Structures and Properties of Copper Alkene Complexes. Preorganization Effects and the Binding of Different Isomers of Cyclododecatriene to Copper Triflate

Brian J. Bellott and Gregory S. Girolami*

School of Chemical Sciences, University of Illinois at Urbana—Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801

The single-crystal X-ray structures of the copper 1,5,9-cyclododecatriene complexes (*cis,cis,trans*-$C_{12}H_{18}$)Cu(OTf), cct-**1**, (*cis,trans,trans*-$C_{12}H_{18}$)Cu(OTf), ctt-**1**, and (*trans,trans,trans*-$C_{12}H_{18}$)Cu(OTf), ttt-**1**, have been determined. In all three compounds, the triflate ligand and all three C=C double bonds of the triene are bound to the copper center, which adopts a distorted tetrahedral coordination geometry. The Cu−C distances are 2.190−2.217 Å and the Cu−O distances are 2.096−2.135 Å. The complex ctt-**1** is a nonelectrolyte in nitromethane. The ^1H and ^{13}C NMR spectra of ctt-**1** and ttt-**1** show that the two faces of the trienes, which are inequivalent in the solid state structure, are equivalent in solution even at −70 °C, suggesting that these molecules undergo a dynamic exchange process that is rapid on the NMR time scale (the two faces of cct-$C_{12}H_{18}$ are inequivalent even for the free triene, and so dynamic processes in its copper complex are not so easily observed). Most likely, the dynamic processes in ctt-**1** and ttt-**1** involve movement of the triflate ligand between one "side" of the molecule and the other by means of a dissociative process, although dissociation of one or more double bonds of the alkene from the copper center, followed by an intramolecular rearrangement, cannot be ruled out. ^{63}Cu NMR chemical shifts are also reported. Competition studies in toluene show that the free energy of ctt-**1** is about 1 kcal mol^{-1} lower (i.e., more stable) than expected from the relative energies of the free trienes. This stabilization can be attributed to a preorganization effect.

Introduction

Copper alkene complexes play a number of important roles in chemistry and biology, including serving as the active site in the ethylene receptor ETR 1, which plays a key role in fruit ripening, seed germination, flowering, and other functions.[1−3] In addition, copper alkene complexes are useful as catalysts for such reactions as conjugate additions to α,β-unsaturated ketones,[4] the aziridination of alkenes,[5−7] and the photoconversion of norbornadiene to quadricyclane.[8] Copper alkene complexes are also useful in chiral separations,[9] as reagents for the activation of dioxygen,[10] and for their fluorescent properties[11,12] and ferroelectric behavior.[13] Finally, copper alkene complexes have been studied as chemical vapor deposition precursors[14] and as atomic layer deposition (ALD) precursors[15,16] for copper metal.

Copper compounds bearing one ethylene ligand are well known.[10,17−26] There are only two examples of copper com-

* Corresponding author. E-mail: girolami@scs.uiuc.edu.

(1) Rodriguez, F. I.; Esch, J. J.; Hall, A. E.; Binder, B. M.; Schaller, G. E.; Bleeckert, A. B. *Science* **1999**, *283*, 996–998.

(2) Beyer, E. M.; Blomstrom, D. C. In *Plant Growth Substances*; Skoog, F., Ed.; Springer-Verlag: New York, 1979; pp 208−218.

(3) Abeles, F. B.; Morgan, P. W.; Selveit, M. E. *Ethylene in Plant Biology*, 2nd ed.; Academic Press: San Diego, 1994.

(4) Perez, P. J.; Diaz-Requejo, M. M. In *Comprehensive Organometallic Chemistry III*; Elsevier: Amsterdam, 2007; Vol. 2, pp 153−195.

(5) Li, Z.; Quan, R. W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5889–5890.

(6) Brandt, P.; Soedergren, M. J.; Andersson, P. G.; Norrby, P.-O. *J. Am. Chem. Soc.* **2000**, *122*, 8013–8020.

(7) Gillespie, K. M.; Sanders, C. J.; O'Shaughnessy, P.; Westmoreland, I.; Thickitt, C. P.; Scott, P. *J. Org. Chem.* **2002**, *67*, 3450–3458.

(8) Wang, X.-S.; Zhao, H.; Li, Y.-H.; Xiong, R.-G.; You, X.-Z. *Top. Catal.* **2005**, *35*, 43–61.

(9) Cavallo, L.; Cuccolito, M. E.; De Martino, A.; Giordano, F.; Orabona, I.; Vitagliano, A. *Chem.−Eur. J.* **2000**, *6*, 1127–1139.

