

Copper(II) Complexes of Novel 1,5-Diaza-*cis*-decalin Diamine Ligands: An Investigation of Structure and Reactivity

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Copper complexes of 1,5-diaza-*cis*-decalin diamines are highly effective in the oxidative asymmetric biaryl couplings of 3-substituted 2-naphthols. On the basis of the demonstrated success of these complexes as catalysts, an effort has been made to identify the copper species present in the reaction and to construct plausible models for the presumed catalyst–substrate complexes. Crystal structures of a series of 1,5-diaza-*cis*-decalin and *N,N*-dialkyl-1,5-diaza-*cis*-decalin Cu(II) complexes have been obtained. The amine substitution determines the type of copper coordination complex formed. For the secondary amine compound, 1,5-diaza-*cis*-decalin, 2:1 diamine:copper complexes appear to be the thermodynamically favored forms, but they are not catalytically active. Crystals of a catalytically competent trimeric 1:1 diamine:copper complex containing bridging hydroxo groups were also generated from 1,5-diaza-*cis*-decalin. For *N,N*-dimethyl-1,5-diaza-*cis*-decalin, a 1:1 diamine:copper bis- μ -hydroxo dimeric complex forms. Larger *N*-alkyl groups prevent formation of 2:1 diamine:copper complexes as well as dimeric or trimeric species. For instance, the *N,N*-diethyl-1,5-diaza-*cis*-decalin forms a monomeric 1:1 diamine:copper adduct. On the basis of these structures a model of the catalyst–substrate complex has been proposed that is consistent with the observed enantioselection. The absolute configurations of the diamines in each copper complex were the same even when the complexes were generated from the racemic diamine, with the exception of the bridging dimer. This observation may serve to explain the nonlinear effects in the asymmetric biaryl couplings catalyzed by the 1,5-diaza-*cis*-decalin copper complexes.

Introduction

Many structures of oxidatively active copper complexes containing small molecule ligands have been described.¹ These complexes have been examined primarily as models of the larger and more complex copper enzyme active sites. Studies of these enzymatic systems are driven by their ability to utilize oxygen as a terminal oxidant in catalytic transformations. The development of small molecule catalysts with similar characteristics is a goal of intense interest.¹ However, the attractive features of utilizing oxygen as an oxidant (ready availability, cost, stability compared to peroxides, etc.) in copper-catalyzed reactions are offset by a lack of understanding of the mechanism of oxygen incorporation, metal oxidation, ligand exchange, and substrate oxidation.

Even though the structures of a small number of chiral saturated diamine copper complexes have been described, the utility of such complexes in oxidative catalysis has not been extensively explored.² In addition, the relationship between structure and reactivity/selectivity of demonstrated copper catalysts has not

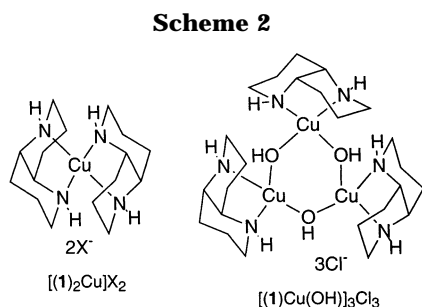
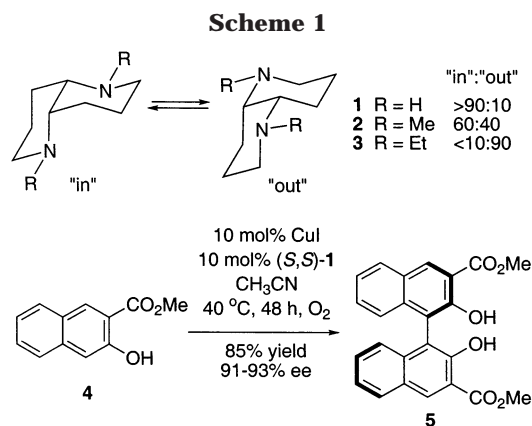
been studied. In our work, we have found that copper(II) complexes generated from a chiral diamine, 1,5-diaza-*cis*-decalin (**1**), are efficient and selective catalysts for the formation of chiral 3,3'-disubstituted BINOL derivatives (Scheme 1).³ To gain a more complete understanding of the multistep catalytic cycle involved in this reaction, we have undertaken a study of the solid- and solution-state structures of the copper complexes derived from a series of 1,5-diaza-*cis*-decalins (**1**–**3**, Scheme 1).

The results obtained from this study are expected to be helpful in the development of more selective catalysts for this type of transformation as well as for the development of other oxidizing copper catalysts for related transformations. In addition, insight into the redox chemistry in related enzymatic copper systems may be gained.

(1) For reviews, see: (a) Solomon, E. I.; Chen, P.; Metz, M.; Lee, S.-K.; Palmer, A. E. *Angew. Chem., Int. Ed.* **2001**, *40*, 4570–4590. (b) Solomon, E. I.; Sundaram, U. M.; Machonkin, T. E. *Chem. Rev.* **1996**, *96*, 2563–2605. (c) Klinman, J. P. *Chem. Rev.* **1996**, *96*, 2541–2561. (d) Kitajima, N.; Moro-oka, Y. *Chem. Rev.* **1994**, *94*, 737–757.

(2) For some examples, see: (a) DuBois, J. L.; Mukherjee, P.; Stack, T. D. P.; Hedman, B.; Solomon, E. I.; Hodgson, K. O. *J. Am. Chem. Soc.* **2000**, *122*, 5775–5787. (b) Henson, M. J.; Mukherjee, P.; Root, D. E.; Stack, T. D. P.; Solomon, E. I. *J. Am. Chem. Soc.* **1999**, *121*, 10332–10345. (c) Root, D. E.; Henson, M. J.; Machonkin, T.; Mukherjee, P.; Stack, T. D. P.; Solomon, E. I. *J. Am. Chem. Soc.* **1998**, *120*, 4982–4990. (d) Mahadevan, V.; Hou, Z.; Cole, A. P.; Root, D. E.; Lal, T. K.; Solomon, E. I.; Stack, T. D. P. *J. Am. Chem. Soc.* **1997**, *119*, 11996–11997. (e) DuBois, J. L.; Mukherjee, P.; Collier, A. M.; Mayer, J. M.; Solomon, E. I.; Hedman, B.; Stack, T. D. P.; Hodgson, K. O. *J. Am. Chem. Soc.* **1997**, *119*, 8578–8579. (f) Cole, A. P.; Root, D. E.; Mukherjee, P.; Solomon, E. I.; Stack, T. D. P. *Science* **1996**, *273*, 1848–1850.

(3) Li, X.; Yang, J.; Kozlowski, M. C. *Org. Lett.* **2001**, *3*, 1137–1140.



Results and Discussion

Synthesis and Crystal Structures of the 1,5-Diaza-*cis*-decalin Copper(II) Complexes. The 1,5-diaza-*cis*-decalins are conformationally flexible and can occur in two conformational forms, "in" and "out" in varying ratios depending on the R substituents (Scheme 1).⁴ We proposed that azaphilic metals would perturb the conformational equilibrium by selectively coordinating the "in" form in a bidentate manner. To investigate this proposal, we undertook the synthesis and characterization of a number of metal complexes of **1**–**3**. In all instances, adducts of the "in" form were observed. Below, we describe the copper(II) complexes in further detail.

The copper(II) complexes of the 1,5-diaza-*cis*-decalins were synthesized by two methods. In the first, copper(II) salts, such as Cu(OTf)₂ and Cu(BF₄)₂, were used directly as the metal source. In the second, copper(I) salts, such as CuCl and CuI, were used, which spontaneously oxidized to the corresponding copper(II) species under aerobic conditions. Both types of species are catalytically active in the conversion of **4** to **5** (Scheme 1), albeit to different extents.³ Single crystals of the copper(II) complexes were formed by evaporation or vapor diffusion.

For the secondary diamine **1**, 2:1 diamine:copper complexes and a 1:1 diamine:copper trimer with μ -hydroxo bridging ligands formed under different conditions (Scheme 2). The molecular structures of all the [(1)₂Cu]X₂ complexes are similar, and an ORTEP drawing of the representative [(1)₂Cu]Cl₂ is illustrated in Figure 1. Table 1 lists selected geometrical parameters. These 2:1 complexes contain one copper(II) atom, which coordinates four nitrogen atoms from two molecules of secondary diamine **1**; the counterions Cl, I, OTf, and BF₄ do not coordinate to the copper center.

