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Ring-in-Ring Structures from Phenanthroline Macrocycles with Exo- and Endotopic Binding Sites

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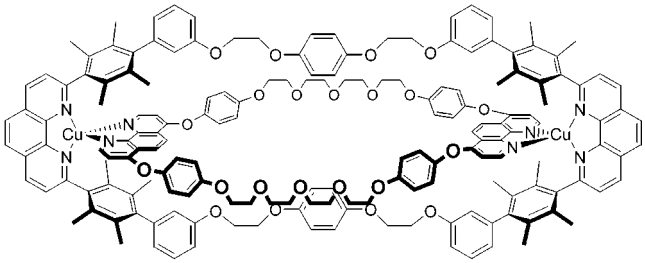
ABSTRACT



Three metallosupramolecular ring-in-ring structures are assembled using the HETPHEN concept (in the presence of copper(I)) with macrocyclic phenanthrolines exhibiting exotopic and endotopic coordination sites.

The seminal work by Sauvage in 1983[1] on the high-yield formation of catenanes via the intermediate formation of catenates has moved phenanthrolines and bipyridines into the focus of metallosupramolecular chemistry.[2] By using the templating effect of tetrahedrally coordinating metal ions, mostly copper(I) and silver(I), many additional challenging structures, such pseudorotaxanes,[3] grids,[4] double/triple helicates,[5] knots,[6] and huge wheels,[7] were realized by several groups in the ensuing years. Many of those structures contain as a key element heteroleptic complexes $[M(diim1)(diim2)]^{n+}$ (diim = diimines, such as phenanthrolines, bipyridines) whose formation is guided by the principles of maximum site occupancy and cooperativity but interestingly not by independent, well-directed tactics.

A while ago, we developed the HETPHEN concept, which allows the preparation of heteroleptic bisphenanthroline or bisbipyridine copper(I)[8] and silver(I)[9] complexes. It occurred to us that the enforced formation of heteroleptic diimine complexes should allow access to structural motifs that on

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(1) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Kintzinger, J. P. *Tetrahedron Lett.* **1983**, *24*, 5095.

(2) Recent reviews covering this wide field, see: (a) Lehn, J.-M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH: New York, 1995. (b) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417. (c) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (d) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483. (e) Kaes, C.; Katz, A.; Hosseini, W. *Chem. Rev.* **2000**, *100*, 3553.

(3) Collin, J. P.; Gavina, P.; Sauvage, J. P. *Chem. Commun.* **1996**, 2005. Baxter, P. N. W.; Sleiman, H.; Lehn, J. M.; Rissanen, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1294.

(4) Baxter, P. N. W.; Lehn, J. M.; Fischer, J.; Youinou, M. T. *Angew. Chem., Int. Edit. Engl.* **1994**, *33*, 2284. Baxter, P. N. W.; Lehn, J. M.; Baum, G.; Fenske, D. *Chem. Eur. J.* **2000**, *6*, 4510.

(5) Constable, E. C.; Hannon, M. J.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1993**, 1883. Kramer, R.; Lehn, J. M.; Marquisrigault, A. *Proc. Natl. Acad. Sci.* **1993**, *90*, 5394. Constable, E. C.; Hannon, M. J.; Edwards, A. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1994**, 2669. Greenwald, M.; Wessely, D.; Katz, E.; Willner, I.; Cohen, Y. *J. Org. Chem.* **2000**, *65*, 1050.

(6) Meyer, M.; Albrecht-Gary, A. M.; Dietrich-Buchecker, C. O.; Sauvage, J. P. *J. Am. Chem. Soc.* **1997**, *119*, 4599. Rapenne, G.; Dietrich-Buchecker, C.; Sauvage, J. P. *J. Am. Chem. Soc.* **1999**, *121*, 994. Dietrich-Buchecker, C.; Rapenne, G.; Sauvage, J. P.; De Cian, A.; Fischer, J. *Chem.-Eur. J.* **1999**, *5*, 1432.

(7) Iron: Hasenknopf, B.; Lehn, J. M.; Boumediene, N.; Dupont-Gervais, A.; Van Dorsselaer, A.; Kneisel, B.; Fenske, D. *J. Am. Chem. Soc.* **1997**, *119*, 9, 10956. Copper: Funeriu, D. P.; Lehn, J. M.; Baum, G.; Fenske, D. *Chem. Eur. J.* **1997**, *3*, 99.