(10) Dai, X.; Warren, T. H. *Chem. Commun.* **2001**, 1998–1999.

(11) Zhang, J.; Xiong, R.-G.; Chen, X.-T.; Xue, Z.; Peng, S.-M.; You, X.-Z. *Organometallics* **2002**, *21*, 235–238.

(12) Zhang, J.; Xiong, R.-G.; Zuo, J.-L.; You, X.-Z. *Chem. Commun.* **2000**, 1495–1496.

(13) Qu, Z.-R.; Chen, Z.-F.; Zhang, J.; Xiong, R.-G.; Abrahams, B. F.; Xue, Z.-L. *Organometallics* **2003**, *22*, 2814–2816.

(14) Rickerby, J.; Steinke, J. H. G. *Chem. Rev.* **2002**, *102*, 1525–1549.

(15) Park, K.-H.; Marshall, W. J. *J. Am. Chem. Soc.* **2005**, *127*, 9330–9331.

(16) Park, K.-H.; Bradley, A. Z.; Thompson, J. S.; Marshall, W. J. *Inorg. Chem.* **2006**, *45*, 8480–8482.

(17) Thompson, J. S.; Whitney, J. F. *Inorg. Chem.* **1984**, *23*, 2813–2819.

(18) Thompson, J. S.; Swiatek, R. M. *Inorg. Chem.* **1985**, *24*, 110–113.

(19) Dias, H. V. R.; Lu, H.-L.; Kim, H.-J.; Polach, S. A.; Goh, T. K. H. H.; Browning, R. G.; Lovely, C. J. *Organometallics* **2002**, *21*, 1466–1473.

(20) Dias, H. V. R.; Singh, S.; Flores, J. A. *Inorg. Chem.* **2006**, *45*, 8859–8861.

(21) Dias, H. V. R.; Wu, J. *Eur. J. Inorg. Chem.* **2008**, *2008*, 509–522.

(22) Straub, B. F.; Eisentrager, F.; Hofmann, P. *Chem. Commun.* **1999**, 2507–2508.

(23) Suenaga, Y.; Wu, L. P.; Kuroda-sowa, T.; Munakata, M.; Maekawa, M. *Polyhedron* **1996**, *16*, 67–70.

(24) Masuda, H.; Yamamoto, N.; Taga, T.; Machida, K.; Kitagawa, S.; Munakata, M. *J. Organomet. Chem.* **1987**, *322*, 121–129.

(25) Dai, J.; Yamamoto, M.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Munakata, M. *Inorg. Chem.* **1997**, *36*, 2688–2690.

(26) Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Nakamura, M.; Akiyama, S.; Kitagawa, S. *Inorg. Chem.* **1994**, *33*, 1284–1291.

(27) Sullivan, R. M.; Liu, H.; Smith, D. S.; Hanson, J. C.; Osterhout, D.; Ciraolo, M.; Grey, C. P.; Martin, J. D. *J. Am. Chem. Soc.* **2003**, *125*, 11065–11079.

(28) Krossing, I.; Reisinger, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 5725–5728.

Table 1. Crystallographic Data for the Three $Cu(C_{12}H_{18})(OTf)$ Isomers[a]

	$Cu(cct\text{-}C_{12}H_{18})(OTf)$	$Cu(ctt\text{-}C_{12}H_{18})(OTf)$	$Cu(ttt\text{-}C_{12}H_{18})(OTf)$
formula	$C_{13}H_{18}CuF_3O_3S$	$C_{13}H_{18}CuF_3O_3S$	$C_{13}H_{18}CuF_3O_3S$
mol wt	374.87	374.87	374.87
space group	*Pbca*	*P2$_1$/c*	*Cmc2$_1$*
a, Å	8.1718(5)	7.2459(16)	11.345(3)
b, Å	15.3049(9)	13.279(3)	9.915(3)
c, Å	25.0661(16)	15.835(4)	13.767(4)
β, deg	90	99.011(4)	90
V, Å^3	3135.0(3)	1505.0(6)	1548.6(7)
T, K	198(2)	193(2)	193(2)
Z	8	4	4
d_{calcd}, g cm^{-3}	1.589	1.655	1.608
μ, cm^{-1}	1.563	1.628	1.582
size, mm	$0.08 \times 0.08 \times 0.35$	$0.05 \times 0.10 \times 0.40$	$0.09 \times 0.30 \times 0.56$
diffractometer		Siemens SMART	
radiation		Mo Kα, $\bar{\lambda} = 0.710\ 73$ Å	
monochromator		graphite crystal	
no. of reflns, total	34 869	11 663	9332
no. of reflns, unique	2985	2754	1956
variables	263	191	224
R_F (obsd data)	0.0519	0.0334	0.0295
wR$_2$ (all data)	0.1676	0.0640	0.0529

