-$  complexes all exhibit two one-electron reduction steps at virtually the same potential (averaging  $-0.44 \text{ V}$  vs. SCE) as shown for the azido salt (Figure 5b). The Cu(I)/Cu(O) couple was not observed.

Scanning from  $0.0$  to  $+1.5 \text{ V}$ , a ligand-centered irreversible two-electron oxidation wave is observed at  $1.03 \text{ V}$  vs. SCE in the free ligand, which shifts to more positive potentials upon complexation (averaging  $1.23$  and  $1.15 \text{ V}$  vs. SCE for complexes with uncoordinated and coordinated anions, respectively). For complexes with coordinated anions, there is an additional irreversible oxidation wave at approximately  $+0.80 \text{ V}$  vs. SCE.

The electrochemical results can be compared with those of two other types of macrocyclic complexes with widely differing degrees of interactions.<sup>3,25,26</sup> For the rigid macrocycles with strongly interacting metal centers derived from isophthalaldehyde originally reported by Robson<sup>3</sup> and investigated electrochemically by Addison<sup>25</sup> and Gagné,<sup>26</sup> stepwise one-electron reductions are observed. Thus, the observation of two waves for the  $\text{ClO}_4^-$  and  $\text{BF}_4^-$  salts indicate that there is some form of metal-metal interaction or inequivalent copper(II) sites, in accordance with the treatise by Bard, Anson, and co-workers on electron transfer in molecules with multiple, noninteracting redox centers.<sup>27</sup> At the other range of both macrocyclic flexibility and metal-metal interaction is the dicopper complex of  $[\text{24-ane-N}_2\text{S}_4]$ .<sup>28</sup> For the tetraazido complex,

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in which the metal-metal separation more closely approaches that of the bis-(dipyromethene) macrocycles at 5.145 (1) Å, the copper(II) ions are reduced to copper(I) via one dielectronic step.

The variability of the nature of the two one-electron reductions of the dicopper(II) sites suggests the utility of these complexes as catalysts for the activation of small molecules via concurrent two-electron reductions. Of considerable interest, in view of the simultaneous one-electron reduction steps in the  $\text{Cl}^-$ ,  $\text{N}_3^-$ , and  $\text{NCS}^-$  salts, is the potential of these complexes to catalyze the oxidation of organic substrates. Preliminary results in this direction indicate that the azido complex catalyzes the oxidation of 3,5-di-*tert*-butylcatechol in the presence of molecular oxygen. These studies will be reported in detail elsewhere.

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**Registry No.** 1 ( $n = 3$ ), 98737-20-3; 3,3'-diethyl-5,5'-diformyl-4,4'-dimethyldipyromethane, 967-68-0; 1,3-propanediamine, 109-76-2;  $\text{Pb}_2(\text{bi-dptmd})(\text{SCN})_2$ , 98759-99-0;  $\text{Zn}_2(\text{bi-dptmd})(\text{Cl})_2$ , 98760-00-0;  $\text{Cu}_2(\text{bi-dptmd})(\text{Cl})_2$ , 98760-01-1;  $\text{Cu}_2(\text{bi-dptmd})(\text{ClO}_4)_2$ , 98760-02-2;  $\text{Cu}_2(\text{bi-dptmd})(\text{BF}_4)_2$ , 93081-48-2;  $\text{Cu}_2(\text{bi-dptmd})(\text{N}_3)_2 \cdot \frac{1}{2}\text{CH}_3\text{OH}$ , 98760-04-4;  $\text{Cu}_2(\text{bi-dptmd})(\text{SCN})_2$ , 98760-05-5;  $\text{Zn}_2(\text{bi-dpen})(\text{Cl})_2$ , 98760-06-6;  $\text{Cu}_2(\text{bi-dpen})(\text{ClO}_4)_2$ , 98777-04-9;  $\text{Cu}_2(\text{bi-dptmd})(\text{N}_3)_2$ , 98760-03-3; ethylenediamine, 107-15-3.

**Supplementary Material Available:** Tables of elemental analyses, solution conductivities, structure factors, thermal parameters, hydrogen atom parameters, and torsional angles (41 pages). Ordering information is given on any current masthead page.