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the basis of maximum site occupancy and cooperativity would not form. In the following we like to describe our efforts to realize ring-in-ring structures (Figure 1), thus demonstrating the assets and merits of the HETPHEN approach.

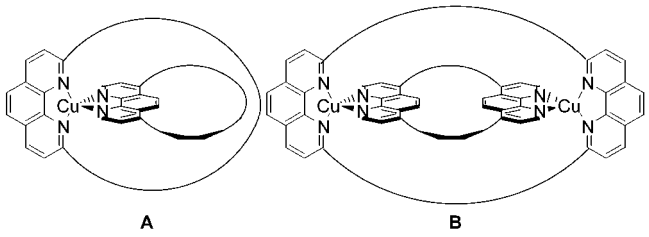


Figure 1. Pictorial representation of mononuclear and dinuclear ring-in-ring structures.

An analysis of **A** and **B** reveals that for the preparation of ring-in-ring structures macrocyclic phenanthrolines with endotopic and equally macrocyclic phenanthrolines with exotopic binding sites are needed. In line with the HETPHEN concept[8,9] one of the macrocyclic ligands has to bear sterically shielded 2,9-aryl substituents at each binding site to avoid competing formation of homoleptic complexes. The other macrocyclic ligand has to carry unshielded phenanthroline coordination sites. As exotopic ligands **1** and **2** had been prepared[10] earlier we chose as counterparts the endotopic phenanthrolines **3a,b** and **4**.

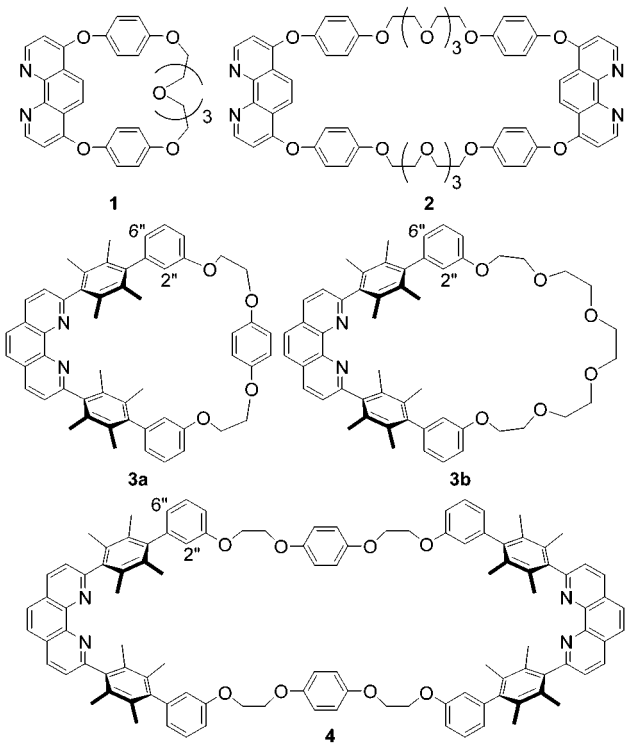
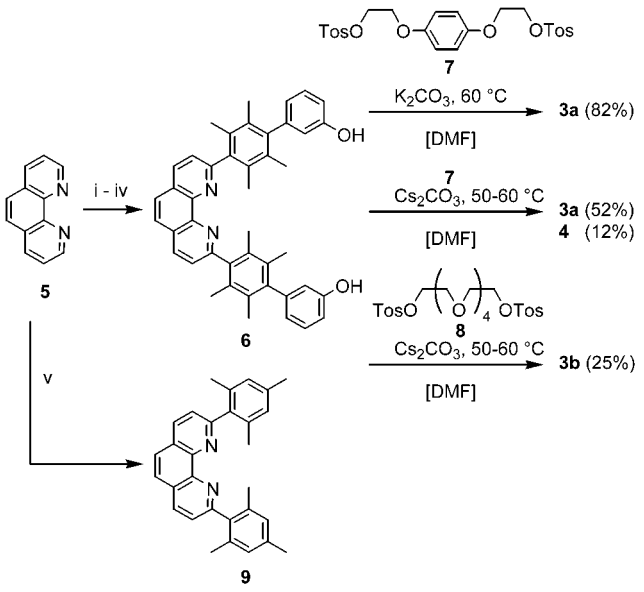


Figure 2. Macrocyclic phenanthrolines with exotopic and endotopic coordination sites.