[a] $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$, $wR_2 = \{\sum [w(F_o{}^2 - F_c{}^2)^2]/\sum [w(F_o{}^2)^2]\}^{1/2}$.

plexes that bear more than one ethylene ligand, $(C_2H_4)_2CuAlCl_4$ and $[Cu(C_2H_4)_3][Al\{OC(CF_3)_3\}_4]$.[27] There are also two known tris-ethylene complexes of silver and gold.[28,29]

Little is known about copper complexes of polyenes, especially those in which the copper center is bound to two or more C=C double bonds. Only seven such compounds have been crystallography characterized: $[Cu(cod)_2][ClO_4]$, where cod = 1,5-cyclooctadiene;[30] $Cu_2(cod)_2X_2$, where X = Cl, Br, or I;[30] $Cu(tbc)(OTf)$, where tbc = 1,2,5,6,9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-triyne;[31] $[Cu(ccc\text{-}C_{12}H_{18})(MeOH)][BF_4]$, and $[Cu(ccc\text{-}C_{12}H_{18})][Al\{OC(CF_3)_3\}_4]$, where ccc-$C_{12}H_{18}$ is *cis,cis,cis*-1,5,9-cyclododecatriene.[32] In many copper complexes of polyenes, each copper center is bound to only one C=C double bond.[33-38] In other copper complexes of polyenes, the number of metal−alkene interactions has not been established.[39-42]

The alkene 1,5,9-cyclododecatriene, $C_{12}H_{18}$, exists in four isomeric forms that differ in the configurations of the double bonds: these four isomers can be designated as ccc, cct, ctt, and ttt, where c and t refer to *cis* and *trans*, respectively. Three of these four trienes (all except the ccc isomer) are prepared by the catalytic cyclotrimerization of butadiene; typically, "naked"

nickel serves as the catalyst.[43,44] Of the four isomers, ttt-$C_{12}H_{18}$ is the principal product of the nickel-based cyclotrimerization catalysis. Cyclododecatrienes have numerous uses:[45,46] for example, they can be converted into valuable chemicals such as brominated flame retardants[47] and ingredients for the perfume industry,[48] and they have also been discussed as starting materials for the preparation of the polyamide precursors laurolactam and dodecanedioc acid.[49-51]

In 1973, Salomon and Kochi[42] described the isolation of adducts of copper(I) triflate with the cct, ctt, and ttt isomers of cyclododecatriene. The compounds, which were prepared by treating a benzene solution of Cu(benzene)(OTf) with the appropriate cyclododecatriene isomer, were characterized by IR and ^{1}H and ^{13}C NMR spectroscopy.[42,52] We now describe the solid state structures of the cct, ctt, and ttt isomers of these complexes and also assess by means of equilibrium competition experiments how strongly each of the three cyclododecatriene isomers binds to the copper center in solution. The results shed new light on the nature of copper−alkene bonding.

Results and Discussion

X-ray Crystal Structures of Copper Cyclododecatriene Complexes. By following Salomon and Kochi's procedure, we obtained crystalline samples of the 1,5,9-cyclododecatriene complexes Cu(*cis,cis,trans*-$C_{12}H_{18}$)(OTf), cct-**1**, Cu(*cis,trans,trans*-$C_{12}H_{18}$)(OTf), ctt-**1**, and Cu(*trans,trans,trans*-$C_{12}H_{18}$)-(OTf), ttt-**1**, and carried out single-crystal X-ray diffraction studies of each (Tables 1 and 2). In all three structures, the copper is bound to all three C=C bonds and to the oxygen of the triflate ligand in a distorted tetrahedral geometry. In the crystal of ttt-**1**, the molecule resides on a mirror plane despite the fact that individual molecules lack mirror symmetry. This means that each site is modeled as a superposition of opposite enantiomers. A satisfactory disorder model was devised, but the metric parameters for this compound are somewhat less

(29) Dias, H. V. R.; Fianchini, M.; Cundari, T. R.; Campana, C. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 556–559.

(30) Kok, J. M.; Skelton, B. W.; White, A. H. *J. Cluster Sci.* **2004**, *15*, 365–376.

(31) Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *Inorg. Chem.* **1988**, *27*, 2201–2202.

(32) Chernyshova, E. S.; Goddard, R.; Poerschke, K.-R. *Organometallics* **2007**, *26*, 4872–4880.