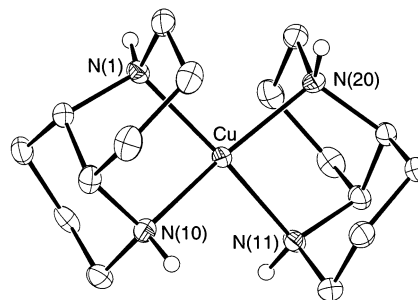


Figure 1. ORTEP drawing of representative complex [(1)₂Cu]Cl₂ from the series [(1)₂Cu]X₂ (X = Cl, I, OTf, BF₄) with 30% probability thermal ellipsoids. Non-heteroatom hydrogens and the counterions (noncoordinating) are omitted for clarity.

For the [(1)₂Cu]X₂ complexes, the Cu–N bond distances are typical,⁵ ranging from 2.02 to 2.04 Å. The ligand N–Cu–N angles (83.5–84.4°) do not vary significantly and are typical for this type of five-membered copper chelate. The N–Cu–N bond angles between the trans nitrogen atoms are 162.0–165.7°, leading to a distorted square planar coordination environment. This distortion is moderate, as judged by the dihedral angles (23.2–26.8°) between the planes defined by the diamine nitrogens and copper. As expected for a series of structures that differ only in the composition of the noncoordinating counterions, the copper bond distances and angles are similar over the entire series. Indeed, the chloride, iodide, and tetrafluoroborate crystals are all orthorhombic. These complexes were generated from (S,S)-**1**, and, as expected, both ligands in the complex possess this configuration and only one enantiomer of the chiral diamine copper complex is present in the unit cell. On the other hand, the triflate adduct (tetragonal) and a second tetrafluoroborate adduct (data not shown) that were generated from racemic **1** are characterized by the presence of two enantiomeric copper diamine complexes in the unit cell; however, the configurations of the two diamine ligands within each complex are the same. In other words, only the homo 2:1 diamine:copper complexes are observed.

For the 1:1 diamine:copper complex (Figure 2), an unusual trimer, [(1)Cu(OH)]₃Cl₃, was observed. Table 2 lists selected geometrical parameters. Two almost identical forms of [(1)Cu(OH)]₃Cl₃ are found in the asymmetric unit of this compound, both of which lie on a crystallographic 3-fold axis and, accordingly, have exact 3-fold symmetry. The three Cu atoms are located at the vertexes of an equilateral triangle and are bridged by three hydroxo ligands. While a number of equilateral triangular Cu₃ structures have been reported,⁵ most are characterized by higher coordination geometries at the copper centers;⁶ either the bridging ligands are μ_3 or additional bridging ligands are present. As a consequence, the central ring comprised of alternating copper and oxygen centers is typically characterized by relatively acute O–Cu–O (90–97°) and Cu–O–Cu (92–100°) bond angles. The μ_3 bridging in such complexes

(5) Hathaway, B. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, N. A., Eds.; Pergamon Press: Oxford, 1987; Chapter 53.

(6) Kodera, M.; Tachi, Y.; Kita, T.; Kobushi, H.; Sumi, Y.; Kano, K.; Shiro, M.; Koikawa, M.; Tokii, T.; Ohba, M.; Okawa, H. *Inorg. Chem.* **2000**, *39*, 226–234, and references therein.

(4) Ganguly, B.; Freed, D. A.; Kozłowski, M. C. *J. Org. Chem.* **2001**, *66*, 1103–1108.

Table 1. Selected Bond Distances (Å) and Angles (deg) of [(1)₂Cu]X₂

	[(1) ₂ Cu]Cl ₂	[(1) ₂ Cu]I ₂	[(1) ₂ Cu](OTf) ₂	[(1) ₂ Cu](BF ₄) ₂
Cu–N(10)	2.017(3)	2.025(4)	2.028(3) ^a	2.021(4)
Cu–N(20)	2.022(3)	2.016(4)		2.036(4)
Cu–N(1)	2.022(3)	2.039(4)		2.030(4)
Cu–N(11)	2.037(3)	2.031(4)		2.030(4)
N(10)–Cu–N(1)	84.38(12)	83.9(2)	83.5(2) ^a	84.01(14)
N(20)–Cu–N(11)	84.30(11)	84.2(2)		83.7(2)
N(20)–Cu–N(1)	97.29(11)	98.5(2)	98.8(2) ^a	98.81(14)
N(10)–Cu–N(11)	98.19(12)	98.7(2)		99.0(2)
N(10)–Cu–N(20)	163.32(13)	163.0(2)	163.7(2) ^a	162.33(14)
N(1)–Cu–N(11)	165.72(13)	162.5(2)		161.97(14)
N(10)–Cu–N(1)/ N(20)–Cu–N(11) ^b	23.2(1)	26.0(3)	24.6	26.8(1)

^a Due to symmetry, the measurements are identical. ^b Dihedral angle between the two indicated planes.

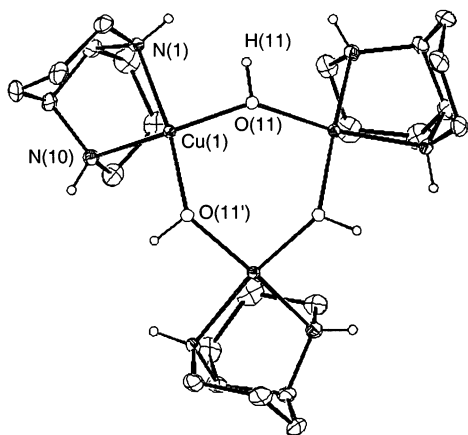


Figure 2. ORTEP drawing of the first molecule in the unit cell of [(1)Cu(OH)]₃Cl₃ with 30% probability thermal ellipsoids. Non-heteroatom hydrogens and the counterions (noncoordinating) are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Two Molecules in the Unit Cell of Tris- μ -hydroxo Trimer [(1)Cu(OH)]₃Cl₃

molecule 1		molecule 2	
Cu(1)–N(1)	2.022(3)	Cu(2)–N(12)	2.032(2)
Cu(1)–N(10)	2.037(2)	Cu(2)–N(21)	2.029(2)
Cu(1)–O(11)	1.912(2)	Cu(2)–O(22)	1.913(2)
Cu(1)–O(11')	1.920(2)	Cu(2)–O(22')	1.915(2)
Cu(1)–Cu(1')	3.499(1)	Cu(2)–Cu(2')	3.485(1)
N(1)–Cu(1)–N(10)	83.60(10)	N(12)–Cu(2)–N(21)	83.74(10)
O(11)–Cu(1)–O(11')	93.17(11)	O(22)–Cu(2)–O(22')	92.72(11)
O(11')–Cu(1)–N(1)	168.26(10)	O(22')–Cu(2)–N(21)	169.88(10)
O(11)–Cu(1)–N(1)	93.00(9)	O(22)–Cu(2)–N(21)	91.52(9)
O(11')–Cu(1)–N(10)	93.00(9)	O(22')–Cu(2)–N(12)	93.11(9)
O(11)–Cu(1)–N(10)	164.38(10)	O(22)–Cu(2)–N(12)	171.54(9)
Cu(1)–O(11)–Cu(1')	131.82(11)	Cu(2)–O(22)–Cu(2')	131.17(10)
Cu(1)–O(11)–H(11)	115.1(2)	Cu(2)–O(22)–H(22)	122.6(2)
Cu(1')–O(11)–H(11)	101.38(14)	Cu(2')–O(22)–H(22)	98.20(13)
N(1)–Cu(1)–N(10) vs O(11)–Cu(1)–O(11') ^a	18.7(2)	N(12)–Cu(2)–N(21) vs O(22)–Cu(2)–O(22') ^a	11.7(3)

^a Dihedral angle between the two indicated planes.