Scheme 1[a]



[a] (i) dibromodurene, ^{n}BuLi, rt; MnO_2, 70%; (ii) dibromodurene, ^{n}BuLi, rt; MnO_2, 51%; (iii) 3-methoxyphenyl boronic acid, $Pd(PPh_3)_4$ (3 mol %), Na_2CO_3, toluene, methanol, H_2O, 48 h, 80−90 °C, 93%; (iv) BBr_3, CH_2Cl_2, 48 h, −78 °C, 93%; (v) see ref 9.

Phenanthrolines **3a,b** were prepared starting from the parent phenanthroline (**5**) in five steps via compound **6**. For the final step we followed high-dilution conditions as successfully applied by Sauvage[11] for similar systems. Slow addition (100 h) of **6** and **7** to a warm suspension of potassium carbonate in DMF afforded **3a** in 82% yield after chromatographic purification. Similarly, **3b** was furnished by slow (50 h) addition of pentaethylenegylcol ditosylate (**8**) and **6** to cesium carbonate in DMF. After two chromatographic separations **3b** was received in 25% yield.

The preparation of **4** was effected by using cesium ions as a template in the macrocyclization of **6** and **7**. Although **3a** was a major product in this reaction, the purification of the minor product **4** was possible through size exclusion chromatography. The structural assignment of **3a** as the [1 + 1] adduct and **4** as the [2 + 2] product is based on the size exclusion chromatographic retention times as well as on the isotopic pattern in the electrospray mass spectra. Moreover, ^{1}H NMR spectra exhibit distinct resonances for some of the protons: for example, **4** displays only one signal for the methyl groups (δ = 1.97 ppm) but two for the CH_{Ar} of the bridging hydroquinone ether unit (δ = 6.87 and 6.97 ppm). On the contrary, **3a** features two different signals for the methyl groups (δ = 1.95 and 1.99 ppm) but only one singlet for the CH_{Ar} at δ = 6.99 ppm. To probe the steric

(8) Schmittel, M.; Ganz, A. *Chem. Commun.* **1997**, 999.
(9) Schmittel, M.; Ganz, A.; Fenske, D.; Herderich, M. *J. Chem. Soc., Dalton Trans.* **2000**, 353.
(10) Schmittel, M.; Ganz, A. *Synlett* **1997**, 710−712. Schmittel, M.; Ammon, H. *Synlett* **1999**, 750. Schmittel, M.; Michel, C.; Ganz, A.; Herderich, M. *J. Prakt. Chem.* **1999**, *341*, 228.
(11) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Kern, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 3043.

shielding of the 2,9-duryl groups in ligands **3**, **4**, and **6**, the phenanthroline **6** was reacted in large excess with $[Cu(CH_3CN)_4]^+$. Both, UV−vis and ESI clearly indicated that the homoleptic complex $[Cu(\mathbf{6})_2]^+$ did not form. On the other side, reaction of **5** + **3a** or **6** in the presence of $[Cu(CH_3CN)_4]^+$ afforded the heteroleptic complexes in high yields, e.g., $[Cu(\mathbf{3a})(\mathbf{5})]^+$ and $[Cu(\mathbf{5})(\mathbf{6})]^+$ (94%). Hence, as already reported for other sterically shielded phenanthroline and bipyridine ligands the formation of the bishomoleptic[8,9] complexes $[Cu(\mathbf{3a})_2]^+$ and $[Cu(\mathbf{6})_2]^+$, respectively, is kinetically prevented, thus rendering the heteroleptic species the only products.

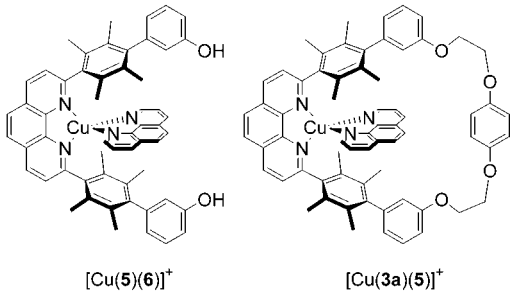


Figure 3. Two model complexes. For $[Cu(\mathbf{5})(\mathbf{6})]^+$ only the *in-in* isomer (with regard to the phenolic OH functionalities) is shown.