(33) Franceschi, F.; Guardigli, M.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1997**, *36*, 4099–4107.

(34) Krisyuk, V. V.; Turgambaeva, A. E.; Rhee, S.-W. *Polyhedron* **2004**, *23*, 809–813.

(35) Chen, T. Y.; Omnes, L.; Vaisserman, J.; Doppelt, P. *Inorg. Chim. Acta* **2004**, *357*, 1299–1302.

(36) Schmidt, G.; Behrens, U. *J. Organomet. Chem.* **1995**, *503*, 101–109.

(37) Baenziger, N. C.; Richards, G. F.; Doyle, J. R. *Inorg. Chem.* **1964**, *3*, 1529–1535.

(38) Baenziger, N. C.; Haight, H. L.; Doyle, J. R. *Inorg. Chem.* **1964**, *3*, 1535–1541.

(39) Haight, H. L.; Doyle, J. R.; Baenziger, N. C.; Richard, G. F. *Inorg. Chem.* **1963**, *2*, 1301.

(40) Paiaro, G.; Netto, N.; Musco, A.; Palumbo, R. *Ric. Sci., Rend., Sez. A* **1965**, *8*, 1441–1450.

(41) Chow, Y. L.; Cheng, X.-E.; Buono-Core, G. E. *Organometallics* **1987**, *6*, 1126–1129.

(42) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889–1897.

(43) Jolly, P. W.; Wilke, G. In *The Organic Chemistry of Nickel*; Academic Press: New York, 1975; Vol. 2, pp 133−212.

(44) Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, pp 671−711.

(45) Kosswig, K. *Chem.-Ztg.* **1972**, *96*, 373–383.

(46) Zakharkin, L. I.; Guseva, V. V. *Russ. Chem. Rev.* **1978**, *47*, 955–974.

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Three Cu(C₁₂H₁₈)(OTf) Isomers[a]
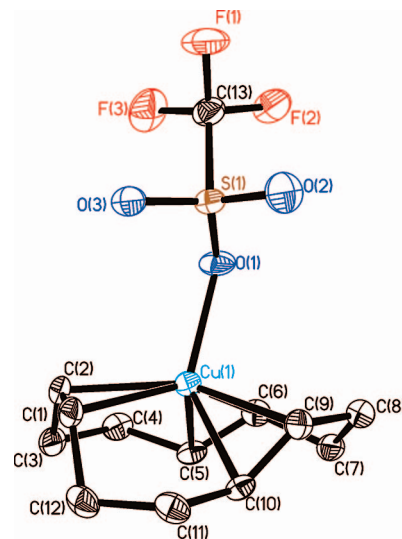
distance/angle	Cu(cct-C$_{12}$H$_{18}$) (OTf)	Cu(ctt-C$_{12}$H$_{18}$) (OTf)	Cu(ttt-C$_{12}$H$_{18}$) (OTf)
Cu(1)−O(1)	2.108(5)	2.080(2)	2.076(11)
Cu(1)−C(1)	2.230(7)	2.156(3)	2.206(9)
Cu(1)−C(2)	2.208(7)	2.151(3)	2.206(7)
Cu(1)−C(5)	2.267(6)	2.313(3)	2.233(8)
Cu(1)−C(6)	2.259(7)	2.258(3)	2.167(14)
Cu(1)−C(9)	2.232(8)	2.197(3)	2.175(10)
Cu(1)−C(10)	2.199(7)	2.190(3)	2.193(17)
C(1)−C(2)	1.314(10)	1.350(5)	1.345(10)
C(5)−C(6)	1.310(9)	1.338(4)	1.337(10)
C(9)−C(10)	1.274(10)	1.350(4)	1.337(10)
O(1)−Cu(1)−C(1)	114.4(3)	117.0(1)	87.8(3)
O(1)−Cu(1)−C(2)	114.1(2)	105.7(1)	104.9(3)
O(1)−Cu(1)−C(5)	105.3(2)	117.1(1)	98.0(3)
O(1)−Cu(1)−C(6)	93.1(3)	90.5(1)	122.0(4)
O(1)−Cu(1)−C(9)	101.8(3)	98.5(1)	106.7(4)
O(1)−Cu(1)−C(10)	131.6(3)	133.3(1)	120.0(3)
Cu(1)−O(1)−S(1)	125.4(5)	120.0(1)	130.3(8)

[a] When disorder is present, the distance given is that for the major occupancy site.
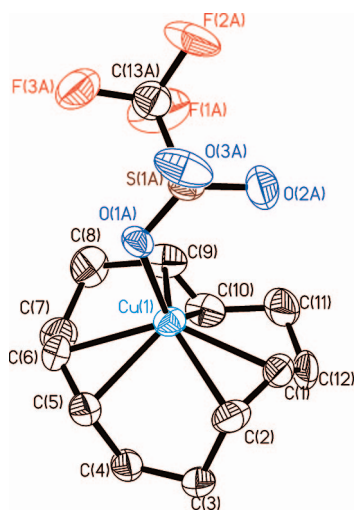
Figure 1. ORTEP representation of Cu(cct-C$_{12}$H$_{18}$)(OTf) with 30% probability thermal ellipsoids. The hydrogen atoms and the minor disordered component of the triflate group have been omitted for clarity.