## Experimental and Theoretical Studies of Dinuclear Gold(I) and Gold(II) Phosphorus Ylide Complexes. Oxidative Addition, Halide Exchange, and Structural Properties Including the Crystal and Molecular Structures of $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2$ and $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2(\text{CH}_3)\text{Br}^\dagger$

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**Abstract:** The reactions of the dinuclear phosphorus ylide gold(I) complexes  $[\text{Au}(\text{CH}_2)_2\text{P}(\text{Me})_2]_2$ , **1**, and  $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2$ , **2**, with the alkyl halides MeI,  $(\text{Me})_3\text{SiCH}_2\text{I}$ , and  $\text{PhCH}_2\text{Br}$  have been studied. It is observed by  $^1\text{H}$  NMR spectroscopy that equilibrium is rapidly achieved between the Au(I) dimer (**1** or **2**), the free alkyl halide, and the Au(II) alkyl halide adduct. This appears to be the first example of a reversible two-center two-electron oxidative addition of an alkyl halide to a dinuclear complex. The MeI adduct reductively eliminates alkyl halide when the solid is heated. When  $\text{CDCl}_3$  solutions of the Au(II) alkyl halide adducts are heated or exposed to light, the Au(II) dihalide dimers, along with other products, are formed. Catalytic halogen exchange between  $\text{CH}_3\text{Br}$  and  $\text{CD}_3\text{I}$  is observed in solution in the presence of **2**. This process is thought to involve an  $\text{S}_{\text{N}}2$  reaction between the free alkyl halide and the postulated intermediate  $\{[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2(\text{Me})\}$  [I]. Halogen exchange between  $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2\text{Br}_2$  and MeI is observed only when **2** is present. One-electron transfer from **2** to the alkyl halide is suggested as the initial step in the overall two-center two-electron oxidative addition reaction. Cyclic voltammetry of **2** and the dihalide adducts suggests consecutive one-electron steps are involved in the electrochemical oxidations and reductions. Although the alkyl halides show resolved oxidation and reduction waves, the processes are irreversible. No free halide is observed in the presence of excess  $\text{CH}_3\text{Br}$  or  $\text{CH}_3\text{I}$ . The ready ionization of the Au-halide bonds in the alkyl halide adducts appears related to the exceptional structural *trans* effect observed in these compounds. In general the Au-halide bond lengths observed in the dinuclear C-Au-Au-halide species are 5-10% longer than the *trans* Au-halide bonds in mononuclear C-Au-halide compounds. Molecular orbital calculations (Atom Superposition and Electron Delocalization) have been used to indicate the character of the bonding in the alkyl halide and dihalide Au(II) complexes. The trends observed in the energy levels correlate well with electrochemical reduction potentials for the dihalides. The structures of  $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2$ , **2**, and  $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2(\text{Me})\text{Br}$ , **2-MeBr**, have been determined by a single-crystal X-ray diffraction study. Crystal data for **2**:  $\text{C}_{28}\text{H}_{28}\text{Au}_2\text{P}_2$ , crystallizes in the monoclinic space group  $P2_1/n$  with  $a = 8.576$  (1) Å,  $b = 9.378$  (2) Å,  $c = 15.915$  (3) Å,  $\beta = 96.48$  (1)°, and  $Z = 2$ . Refinement with 2039 reflections with  $F_o^2 > 3\sigma(F_o^2)$  yielded  $R = 0.028$  and  $R_w = 0.027$ . Crystal data for **2-MeBr**:  $\text{C}_{29}\text{H}_{31}\text{P}_2\text{Au}_2\text{Br}$ , crystallizes in the monoclinic space group  $Cc$  with  $a = 13.385$  (2) Å,  $b = 12.340$  (1) Å,  $c = 17.360$  (3) Å,  $\beta = 103.65$  (1)°, and  $Z = 4$ . Refinement with 2629 reflections with  $F_o^2 > 3\sigma(F_o^2)$  yielded  $R = 0.061$  and  $R_w = 0.059$ .

Organogold chemistry<sup>1</sup> and the study of dinuclear transition-metal complexes<sup>2</sup> are both among the rapidly developing areas of organometallic and metal cluster chemistry. While many mechanistic studies have been reported on mononuclear metal

systems which undergo oxidative addition-reductive elimination steps,<sup>3</sup> only recently have reports appeared of oxidative addition

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