Because of the possibility to form stereogenic axes along the phenanthroline−durene and durene−phenol bonds, three different diastereomers were observed in $[Cu(\mathbf{5})(\mathbf{6})]^+$. On the basis of COSY and NOESY experiments the diastereomers were identified as *out-out* (37%), *in-out* (47%), and *in-in* (16%) conformers. For $[Cu(\mathbf{3a})(\mathbf{5})]^+$ the NMR revealed a symmetric species.

That the HETPHEN concept also works with macrocyclic phenanthrolines **1** and **2** was demonstrated earlier.[8] Using X-ray structural analysis the complex $[Cu_2(\mathbf{2})(\mathbf{9})_2]^{2+}$ was now investigated more closely (Table 1, Figure 4). The distortion at the copper centers are rather distinct as specified by the Dobson[12] angles: $\theta_x = 92.4°$, $\theta_y = 105.9°$, and $\theta_z = 93.7°$. As a consequence of $\theta_y = 105.9°$ $[Cu_2(\mathbf{2})(\mathbf{9})_2]^{2+}$ shows an interesting parallel arrangement of one mesityl group with the second phenanthroline ligand indicative of a $\pi-\pi$ interaction that is also known from simple heteroleptic complexes.[13]

Table 1. Some Selected Data from the X-ray Structural Analysis of $[Cu(\mathbf{2})(\mathbf{9})]^+$

bond	length (pm)	angle	angle (deg)
Cu−N(1)	210.7 (4)	N(2)−Cu−N(1)	82.5 (2)
Cu−N(2)	198.4 (4)	N(2)−Cu−N(3)	129.5 (2)
Cu−N(3)	204.0 (4)	N(2)−Cu−N(4)	136.3 (2)
Cu−N(4)	202.9 (4)	N(3)−Cu−N(1)	115.4 (2)
		N(4)−Cu−N(1)	112.8 (2)
		N(4)−Cu−N(3)	82.4 (2)

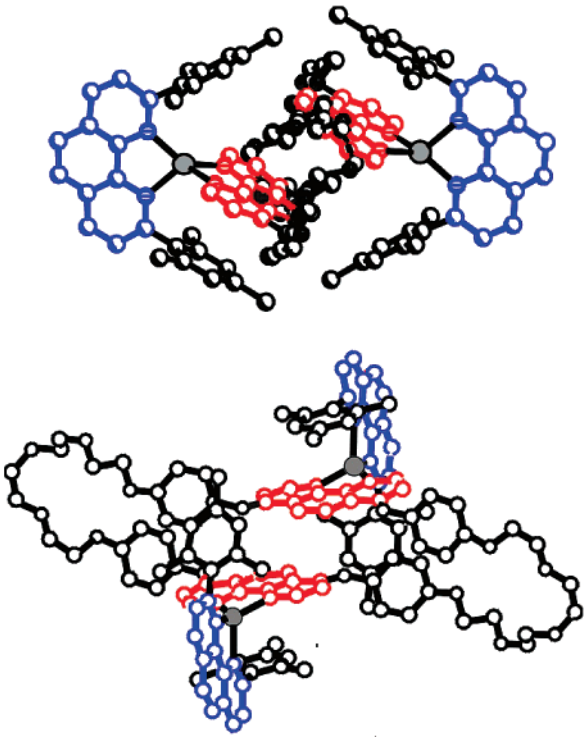


Figure 4. X-ray structure of $[Cu_2(\mathbf{2})(\mathbf{9})_2]^+$ (view from two sides).

The X-ray structure of $[Cu_2(\mathbf{2})(\mathbf{9})_2]^{2+}$ is additionally characterized by a parallel arrangement of the two phenanthroline subunits (red) and of the hydroquinone moieties of the polyether units.