is proposed to stabilize the Cu₃ core structure and control the valence state of the Cu(II) ions. In the case of [(1)Cu(OH)]₃Cl₃, the sterically hindered diamine **1** prevents further coordination and the copper centers are tetracoordinate with a distorted square planar geometry (11.7° and 18.7° out-of-plane distortion). The chloride counterions do not coordinate to the copper(II) atoms, as was also the case in the 2:1 diamine:copper [(1)₂Cu]X₂ complexes (Figure 1). Rather, the chloride ions are incorporated into a helical structure arising from hydrogen bonding with alternating water molecules. Thus, [(1)Cu(OH)]₃Cl₃ is a rare example of an equilateral triangular Cu(II)₃ complex with no μ_3 -bridging. Such a result with hydroxo bridging ligands is even more

unusual in light of the high propensity for unhindered hydroxos to participate in further Cu bridging. Consequently, the usual avenue for stabilization of the Cu₃ core structure is absent in [(1)Cu(OH)]₃Cl₃. Another common mode for stabilization of the Cu₃ core is afforded by multidentate ligands containing μ_2 copper bridging alkoxy groups,⁷ which can lead to more planar Cu₃O₃ cores (O–Cu–O 90–96° and Cu–O–Cu 116–145°). However, this motif is also not present in [(1)Cu(OH)]₃Cl₃. As such, the structure of [(1)Cu(OH)]₃Cl₃ is exceptional, and the primary means of stabilization appears to arise from the structural constraints imposed by diamine ligand **1**.

The copper centers of trimer [(1)Cu(OH)]₃Cl₃ differ from those in the 2:1 complexes (1)₂CuX₂ described above in that a second diamine (**1**) has been replaced by two hydroxo bridges in the trimer. Despite the change in the formal copper charge from +2 (2:1 complexes) to +1 (trimer), the Cu–N bond distances (2.02–2.04 Å) in the trimer are similar to those of the 2:1 complexes. As expected, the Cu–O bond distances (1.91–1.92 Å) for the –1 hydroxo ligands are shorter than the Cu–N distances. The N–Cu–N bond angles (83.6–83.7°) appear characteristic for the diaza-*cis*-decalin ligands and are similar to those of the 2:1 complexes. The O–Cu–O bond angles (92.7–93.2°) are slightly larger than the comparable N–Cu–N angles in the 2:1 complexes. The Cu–O–Cu angles (131.2–131.8°) are fairly large for bridging hydroxo ligands in copper(II) species, and the Cu–Cu distances (3.49–3.50 Å) are also longer than usual.^{6–8} These somewhat unusual bond lengths and angles arise from repulsion between the sterically large diamine ligands, which causes distortion of the Cu₃O₃ structure to a flatter chairlike form. This distortion results in copper geometries closer to square planar in the trimer compared to the 2:1 complexes (trimer dihedrals = 11.7–18.7°; 2:1 complex dihedrals = 23.2–26.8°). The trimer can accommodate less distorted square planar geometries because of the smaller steric demand of the two bridging hydroxo ligands relative to the second diamine ligand found in the 2:1 complexes.

For *N,N*-dimethyl diamine **2**, a bis(μ_2 -hydroxo) copper(II) dimer [(2)Cu(OH)]₂(OTf)₂ was formed (Figure 3). The copper(II) atoms are tetracoordinate, and the coun-

(7) For examples see: (a) Klaassen, M.; Klüfers, P. *Z. Anorg. Allg. Chem.* **1993**, *619*, 661–668. (b) Wang, S.; Pang, Z.; Smith, K. D. L.; Wagner, M. L. *J. Chem. Soc., Dalton Trans.* **1994**, 955–964. (c) Klüfers, P.; Piotrowski, H.; Schuhmacher, J. *Z. Anorg. Allg. Chem.* **1997**, *623*, 191–199.

(8) Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107–2110.

Table 3. Selected Bond Distances (Å) and Angles (deg) of Bis- μ -hydroxo Dimer Complexes [(2)Cu(OH)]₂(OTf)₂, [(TMCDA)Cu(OH)]₂(OTf)₂^{2f} and [(Sp)Cu(OH)]₂(ClO₄)₂¹¹

	[(2)Cu(OH)] ₂ (OTf) ₂	[(TMCDA)Cu(OH)] ₂ (OTf) ₂	[(Sp)Cu(OH)] ₂ (ClO ₄) ₂
Cu–N(10)	1.998(9)	2.01	1.98(1)
Cu–N(10')	1.998(9)	2.02	2.03(1)
Cu–N(1)	2.049(11)	2.00	2.02(1)
Cu–N(1')	2.049(11)	1.98	2.02(1)
Cu–O(1)	1.894(8)	1.93	1.925(9)
Cu–O(1')	1.901(8)	1.91	1.93(1)
Cu'–O(1)	1.903(8)	1.92	1.909(10)
Cu'–O(1')	1.894(8)	1.89	1.951(10)
Cu–Cu'	2.972(2)	2.99	2.952(4)
N(1)–Cu–N(10)	85.7(4)	87.8	90.6(5)
N(1')–Cu–N(10')	85.7(4)	85.9	90.3(5)
O(1)–Cu–O(1')	77.0(4)	76.5	79.5(4)
O(1)–Cu'–O(1')	77.0(4)	77.4	79.4(4)
O(1)–Cu–N(10)	173.5(4)	171.2, 171.2	103.0(5)
O(1')–Cu–N(10)	99.1(4)	96.5, 98.9	101.2(5)
O(1)–Cu–N(1)	98.8(4)	99.5, 98.9	105.6(5)
O(1')–Cu–N(1)	171.5(4)	174.6, 171.0	101.4(5)
Cu–O(1)–Cu'	103.0(4)	102.0, 103.7	99.2(10)
N(1)–Cu–N(10) vs O(1)–Cu–O(1') ^a	10(2) 10(2)	6.8 12.0	42(1) 50(1)

^a Dihedral angle between the two indicated planes.

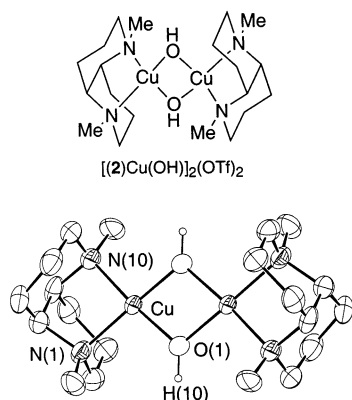
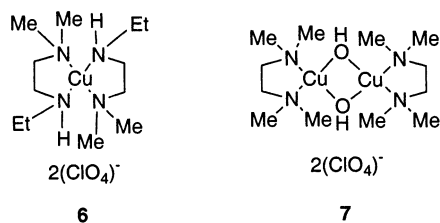


Figure 3. ORTEP drawing of [(2)Cu(OH)]₂(OTf)₂ with 30% probability thermal ellipsoids. Non-heteroatom hydrogens and the counterions (noncoordinating) are omitted for clarity.

terions do not coordinate to the copper(II) centers, similar to the complexes described above containing **1**.

The change in coordination structure from a 2:1 complex to a dimer upon alkylation of the 1,5-diaza-*cis*-decalin nitrogens is a consequence of the steric demand of the diamine ligands and is analogous to reported structural perturbations in related 1,2-diamine copper complexes. For example, *N,N*-dimethyl-*N*-ethylethylenediamine forms a 2:1 diamine:copper complex (**6**).⁹ However, *N,N,N,N*-tetramethylethylenediamine invariably affords the μ -hydroxo-bridged dimeric copper(II) complex (**7**).¹⁰ Steric interactions clearly play an important role in the formation of these copper(II) complexes. Formation of a monomeric complex can be achieved by taking advantage of this trend (i.e., replace *N*-Me with *N*-Et, see below).