Figure 2. ORTEP representation of Cu(ctt-C$_{12}$H$_{18}$)(OTf) with 30% probability thermal ellipsoids. The hydrogen atoms have been omitted for clarity.
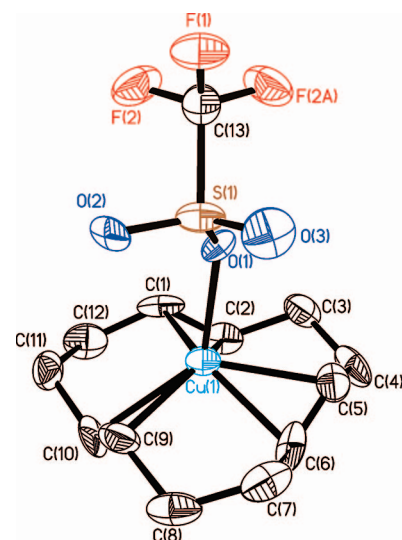
Figure 3. ORTEP representation of Cu(ttt-C$_{12}$H$_{18}$)(OTf) with 30% probability thermal ellipsoids. The hydrogen atoms and the second minor component of the triflate group have been omitted for clarity.

precise than for the other two isomers. In crystals of cct-**1**, the triflate group shows some conformational disorder, but both conformers have similar Cu−O bond distances.

In cct-**1** (Figure 1), the two *cis* double bonds and their vicinal carbon atoms form a tub-like geometry. In ctt-**1** (Figure 2), the C$_{12}$H$_{18}$ ligand adopts a distorted *syn*-fused tub-chair conformation, with the *cis* double bond being at the end of the tub farthest from the fusion points. Interestingly, in this complex, one of the two *trans* double bonds forms significantly longer Cu−C distances (2.28 Å) than does the other *trans* double bond (2.19 Å). In ttt-**1** (Figure 3), the C$_{12}$H$_{18}$ ligand adopts an all-chair

conformation with local 3-fold symmetry. This conformation is similar to that seen in the corresponding Ni⁰ complex Ni(ttt-C$_{12}$H$_{18}$)(PMe$_3$).[53] The average C=C bond length of 1.340(10) Å in ttt-**1** is essentially the same as that of 1.32 Å in the free ligand[54] within experimental error.

The Cu−O bond lengths to the triflate ligand are 2.108(5) Å in cct-**1**, 2.080(2) Å in ctt-**1**, and 2.076(11) Å in ttt-**1**. The average Cu−C distances to the C=C double bonds are 2.232 (cct-**1**), 2.211 (ctt-**1**), and 2.197 Å (ttt-**1**); for comparison, the average Cu−C distances to the C=C double bonds in the all-*cis* complexes [Cu(ccc-C$_{12}$H$_{18}$)(MeOH)][BF$_4$] and [Cu(ccc-C$_{12}$H$_{18}$)]-[Al{OC(CF$_3$)$_3$}$_4$] are 2.222(2) and 2.193(4) Å, respectively.[32] The Cu−O and Cu−C distances in all of these complexes are essentially insensitive to the isomeric form of the triene.

Solution State Dynamics of Copper Cyclododecatriene Complexes. Variable-temperature ¹H and ¹³C NMR spectra of the free trienes and their copper complexes have been measured