To obtain ring-in-ring structures we first reacted the small monophenanthroline macrocycles **3a,b** containing endotopic ligand sites with macrocycle **1** in the presence of $[Cu(CH_3CN)_4]BF_4$. After chromatography (SiO_2, dichloromethane:methanol = 10:1) the red complexes $[Cu(\mathbf{1})(\mathbf{3a})]^+$ (68%) and $[Cu(\mathbf{1})(\mathbf{3b})]^+$ (33%) were afforded. ^{1}H NMR signals clearly indicate the formation of the heteroleptic complexes as evidenced in particular from the characteristic shifts of the 2″-H and the 6″-H (Table 2, Figure 2).

Analogously, reaction of the bisendotopic bisphenanthroline **4** with the bisexotopic counterpart **2** and $[Cu(CH_3CN)_4]BF_4$ furnished the red complex $[Cu_2(\mathbf{2})(\mathbf{4})]^{2+}$ after chromatography in 79% yield (Figure 5).

Table 2. Characteristic ^{1}H NMR Shifts of 2″-H and 6″-H (in ppm) in the Various Ring-in-Ring Structures (in $CDCl_3$)

ligand or complex	δ (2″-H)	δ (6″-H)
macrocyle **3a**	6.67	6.92
macrocyle **3b**	6.66	6.89
$[Cu(\mathbf{3a})(\mathbf{5})]^+$	5.14	6.30
$[Cu(\mathbf{1})(\mathbf{3a})]^+$	5.45	6.39
$[Cu(\mathbf{1})(\mathbf{3b})]^{+\,a}$	5.47	6.39
macrocyle **4**	6.69	6.83
$[Cu_2(\mathbf{2})(\mathbf{4})]^{2+\,b}$	4.89/5.25/5.33	6.42/6.44/6.48

[a] D_6-acetone. [b] Three signals due to three conformers.

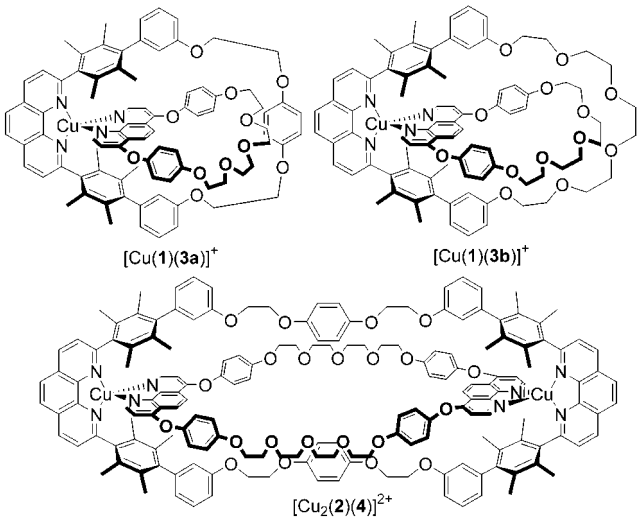
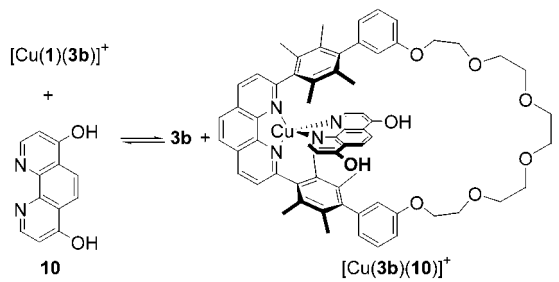


Figure 5. Ring-in-ring structures.

Comparing the various complexes [Cu(**3a**)(**5**)]$^+$, [Cu(**1**)(**3a**)]$^+$, [Cu(**1**)(**3b**)]$^+$, and [Cu_2(**2**)(**4**)]$^{2+}$ both by NMR and ESI (electrospray ionization) reveals a more detailed picture. Accordingly, the unstrained complex [Cu(**3a**)(**5**)]$^+$ is basically undissociated as evidenced by one set of sharp signals in the ^{1}H NMR and a m/z = 1033.2 (M^+, 100%) in the ESI experiment. In contrast, the two monophenanthroline ring-in-ring structures [Cu(**1**)(**3a**)]$^+$ and [Cu(**1**)(**3b**)]$^+$ are showing weak M^+ signals along with strong signals for [Cu(**3a**)]$^+$ and [Cu(**3b**)]$^+$ (100%). Also, the NMR not only shows the set of signals required for [Cu(**1**)(**3a**)]$^+$ and [Cu(**1**)(**3b**)]$^+$, respectively, but also a minor set of signals (10−15%) that can be assigned to [Cu(**3a**)]$^+$ and [Cu(**3b**)]$^+$. Quite clearly, these two complexes are in equilibrium with their components, most likely as a result of strain caused by the interaction of the two ring systems. PM3 calculations[14]