The structure of complex [(2)Cu(OH)]₂(OTf)₂ is typical of μ -hydroxo-bridged dimeric copper(II) complexes.⁵ Comparison to the known bis(μ_2 -hydroxo) copper(II) dimeric complexes of the chiral saturated diamines (–)-sparteine¹¹ and *N,N,N,N*-tetramethyl-(1*R*,2*R*)-cyclohexanediamine (TMCDA)^{2f} (Table 3) reveals that the Cu–N bond distances are similar while the Cu–O bond distances are slightly shorter in the dimer of **2**. From these distances, it appears that the steric size of the ligand with respect to the hydroxo bridging is sparteine > TMCDA > **2**. The N–Cu–N and O–Cu–O bond angles of **2** (85.7° and 77.0°) are similar to those of TMCDA (85.9–87.8° and 76.5–77.4°) but are smaller than those of sparteine (90.3–90.6° and 79.4–79.5°). The Cu–O–Cu angles and Cu–Cu separations are similar for all three complexes; they are completely characteristic for this type of coordination complex⁸ and are smaller than those found in the trimeric complex (see above). The largest difference between these structures is found in the dihedral angle between the N–Cu–N and O–Cu–O planes, which is small in the complexes of **2** (10°) and TMCDA (6.8–12.0°), but is considerably larger in that of sparteine (42–50°). The size and shape of sparteine forces a tetrahedral distortion at the copper centers that is largely absent in these other ligands. Overall, the dimer of **2** is more similar to that of TMCDA versus sparteine, and in overall steric terms **2** is intermediate to TMCDA and sparteine. These structural results highlight the difference between the 1,5-diaza-*cis*-decalins and sparteine which is reflected in the wide range of enantioselectivities (see reaction in Scheme 1)^{3,12} introduced by the corresponding diamine copper catalysts.

With *N,N*-diethyl diamine **3**, a 1:1 diamine:copper monomeric complex was formed even when starting from copper(I) chloride (Figure 4). X-ray analysis of this copper(II) complex showed that the copper(II) atom is tetracoordinate, but now counterions fill the remaining

(9) Tsiamis, C. *Inorg. Chim. Acta* **1992**, 198–200, 651–661.

(10) Arcus, C.; Fivizzani, K. P.; Pavkovic, S. F. *J. Inorg. Nucl. Chem.* **1977**, 39, 285–287.

(11) Funahashi, Y.; Nakaya, K.; Hirota, S.; Yamauchi, O. *Chem. Lett.* **2000**, 1172–1173.

(12) Nakajima, M.; Miyoshi, I.; Kanayama, K.; Hashimoto, S.-I.; Noji, M.; Koga, K. *J. Org. Chem.* **1999**, 64, 2264–2271.

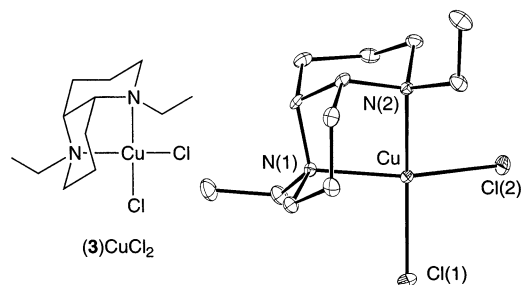


Figure 4. ORTEP drawing of **(3)**CuCl₂ with 30% probability thermal ellipsoids. Hydrogens are omitted for clarity.

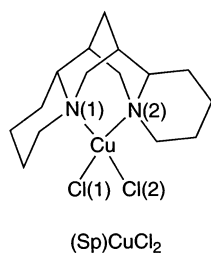
Table 4. Selected Bond Distances (Å) and Angles (deg) of Complexes **(3)CuCl₂ and **(Sp)**CuCl₂¹¹**

	(3) CuCl ₂	(Sp) CuCl ₂ ¹¹
Cu–N(1)	2.072(2)	1.993(5)
Cu–N(2)	2.072(2)	2.017(5)
Cu–Cl(1)	2.2455(7)	2.262(2)
Cu–Cl(2)	2.2455(7)	2.224(2)
N(1)–Cu–N(2)	84.74(9)	90.5(2)
N(1)–Cu–Cl(1)	94.01(5)	101.2(2)
N(1)–Cu–Cl(2)	157.63(5)	134.9(2)
N(2)–Cu–Cl(1)	157.63(5)	121.9(2)
N(2)–Cu–Cl(2)	94.01(5)	104.7(2)
Cl–Cu–Cl	95.38(4)	105.60(8)
N–Cu–N vs Cl–Cu–Cl ^a	30.94(4)	68.5

^a Dihedral angle between the two indicated planes.

coordination sites of the copper, which is different from the copper(II) complexes of diamines **1** and **2**. Clearly, the coordination chemistry of these copper(II) species is very sensitive to the stereochemical environment of the 1,5-diaza-*cis*-decalins.

This structure was compared to that of the reported [(*Sp*)CuCl₂] complex (Table 4).^{11,13} The Cu–N bond



distance (2.07 Å) is longer than that in the (–)-sparteine complex (1.99–2.02 Å), while the Cu–Cl bond distance (2.25 Å) is similar to that in the (–)-sparteine complex (2.22–2.26 Å). The N–Cu–N and Cl–Cu–Cl bond angles (84.7° and 95.4°) are smaller than those of (–)-sparteine complex (90.5° and 105.6°). The smaller N–Cu–N bond angles, on average, for the 1,5-diaza-*cis*-decalin structures relative to the sparteine structures indicate that 1,5-diaza-*cis*-decalin has a smaller bite angle relative to sparteine.¹⁴ The dihedral angle between the N–Cu–N and Cl–Cu–Cl planes is fairly

(13) (a) Childers, L. S.; Folting, K.; Merritt, L. L., Jr.; Streib, W. E. *Acta Crystallogr. B* **1975**, *31*, 924. (b) Lopez, S.; Muravyov, I.; Pulley, S. R.; Keller, S. W. *Acta Crystallogr.* **1998**, *C54*, 355–357.

(14) We observe the same trends (smaller bite angle with the 1,5-diaza-*cis*-decalins) in a comparison of the PdCl₂ complexes of sparteine (Jensen, D. R.; Pugsley, J. S.; Sigman, M. S. *J. Am. Chem. Soc.* **2001**, *123*, 7475–7476) with **1** and **2** (Kozlowski, M. C.; Li, X. Unpublished results).

large in the complex with **3** (30.9°), but is even larger in that of sparteine (68.5°). As was the case for the dimeric structures, sparteine forces a much larger tetrahedral distortion at the copper(II) center compared to **3**.

Active Species (1:1 vs 2:1). As a first step in our study of the mechanism of the oxidative biaryl couplings catalyzed by the **1**·copper(II) complexes, we wished to establish the stoichiometry between the ligand and copper present in the active catalyst. We observed that crystallization of the adduct from treatment of **1** with a variety of copper(I) and copper(II) species under aerobic conditions reproducibly provided 2:1 diamine:copper(II) complexes. Apparently, formation of such 2:1 complexes is highly favorable due to the affinity of copper(II) for amine ligands.¹⁵ These complexes were observed in most instances even when a 1:1 ratio of diamine:copper was employed in the preparation, indicating that the 2:1 **1**:copper(II) complexes represent the thermodynamically most stable species in this system. When the crystalline 2:1 diamine:copper complex ((**1**)₂Cu]Cl₂) was redissolved and employed in the oxidative asymmetric biaryl coupling of methyl 3-hydroxynaphthalene-2-carboxylate (**4**, Scheme 1), no reaction was observed.

Due to this result, we performed a further series of experiments (Table 5). The first 10 entries list the results from catalysts containing diamine **1** in the oxidative asymmetric biaryl coupling of **4** (Scheme 1). These entries are divided into sets of two, which differ only in the diamine to copper stoichiometry (L:Cu = 1:1 or 2:1). When Cu(OTf)₂ was employed as the metal source for the catalyst, very little reaction was observed with either stoichiometry (Table 5, entries 1, 2). In contrast, the CuCl-derived catalyst was very sensitive to the stoichiometry. Higher conversions were routinely observed with the 1:1 stoichiometry at both 40 and 80 °C (Table 5, entries 3–6), while the enantioselectivity was unaffected by the stoichiometry. Analogous results were observed with CuI-derived catalysts (entries 9, 10). The similar levels of enantioselection with the 1:1 and 2:1 diamine:copper catalyst formulations suggest the intervention of the same catalyst species (probably a 1:1 adduct) regardless of the in situ catalyst stoichiometry.