(47) Smith, K.; Liu, C.-H.; El-Hiti, G. A.; Kang, G. S.; Jones, E.; Clement, S. G.; Checquer, A. D.; Howarth, O. W.; Hursthouse, M. B.; Coles, S. J. *Org. Biomol. Chem.* **2005**, *3*, 1880–1892.
(48) Munro, D. U.S. Patent 6,551,988, 2003.
(49) Balbolov, E.; Skumov, M. *J. Mol. Catal. A: Chem.* **1999**, *137*, 77–83.
(50) Sporka, K.; Hanika, J.; Ruzicka, V. *Tech. Chem. (Prague)* **1978**, *68*, 16–20.
(51) Tsyskovskii, V. K. *Plast. Massy* **1969**, 18–21.
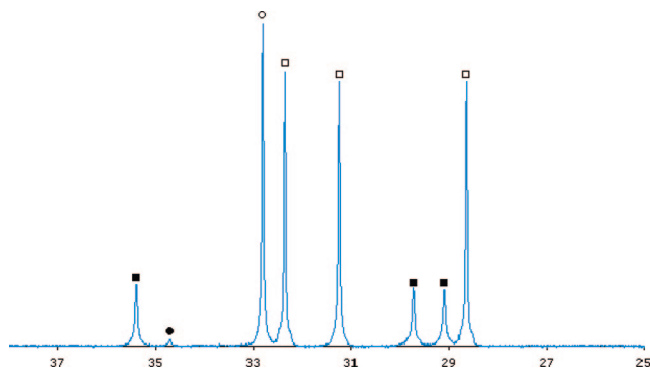(52) Salomon, R. G.; Kochi, J. K. *J. Organomet. Chem.* **1974**, *64*, 135–143.

Figure 4. $^{13}C\{^1H\}$ NMR spectrum (C_7D_8, −70 °C) in the methylene region of the equilibrium mixture obtained by adding 3 equiv of ctt-$C_{12}H_{18}$ to Cu(ttt-$C_{12}H_{18}$)(OTf). Key: ○ = ttt-$C_{12}H_{18}$, □ = ctt-$C_{12}H_{18}$, ● = Cu(ttt-$C_{12}H_{18}$)(OTf), ■ = Cu(ctt-$C_{12}H_{18}$)(OTf).

to determine whether the complexes engage in chemical exchange processes. For each free triene, the number of different ^{13}C environments seen at room temperature is as follows: six for cct-$C_{12}H_{18}$ (three methylenes and three methines), six for ctt-$C_{12}H_{18}$ (ditto), and two for ttt-$C_{12}H_{18}$ (one methylene and one methine).[55−57] These numbers are consistent with the following time-averaged point group symmetries of the free trienes: C_2 for cct-$C_{12}H_{18}$ (the 2-fold rotation axis bisects the *trans* double bond), C_s for ctt-$C_{12}H_{18}$ (the mirror plane bisects the *cis* double bond), and D_3 for ttt-$C_{12}H_{18}$.
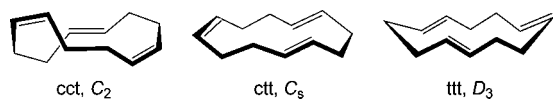
For cct- and ttt-$C_{12}H_{18}$, complexation with a copper triflate unit should lower the symmetry of the bound ring relative to free triene by destroying the 2-folds. In contrast, for ctt-$C_{12}H_{18}$, complexation with the copper triflate unit should preserve the symmetry of the triene ring. Thus, if the structures of the complexes in solution are similar to those seen in the solid state, we expect to see the following numbers of ^{13}C NMR environments for the $C_{12}H_{18}$ ligands: 12 for cct-**1**, 6 for ctt-**1**, and 4 for ttt-**1**. Experimentally, both at room temperature and at −75 °C, we see the following numbers of $^{13}C\{^1H\}$ NMR environments: 12 for cct-**1** and six for ctt-**1**, *but only two* for ttt-**1**. Evidently, for ttt-**1**, the two faces of the ttt ligand are equivalent on the NMR time scale.

Identical conclusions were drawn from the variable-temperature ^1H NMR data: for cct-**1** and ctt-**1** the number of environments agrees with the solid state structure, whereas for ttt-**1** the number of environments is half that expected.

To account for the NMR results, there are two principal kinds of explanations, static and dynamic: (1) the solution and solid state structures of ttt-**1** are different, or (2) the solution and solid state structures are the same, but the compound is undergoing a chemical exchange process in solution that is fast on the NMR time scale.

(53) Hoffmann, E. G.; Jolly, P. W.; Küsters, A.; Mynott, R.; Wilke, G. *Z. Naturforsch. B* **1976**, *31*, 1712.

(54) Immirzi, A.; Allegra, G. *Atti Accad. Naz. Lincei, Cl. Sci. Fis. Mat. Nat. Rend.* **1967**, *43*, 338–349.

(55) Rawdah, T. N.; El-Faer, M. Z. *Tetrahedron Lett.* **1996**, *37*, 4267–4270.

(56) Rawdah, T. N.; El-Faer, M. Z. *Tetrahedron Lett.* **1995**, *36*, 3381–3384.