Scheme 2



provide a measure of the steric crowding inside the ring-in-ring structure [Cu(**1**)(**3b**)]$^+$; using a homodesmotic reaction[15] the ring-in-ring structure [Cu(**1**)(**3b**)]$^+$ + **10** is less stable by 9.2 kcal mol^{-1} than the "unstrained" complex [Cu(**3b**)(**10**)]$^+$ + **3b**. The PM3 calculated mimimum structure of [Cu(**1**)(**3b**)]$^+$ reveals clearly how the inner ring **3b** has to fold in order to be accommodated inside of **1**.

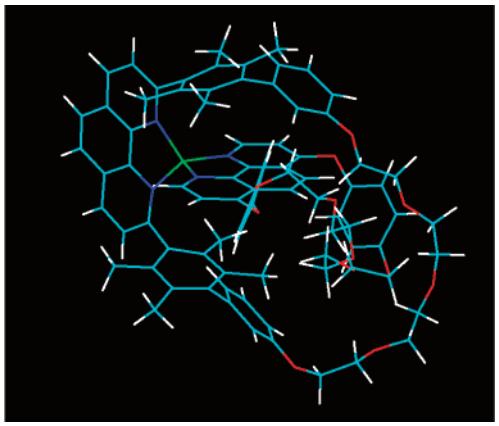


Figure 6. PM3 calculated mimimum structure of [Cu(**1**)(**3b**)]$^+$.

The bisphenanthroline ring-in-ring structure [Cu_2(**2**)(**4**)]$^{2+}$ should be more stable, since the two ring systems are connected via two copper coordination sites. Indeed, the ESI results show the M^{2+} at m/z 1409.5 (100%) as the dominant signal. Also, in CAD experiments a notable decomposition could only be effected at very high voltage (i.e., 90 eV). This, however, did not lead to dissociative loss of one of the ligands but to cleavage of covalent bonds, indicative of strong coordinative bonds.

In the NMR spectrum (see Table 2) [Cu_2(**2**)(**4**)]$^{2+}$ exhibits three sets of signals due to the presence of three conformers. A careful analysis, however, discloses additionally the occurrence of a small percentage of phenanthroline [Cu_2(**4**)]$^{2+}$ (<15%). Why does the complex partly dissociate? As ring strain should be less important in [Cu_2(**2**)(**4**)]$^{2+}$ than in the small mononuclear complexes [Cu(**1**)(**3a**)]$^+$ and [Cu(**1**)(**3b**)]$^+$, it is presumably torsional strain (see the three conformers) and entropic losses (due to rotational constraints of a large number of single bonds in the complex) that cannot be completely compensated by the enthalpic driving force of the coordinative bonds.

In conclusion, we have demonstrated that the HETPHEN concept can be used to prepare supramolecular mononuclear and dinuclear ring-in-ring structures.

Acknowledgment. We are indebted to the DFG and the Fonds der Chemischen Industrie for support. M.S. would like to thank Waldemar Adam on the occasion of his 65th birthday for much helpful advice on physical organic chemistry and an inspiring scientific opus.

Supporting Information Available: Full experimental material on all new substrates and X-ray data for [Cu_2(**2**)(**9**)$_2$]$^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Dobson, J. F.; Green, B. E.; Healy, P. C.; Kennard, C. H. L.; Pakawatchai, C.; White, A. H. *Aust. J. Chem.* **1984**, *37*, 649.
(13) Miller, M. T.; Gantzel, P. K.; Karpishin, T. B. *Inorg. Chem.* **1999**, *38*, 3414.
(14) PM3 calculations were run using Hyperchem 6 with parameters for transition metals.
(15) George P.; Trachtman, M.; Bock, C. W., Brett, A. M. *Theor. Chim. Acta*, **1975**, *38*, 121.