Further support for the assignment of the 1:1 diamine:copper complexes as the active catalyst species was obtained from the reactivity of isolated crystalline derivatives of the 1:1 and 2:1 diamine:copper adducts. Upon subjecting crystals of trimeric [(**1**)Cu(OH)]₃Cl₃ (1:1 diamine:Cu stoichiometry) to the reaction conditions (Table 5, entry 7), a similar reactivity/selectivity profile was observed relative to the catalyst generated in situ with a 1:1 diamine:copper ratio (Table 5, entry 5). On the other hand, when the crystalline 2:1 diamine:copper complex derived from CuCl [(**1**)₂Cu]Cl₂ was redissolved and employed, no product was observed (Table 5, entry 8), which is similar to the results from the catalyst generated in situ with a 2:1 diamine:copper ratio (Table 5, entry 6). Inasmuch as the correlation of reactivity/selectivity between the crystalline and in situ species is good in these systems (see also Table 5, entries 12, 13 and 16, 17), it is plausible that crystallographic structures are representative of the solution structures.

(15) Hatfield, W. E.; Piper, T. S.; Klabunde, U. *Inorg. Chem.* **1963**, *2*, 629–632.

Table 5. Effect of the Diamine, Copper Sources,^a and Stoichiometry on the Coupling Reaction of Methyl 3-Hydroxynaphthalene-2-carboxylate (4**, Scheme 1)^b**

entry	diamine	Cu source	diamine:Cu	catalyst source ^c	<i>T</i> (°C)	<i>t</i> (h)	solvent	yield (%) ^d	ee (%) ^e
1	1	Cu(OTf) ₂	1:1	in situ	80	24	CH ₃ CN	3	16
2	1	Cu(OTf) ₂	2:1	in situ	80	24	CH ₃ CN	3	4
3	1	CuCl	1:1	in situ	80	24	DCE	52	86
4	1	CuCl	2:1	in situ	80	24	DCE	5	86
5	1	CuCl	1:1	in situ	40	24	DCE	40	91
6	1	CuCl	2:1	in situ	40	24	DCE	3	93
7	1	CuCl	1:1	crystal ^f	40	24	DCE	32	90
8	1	CuCl	2:1	crystal ^g	40	24	DCE	0	0
9	1	CuI	1:1	in situ	40	48	CH ₃ CN	85	91
10	1	CuI	2:1	in situ	40	48	CH ₃ CN	32	90
11	1	Cu(BF ₄) ₂	1:1	in situ	40	48	CH ₃ CN	52	90
12	2	Cu(OTf) ₂	1:1	in situ	80	24	DCE	66	0
13	2	Cu(OTf) ₂	1:1	crystal ^h	80	24	DCE	58	2
14	2	Cu(OTf) ₂	2:1	in situ	80	24	DCE	42	5
15	2	Cu(OTf) ₂	3:1	in situ	80	24	DCE	36	4
16	3	CuCl	1:1	in situ	40	48	DCE	74	0
17	3	CuCl	1:1	crystal ⁱ	40	48	DCE	80	0

^a All of the active catalysts are copper(II) adducts. When CuX (X = Cl, I) sources are employed, the catalyst complex is presumably the hydroxo species, Cu(OH)X, which forms in the presence of oxygen. ^b 0.5 mmol **4** (0.1 M), 10 mol % (*S,S*)-diamine, 10 mol % Cu source, O₂. ^c In situ refers to a catalyst solution generated by combining the diamine and Cu source in the ratio indicated in the diamine:Cu column. Crystal refers to the specified crystalline compound. ^d Isolated yields. ^e Enantiomeric excess determined by HPLC (Chiralpak AD). Absolute configuration was *R* for all cases. ^f [(1)Cu(OH)]₃Cl₃. ^g [(1)₂Cu]Cl₂. ^h [(2)Cu(OH)]₂(OTf)₂. ⁱ (3)CuCl₂.

Since the 2:1 complex does form even when a 1:1 diamine:copper stoichiometry is used, the reactivity of the in situ catalyst species reflects both the amount of 1:1 (vs 2:1) complex present and the nature of the counterion. The equilibrium between the 1:1 and 2:1 complexes directly influences the amount of active catalyst (1:1) available. The counterion may influence this equilibrium but likely also plays a role in the inherent reactivity of the 1:1 complex (i.e., softer counterions will stabilize copper(I) intermediates, resulting in more rapid reactions, entry 5 vs 9).³ While the counterion does influence the reactivity of the catalysts, several different counterion formulations give rise to the same enantioselectivity (Table 5, entries 5, 9, 11). Together with the accumulated crystallographic data (counterions noncoordinating, see Figures 1–3), these results suggest that the counterions do not play an intimate role in the stereochemistry-determining step (see below).

With **2**, a different structural type was observed upon crystallization. In this case, a classic copper(II) dimer with bridging hydroxo ligands is seen. Once again, similar reactivity/selectivity profiles were observed for reactions that utilized this crystalline material or the corresponding 1:1 diamine:copper complex prepared in situ (Table 5, entries 12, 13). Notably, the decline in reactivity as the diamine:copper ratio increases is not as marked for the copper(II) complexes of **2** relative to those of **1** (entries 12, 14, 15 vs 3, 4). This result likely reflects the inability of the *N,N*-dimethyl analogue to effectively form 2:1 diamine:copper complexes due to steric repulsion between the *N*-methyl groups in such a complex. As a consequence, the formation of inactive complexes (2:1 diamine:copper) occurs to a lesser extent even when excess diamine is present.

Overall, the reactivity/selectivity trends of the active catalyst species formed during the in situ preparation and upon dissolution of the crystallized 1:1 complexes are the same. The intervention of a 1:1 diamine:copper catalyst is most consistent with these observations.

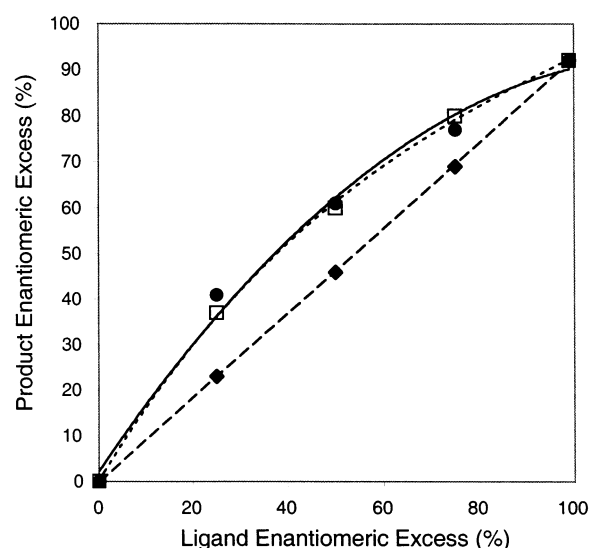


Figure 5. Nonlinear effects with the CuI catalyst derived from diamine **1** in the biaryl coupling of **4** at 40 °C under O₂ in 4:1 ClCH₂CH₂Cl/CH₃CN for 48 h (Scheme 1): (◆) theoretical linear plot (dashed line); (□) premixed ligands with indicated % ee (dotted line); (●) mixtures of the two enantiomerically pure catalyst solutions prepared separately (solid line).

Nonlinear Effects. A mild positive nonlinear effect¹⁶ has been observed for the copper catalysts in the oxidative coupling of **4** (Scheme 1). The same nonlinear effect was observed when a ligand of the indicated enantiomeric excess was utilized in generating the copper catalyst or when two separate enantiomeric copper catalyst solutions were mixed in the appropriate ratios. Thus, the nonlinear effect arises from species that are in rapid equilibrium. If this had not been the

(16) (a) Kagan, H. B. *Synlett* **2001**, 888–899. (b) Blackmond, D. G. *Acc. Chem. Res.* **2000**, *33*, 402–411. (c) Detlef, H.; Hans-Joachim, D.; Fisher, C.; Buschmann, H.; Baumann, W.; Heller, B. *Angew. Chem., Int. Ed.* **2000**, *39*, 495–499. (d) Girard, C.; Kagan, H. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 2922–2959.