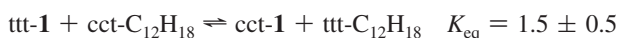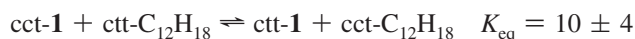(57) Anet, F. A. L.; Rawdah, T. N. *J. Am. Chem. Soc.* **1978**, *100*, 5003–5007.

For the static case, one possibility is that in solution the triflate anion dissociates to give a Cu(ttt-$C_{12}H_{18}$) cation, in which the copper center sits exactly at the center of the ring, thus restoring D_3 point group symmetry. This possibility is ruled out by vapor pressure osmometry experiments, which have shown that the triflate ligand in ttt-**1** is not dissociated in benzene.[42,58] Another static explanation of the NMR data is that the ttt ring has dissociated completely from the copper center. This hypothesis is ruled out by the osmometry result and also by the finding that the ^{13}C NMR chemical shifts of the ttt group in the Cu complex are distinctly different from those seen for the free triene (see above). For the dynamic case, one possible mechanism, reversible dissociation of the triene, was ruled out in separate experiments, which showed that exchange between the bound and free $C_{12}H_{18}$ trienes is slow on the NMR time scale at −75 °C (see below).

The mechanism most likely to account for the equivalence of the two faces of the ttt ligand is movement of the triflate ligand between one side of the molecule and the other, probably by breaking and then re-forming the Cu−O bond. Simultaneously, the copper atom slips through the center of the ttt-$C_{12}H_{18}$ ring and emerges on the other side. This motion does not require breaking of any of the copper−alkene bonds.

For cct-**1**, there is no evidence of an exchange process involving similar movement of the copper atom from one face of the $C_{12}H_{18}$ ring to the other. Unlike the situation for ttt-**1**, such a motion would require breaking of the interactions between the copper atom and the two *cis* C=C double bonds, as well as torsional motions to flip these bonds from one side of the mean ring plane to the other. Evidently, such a dynamic process is slow because the copper−alkene interactions have high dissociation barriers.

We note in passing that the ^{13}C NMR coordination chemical shifts for the olefinic carbons in all three isomers of **1** are ca. −6 ppm (e.g., from δ 132 for free ttt-$C_{12}H_{18}$ to δ 126 for ttt-**1**).[52] The ^1H NMR chemical shifts show more subtle behavior, some moving to higher frequencies and some to lower frequencies when the triene is complexed.

In benzene and at −80 °C in toluene, the ^{63}Cu NMR spectrum of ctt-**1** at room temperature consists of a broad signal at δ 212 with a full width at half-maximum of 6000 Hz, whereas ttt-**1** shows a much sharper resonance at δ 241 with a full width at half-maximum of 500 Hz. The narrower line width of the peak due to ttt-**1** reflects a smaller electric field gradient, which in turn is almost certainly the result of the higher symmetry of the ttt ligand. Consistent with this hypothesis, no ^{63}Cu NMR signal could be observed for cct-**1** at any temperature; presumably its line width is even larger than 6000 Hz. We do not believe that the ^{63}Cu NMR spectra are affected by adventitious formation of paramagnetic Cu^{II} impurities: the Cu($C_{12}H_{18}$)(OTf) complexes are not particularly air sensitive, and the measured line widths were very reproducible from sample to sample.

Equilibrium Binding Studies. Few studies of the binding constants of alkenes to copper have previously been reported. The formation constants for the binding of alkenes to copper(I) centers bearing nitrogen-donating ligands have been determined from vapor pressure measurements.[59] Copper−alkene bonding becomes stronger as the nitrogen-containing ligands become more basic. A similar study of the stabilities of copper(I)
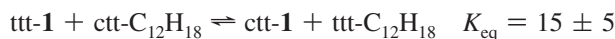
(58) In nitromethane, ctt-**1** is a non-electrolyte (see Experimental Section). For a review of conductivity measurements, see: Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122.

(59) Munakata, M.; Kitagawa, S.; Kosome, S.; Asahara, A. *Inorg. Chem.* **1986**, *25*, 2622–2627.

complexes of alkenes and other small molecules bearing nitrogen donor ligands demonstrated that there is no significant lengthening of the C=C double bond and essentially no metal-to-ligand π-back bonding.[18,60] Finally, the binding ability of alkenes to the Cu(OTf) fragment has been determined by carrying out competition studies in which an excess of an alkene was added to Cu(OTf)(VS), where VS is vinyl sulfonate.[61] The binding strengths of the three alkenes they tested decreased in the order ethylene > 1-butene ≥ 1,3-butadiene.