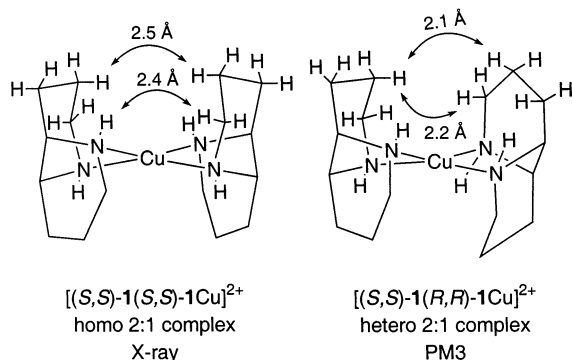


Figure 6. Models of the 2:1 hetero and homo complexes of **1** with Cu^{2+} .

case, then the nonlinear effect should not have been the same when the enantiomeric catalyst solutions were mixed.

A survey of the crystallographic complexes described in this study suggests an origin of the observed nonlinear effects. Two of the 2:1 diamine:copper complexes (triflate and tetrafluoroborate complexes) were generated from racemic **1**. Hence, the formation of 2:1 complexes containing the same diamine enantiomers (homo 2:1) or opposite diamine enantiomers (hetero 2:1) is possible. However, only the homo 2:1 complexes were obtained, and both enantiomers of the homo 2:1 complexes were observed in the unit cells. Molecular models¹⁷ show significant steric interactions between the two ligands of the hetero 2:1 complex (Figure 6). Such interactions are absent in the homo 2:1 complex (Figure 6). On this basis, we conclude that the hetero 2:1 complex is less stable than the homo 2:1 complex. Nonlinear effects arise either from the intervention of two molecules of the catalyst when enantioselection is established (diastereomeric transition states) or from the presence of dimeric/higher order diastereomeric complexes which have different rates of dissociation to the active catalyst. The latter analysis applies to the 2:1 complex since it is not an active catalyst (see above). Since the 2:1 hetero complexes do not appear to form, the nonlinear effects do not arise from this source.

For the trimeric complexes, the reactivity profiles indicate that these species are either the active catalyst or a precursor to the active catalyst. In either case, trimeric species do not account for the nonlinear effect since only the homotrimers form (all the diamines in the trimer are the same enantiomer) when these complexes are prepared from enantiomerically pure or racemic ligand.^{18,19}

The crystal structure from the related *N,N*-dimethyl diamine **2** provides the key to understanding the nonlinear effects. In this case, heterodimer crystals were obtained when a racemic ligand was used in the preparation. *This is the only complex, which contains more than one diamine ligand, in which both enantiomers of the diamine are found in one copper complex.*

(17) PM3(tm) semiempirical calculations with SPARTAN v5.0 (Wavefunction, Inc.: 18401 Von Karman Avenue, Suite 370; Irvine, CA 92612).

(18) A crystal structure of the trimer that was generated from the racemic ligand has also been obtained.

(19) Models indicate that the heterotrimers also have unfavorable steric interactions due to the close proximity between each of the diamine ligands.

Stereochemical models of the hetero- and homodimer complexes indicate a large spatial separation between the two diamines (unlike the 2:1 complexes and the trimers). Under these circumstances, it appears that the heterodimeric crystal is more stable than the homodimer. Calculations indicate that the energies of the heterodimer and homodimer dications are similar.¹⁷ While the copper(II) complexes of **2** provide low enantioselectivity in the oxidative biaryl coupling, the reactivity is similar to that observed with **1**. Thus, it is likely that both complexes (dimeric and trimeric in the solid state) can undergo exchange to the same type of active catalyst species in solution.

VPO measurements indicate that the average solution molecular weight of the catalyst prepared from 1,5-diaza-*cis*-decalin and CuCl under aerobic conditions in a chloroform solution is midway between the dimer and trimer. On this basis, it seems reasonable that the copper complex is in equilibrium between several species in solution. From the crystallographic structures, the presence of 2:1 complexes and trimers is probable. In addition, the dimeric complexes analogous to those seen in the crystal structures of **2** are likely to be present in this solution. If this is the case, then the nonlinear effect could arise from these dimers. If the dimer is the active catalyst, different homo- and heterodimers likely react with different rates (corresponding to different activation energies) since they are diastereomeric. Alternatively, the dimer may not be an active catalyst, but may prove to be a reservoir of inactive species. If the heterodimer is more stable and does not dissociate (or dissociates more slowly) to the active catalyst species, then a positive nonlinear effect would be observed.

Stereochemical Models. With the X-ray structures of these copper(II) complexes in hand, an effort has been made to construct plausible models for the presumed catalyst-substrate complexes to explain the sense of stereoselection in the biaryl coupling. Since the steric demand of the hydroxo bridges in the trimer most closely approximates that of the naphthoate substrate, the trimer was used as a starting point for the construction of stereochemical models. The hydroxo groups of the trimer were replaced by naphthoate **4**, resulting in distorted square planar structure **8** (Figure 7). In this case the top face of the naphthoate portion is less occluded by diamine **1** than the bottom face. We anticipate that electron transfer from the Cu(II) to the substrate occurs to yield a Cu(I) species and that this process will be accompanied by a geometry change at the copper center. It is unlikely that the two ligands (substrate and diamine) will rotate past one another (via a square planar structure) during this geometry change. Rather, the ligands will rotate in the direction of the already observed distortion, yielding **9**. In doing so, the same stereochemical face remains preferentially exposed over the course of the geometry change. Attack of a second substrate from this less hindered top face as illustrated in the stereoview of **9**-substrate is expected to be more facile, which is consistent with the observed stereochemical results.²⁰

(20) The second attacking substrate may also coordinate the copper catalyst or undergo hydrogen bonding with the copper diamine NH groups.

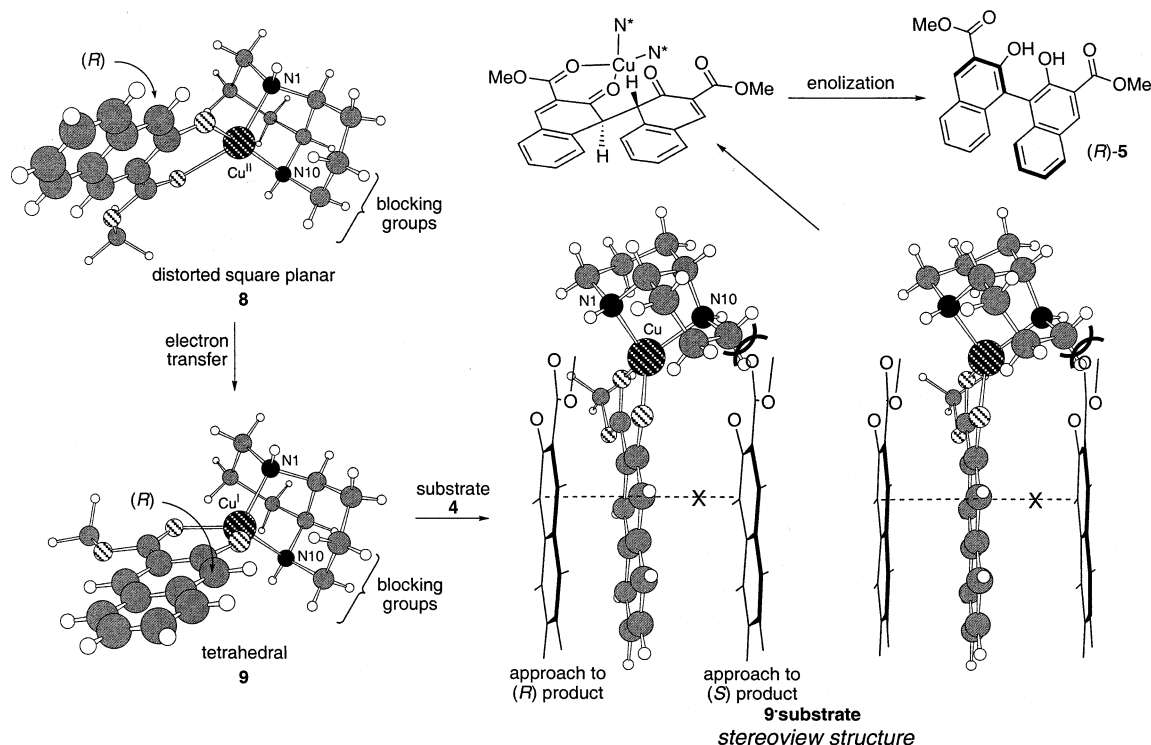


Figure 7. Stereochemical model for the biaryl coupling using (*S,S*)-**1**, which yields (*R*)-**5** (Scheme 1).

Concluding Remarks

Crystal structures of a series of copper(II) complexes of 1,5-diaza-*cis*-decalins have been obtained. The 1,5-diaza-*cis*-decalins have been shown to function as highly stable bidentate ligands via coordination of the “in” conformational form in all cases. The bite angle of the 1,5-diaza-*cis*-decalins (83.5–85.7°) was found to be approximately 5–7° smaller than the bite angle of sparteine (90.3–90.6°), as judged from a number of coordination complexes. By varying the substitution on the nitrogen atoms of 1,5-diaza-*cis*-decalin it is possible to form a range of different copper coordination complexes. From the crystallographic data and solution phase experiments, a picture of the catalytic cycle in the asymmetric oxidative biaryl coupling with 1,5-diaza-*cis*-decalin copper complexes begins to emerge (Figure 8). Several species can form including 2:1 (monomeric) and 1:1 (dimeric, trimeric, and monomeric) diamine:copper complexes. The evidence indicates that the 1:1 diamine:copper complexes are a reservoir of reactive species that likely undergo exchange with the substrate to form **8**. The geometry of proposed intermediate **8**, in turn, is consistent with the observed product configuration. This picture is also consistent with the observed nonlinear effects, in that the dimer may act as a sink for racemic **1**. Further studies are underway to investigate the nature of the carbon–carbon bond forming reaction and to understand the mechanism of catalyst reoxidation by molecular oxygen.

Experimental Section

General Considerations. CuCl and CuI were purchased from Strem. Cu(OTf)₂ was purchased from Acros. Cu(BF₄)₂·H₂O was purchased from Aldrich. 1,5-Diaza-*cis*-decalin (**1**) and *N,N*-dialkyl derivatives **2** and **3** were prepared using the reported methods.^{3,4} The biaryl coupling reactions were moni-

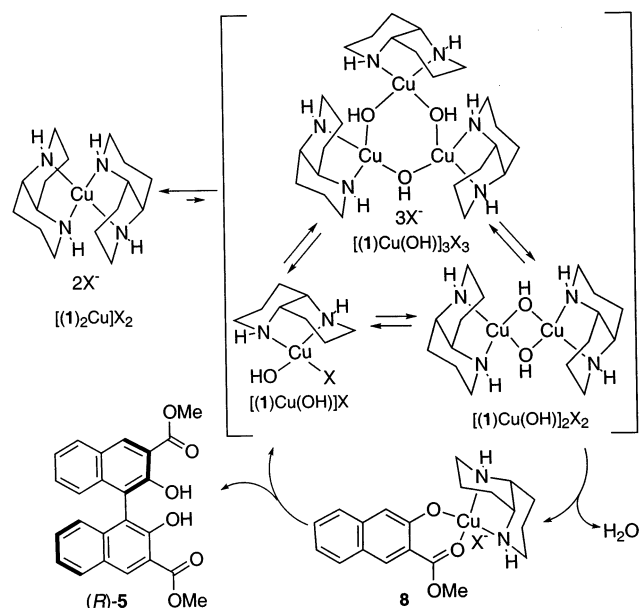


Figure 8. Catalytic cycle for the formation of (*R*)-**5**.

tored as described previously³ using a Waters 600 high-performance liquid chromatograph (HPLC) equipped with a variable wavelength detector ($\lambda = 254$ nm) and an analytical Chiralpak AS column (0.46 cm \times 25 cm) from Daicel.

Preparation of Metal Complexes and Crystals. [(1)₂Cu]Cl₂: To a solution of diamine **1** (1.1 equiv) in CH₂Cl₂ at room temperature open to the atmosphere was added CuCl (1.0 equiv). The mixture was sonicated for 30 min. The deep blue solution was filtered to remove any insoluble particulate matter. Upon standing at room temperature for several days, slow evaporation of the solvent afforded red-purple needles of bis[1,5-diaza-*cis*-decalin- κ *N,N,\kappa**N*]copper(II) dichloride.

[(1)₂Cu]I₂: Diamine **1** (1.1 equiv) in CH₃CN was added to a colorless solution of CuI (1.0 equiv) in CH₃CN at room temperature open to the atmosphere. The purple solution was

Table 6. Experimental Details and Crystal Data for [(1)₂Cu]X₂

	[(1) ₂ Cu]Cl ₂	[(1) ₂ Cu]I ₂	[(1) ₂ Cu](OTf) ₂	[(1) ₂ Cu](BF ₄) ₂
metal source	2:1 Cl CuCl	2:1 I CuI	2:1 OTf Cu(OTf) ₂	2:1 BF ₄ Cu(BF ₄) ₂
ligand used	(<i>S,S</i>)	(<i>S,S</i>)	racemic	(<i>S,S</i>) ^a
ligand config in cryst	(<i>S,S</i>), (<i>S,S</i>)	(<i>S,S</i>), (<i>S,S</i>)	(<i>R,R</i>), (<i>R,R</i>) (<i>S,S</i>), (<i>S,S</i>)	(<i>S,S</i>), (<i>S,S</i>)
cryst cond	evaporation (CH ₂ Cl ₂)	evaporation (CH ₂ Cl ₂)	vapor diffusion (CH ₂ Cl ₂ /Et ₂ O)	vapor diffusion (CH ₂ Cl ₂ /hexanes)
formula	CuC ₁₆ H ₃₄ N ₄ OI ₂	CuC ₁₆ H ₃₄ N ₄ OI ₂	CuC ₁₈ H ₃₂ N ₄ S ₂ O ₆ F ₆	CuC ₁₆ B ₂ H ₃₂ N ₄ F ₈
fw	432.91	615.81	642.14	517.62
cryst type	needle	needle	needle	needle
color	red-purple	red-purple	blue-purple	blue
cryst syst	orthorhombic	orthorhombic	tetragonal	orthorhombic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (#19)	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (#19)	<i>P</i> 4 ₂ / <i>mbc</i> (#135)	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (#19)
<i>a</i> , Å	14.4671(3)	11.2421(1)	12.6921(1)	14.2450(3)
<i>b</i> , Å	17.6860(2)	20.6154(2)		17.7030(4)
<i>c</i> , Å	7.7624(1)	9.5218(1)	16.0685(2)	8.4957(2)
<i>V</i> , Å ³	1986.13(50)	2206.78(4)	2588.47(4)	2142.44(8)
<i>Z</i>	4	4	4	4
<i>D</i> _{calc} , g/cm ³	1.448	1.854	1.648	1.605
<i>R</i> ₁ ^{b,c}	0.0376	0.0334	0.0579	0.0468
<i>wR</i> ₂ ^{b,d}	0.0812	0.0813	0.1316	0.1127
GOF ^e	1.082	1.063	1.167	1.058

^a When a racemic ligand was employed, crystals were obtained (different space group) that contained only the two enantiomeric homo 2:1 diamine:copper complexes. ^b $F > 4\sigma$. ^c $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^d $wR_2 = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$. ^e $GOF = \{\sum w(F_o^2 - F_c^2)^2 / (n - p)\}^{1/2}$ where n = number of reflections and p = the number of parameters refined.

Table 7. Experimental Details and Crystal Data for Complexes [(1)Cu(OH)]₃Cl₃, [(2)Cu(OH)]₂(OTf)₂, and (3)CuCl₂

	[(1)Cu(OH)] ₃ Cl ₃ ^a <i>μ</i> -hydroxo trimer	[(2)Cu(OH)] ₂ (OTf) ₂ ^b <i>μ</i> -hydroxo dimer	[(3)CuCl ₂] monomer
metal source	CuCl	Cu(OTf) ₂	CuCl
ligand used	(<i>S,S</i>)	racemic	racemic
ligand config	(<i>S,S</i>), (<i>S,S</i>), (<i>S,S</i>) ^c	(<i>S,S</i>), (<i>R,R</i>)	(<i>S,S</i>), (<i>R,R</i>)
cryst cond	vapor diffusion (DCE/pentane)	vapor diffusion (CH ₂ Cl ₂ /Et ₂ O)	vapor diffusion (CH ₂ Cl ₂ /MTBE)
formula	Cu ₃ C ₈ H ₁₉ N ₂ O ₂ Cl	Cu ₂ C ₂₂ H ₄₀ N ₄ S ₂ O ₈ F ₆	CuC ₁₂ H ₂₄ N ₂ Cl
fw	274.24	793.78	330.77
cryst type	cube	needle	needle
color	blue	blue-purple	blue-green
cryst syst	rhombohedral	triclinic	orthorhombic
space group	<i>R</i> 3 (#146)	<i>P</i> 1̄ (#2)	<i>C</i> 222 (#20)
<i>a</i> , Å	20.776(3)	8.798(2)	7.737(2)
<i>b</i> , Å		12.136(2)	11.958(3)
<i>c</i> , Å	13.738(2)	7.922 (2)	15.786(4)
<i>V</i> , Å ³	5131.7(13)	819.5(3)	1460.4(7)
<i>Z</i>	18	1	4
<i>D</i> _{calc} , g/cm ³	1.597	1.608	1.504
<i>R</i> ₁ ^{d,e}	0.0251	0.1173	0.0229
<i>wR</i> ₂ ^{d,f}	0.0520	0.3045	0.0450
GOF ^g	1.039	1.097	0.948

^a When a racemic ligand was employed, crystals containing the same structure were obtained that diffracted well, but peculiarities arose in the structure due to twinning and the presence of both enantiomeric forms. ^b $\alpha = 99.93(2)^\circ$, $\beta = 92.063(6)^\circ$, $\gamma = 79.584(14)^\circ$. ^c For both molecules in the asymmetric unit. ^d $F > 4\sigma$. ^e $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^f $wR_2 = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$. ^g $GOF = \{\sum w(F_o^2 - F_c^2)^2 / (n - p)\}^{1/2}$ where n = number of reflections and p = the number of parameters refined.

filtered to remove any insoluble particulate matter. The CH₃CN was removed in vacuo, and the residue was dissolved in CH₂Cl₂. Upon standing at room temperature for several days, slow evaporation of the solvent afforded red-purple needles of bis[1,5-diaza-*cis*-decalin- κ N, κ N]copper(II) diiodide.

[(1)₂Cu](OTf)₂: Diamine **1** (1.1 equiv) in CH₂Cl₂ was slowly added to a colorless solution of Cu(OTf)₂ (1.0 equiv) in CH₂Cl₂ at room temperature under N₂. The purple solution was filtered to remove any insoluble particulate matter. Slow vapor diffusion with Et₂O at room temperature for several days afforded blue-purple needles of bis[1,5-diaza-*cis*-decalin- κ N, κ N]copper(II) bistrifluoromethanesulfonate.

[(1)₂Cu](BF₄)₂: Diamine **1** (1.1 equiv) in CH₂Cl₂ was slowly added to a blue solution of Cu(BF₄)₂·H₂O (1.0 equiv) in CH₃CN at room temperature under N₂. The purple solution was filtered to remove any insoluble particulate matter. The CH₃CN was removed in vacuo, and the residue was dissolved

in CH₂Cl₂. Slow vapor diffusion with hexanes at room temperature for several days afforded blue crystals of bis[1,5-diaza-*cis*-decalin- κ N, κ N]copper(II) bistetrafluoroborate.

[(1)Cu(OH)]₃Cl₃: CuCl (1.0 equiv) was added to diamine (*S,S*)-**1** (1.1 equiv) in ClCH₂CH₂Cl at room temperature. The mixture was sonicated open to the atmosphere for 30 min. The deep blue solution was filtered to remove any insoluble particulate matter. Slow vapor diffusion with pentane at room temperature for several days afforded a dilute blue-green solution, and the solvent was further evaporated slowly over several days to afford blue cubic crystals of tris[*μ*-hydroxy-[(*S,S*)-1,5-diaza-*cis*-decalin- κ N, κ N]copper(II) chloride].

[(2)Cu(OH)]₂(OTf)₂: Diamine **2** (1.1 equiv) in CH₂Cl₂ was slowly added to a colorless solution of Cu(OTf)₂ (1.0 equiv) in CH₂Cl₂ at room temperature under N₂. The purple solution was filtered to remove any insoluble particulate matter. Slow vapor diffusion with Et₂O at room temperature for several days

afforded blue-green cubic crystals of bis{ μ -hydroxy[*N,N*-dimethyl-1,5-diaza-*cis*-decalin- κ *N,N*]}dicopper(II) trifluoromethanesulfonate}.

[(**3**)CuCl₂]: A solution of diamine **3** (0.272 g, 1.38 mmol) in CH₂Cl₂ was added to a stirring solution of CuCl (0.129 g, 1.30 mmol) in CH₃CN at room temperature. The mixture was vigorously stirred open to the atmosphere for 7 h. After the solvents were removed in vacuo, the residue was dissolved in CH₂Cl₂. The deep blue solution was filtered to remove any insoluble particulate matter. Slow vapor diffusion with MTBE at room temperature for 24 h afforded blue-green needles of dichloro[*N,N*-diethyl-1,5-diaza-*cis*-decalin- κ *N,N*]copper(II).

General Procedure for the X-ray Data Collection and Analysis. X-ray intensity data were collected on a Rigaku R-Axis IIC or a Rigaku Mercury CCD area detector employing graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å). Oscillation images were processed using *bioteX* or *CrystalClear*,²¹ producing a listing of unaveraged F^2 and $w(F^2)$ values, which were then passed to the *teXsan*²² program package for further processing and structure solution on a Silicon Graphics computer.

The structures were solved by direct methods (SIR92).²³ Refinement was by full-matrix least squares based on F^2 using SHELXL-93.²⁴ All reflections were used during refinement (F^2 's that were experimentally negative were replaced by $F^2 = 0$). The weighing scheme used was $w = 1/[\sigma^2(F_o^2) + AP^2 + BP]$ where $P = (F_o^2 + 2F_c^2)/3$. See Tables 6 and 7 for descriptions of the crystallographic parameters.

Nonlinear Effects. In the first procedure, diamine **1** (0.1 equiv) with the indicated enantiomeric excess (Figure 5) was

(21) (a) *bioteX*, A suite of Programs for the Collection, Reduction and Interpretation of Imaging Plate Data; Molecular Structure Corporation, 1995. (b) *CrystalClear*, Rigaku Corporation, 1999.

(22) *teXsan*, Crystal Structure Analysis Package; Molecular Structure Corporation, 1985 and 1992.

(23) SIR92. Altomare, A.; Burla, M. C.; Camalli, M.; Casciaro, M.; Giacovazzo, C.; Guagliardi, A.; Polidoro, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(24) Sheldrick, G. M. *SHELXL-93*, Program for the Refinement of Crystal Structures; University of Göttingen: Germany, 1993.

dissolved in ClCH₂CH₂Cl and was added to a freshly prepared room-temperature CH₃CN solution of CuI (0.1 equiv) open to the atmosphere.

In a second procedure, separate solutions of the (*S,S*)- and (*R,R*)-catalysts were prepared from solutions of (*S,S*)-diamine **1** and (*R,R*)-diamine **1** in ClCH₂CH₂Cl by addition to CuI in CH₃CN followed by exposure to air. These solutions were then combined in the appropriate proportions in dry test tubes to generate the catalyst solutions with the indicated ligand enantiomeric excess (Figure 5).

The blue catalyst solutions prepared as described above were added to a 0.10 M solution of substrate (1.0 equiv) in a disposable test tube or vial, and the oxidative coupling reactions were performed as reported previously.³ For both sets of experiments, the overall ratio of the solvents in the final reaction mixture was 4:1 ClCH₂CH₂Cl:CH₃CN.

Vapor Phase Osmometry (VPO) Measurements. The average molecular weight of the complex derived from CuCl and (*S,S*)-**1** under aerobic conditions in solution was determined to be 650 or less by vapor phase osmometry (VPO) measurement. The measurement was performed by INDSPEC Chemical Corporation, Pittsburgh, PA 15238, using a Knauer K-7000 vapor phase osmometer using CHCl₃ as a solvent at 37 °C.

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Supporting Information Available: Text giving full details of the crystallographic methods and tables giving X-ray data. This material is available free of charge on the Internet at <http://pubs.acs.org>.

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