We have carried out a series of competition experiments in order to determine the relative binding energies of the three cyclododecatriene isomers to copper (Figure 1). For example, a sample of ttt-**1** was mixed with 3 equiv of cct-$C_{12}H_{18}$ in C_7D_8, the mixture was allowed to equilibrate, and then the concentrations of the two starting materials as well as the reaction products cct-**1** and ttt-$C_{12}H_{18}$ were measured by integrations of the $^{13}C\{^1H\}$ NMR peaks at −70 °C (we cannot measure concentrations at room temperature by this technique owing to line broadening effects caused by chemical exchange). Proof that competition experiments were under equilibrium conditions was obtained by showing that the same concentrations were obtained from both reaction directions.

From these competition experiments, we find the following equilibrium constants at −70 °C:

$$\text{ttt-}\mathbf{1} + \text{ctt-}C_{12}H_{18} \rightleftharpoons \text{ctt-}\mathbf{1} + \text{ttt-}C_{12}H_{18} \quad K_{eq} = 15 \pm 5$$

$$\text{cct-}\mathbf{1} + \text{ctt-}C_{12}H_{18} \rightleftharpoons \text{ctt-}\mathbf{1} + \text{cct-}C_{12}H_{18} \quad K_{eq} = 10 \pm 4$$

$$\text{ttt-}\mathbf{1} + \text{cct-}C_{12}H_{18} \rightleftharpoons \text{cct-}\mathbf{1} + \text{ttt-}C_{12}H_{18} \quad K_{eq} = 1.5 \pm 0.5$$

The free energy changes associated with each of these equilibria are −1.1, −0.9, and −0.2 (all ± 0.1) kcal mol^{-1}, respectively. These competition experiments show that the copper prefers to bond to the ctt isomer of cyclododecatriene. The equilibrium constants, of course, reflect the free energies of *both* the complexes and the free trienes.

For free 1,5,9-cyclododecatriene, the relative free energies of the various isomers can be derived from the equilibrium concentrations of 900(ttt):100(ctt):2(cct) measured in toluene at 25 °C.[62] Thus, ttt-$C_{12}H_{18}$ is the most thermodynamically stable, with ctt- and cct-$C_{12}H_{18}$ being 1.3 and 3.6 kcal mol^{-1} higher in energy, respectively. (The ccc-$C_{12}H_{18}$ isomer is even less stable, and it is calculated to be 11.5 kcal mol^{-1} higher in energy than ttt-$C_{12}H_{18}$.[63]) Because the free energy of free ctt-$C_{12}H_{18}$ is intermediate between those of the other two isomers, the preference for the Cu center to bind to this isomer must relate to the free energy of the complex ctt-**1**. Quantitative comparisons[64] suggest that ctt-**1** is ∼1 kcal mol^{-1} more stable than what one would expect from the relative energies of the trienes.

For comparison, for nickel(0) complexes of 1,5,9-cyclododecatriene, the Ni ttt isomer is the most stable, and the Ni ctt and Ni cct complexes have free energies of +4.0 and +5.2 kcal

mol^{-1}, respectively, as calculated by a gradient-corrected DFT method.[63,65] These calculations suggest that metals in trigonal-planar coordination environments are most stable when bonded to ttt-$C_{12}H_{18}$, whereas our results suggest that metals in tetrahedral coordination environments are most stable when bonded to *either* ctt- or ttt-$C_{12}H_{18}$. Besides their different coordination numbers and geometries, however, these nickel and copper complexes differ in another way: back-bonding to the alkene is more important for nickel(0) than for copper(I). It is difficult to imagine, however, how this factor can explain why ctt-$C_{12}H_{18}$ binds to tetrahedral copper(I) somewhat more strongly than expected.

The stronger bonding between Cu and ctt-$C_{12}H_{18}$ can best be attributed to a preorganization effect.[66] Both cct- and ttt-$C_{12}H_{18}$ must distort to a higher energy conformation in order to bind effectively to the copper center. (That cct- and ttt-$C_{12}H_{18}$ are the only two isomers that must distort is related to the conclusion from the NMR studies that the symmetries of these two rings—but not that of ctt-$C_{12}H_{18}$—are lowered upon complexation with copper triflate.) The necessity to undergo a conformational change is particularly easy to see for cct-$C_{12}H_{18}$, in which the two *cis* double bonds lie on opposite sides of the mean ring plane, as opposed to the conformation seen crystallographically for cct-**1**, in which both *cis* double bonds are on the same side of the mean ring plane. A conformational change (albeit a more subtle one) is also necessary for ttt-$C_{12}H_{18}$ to bind to a copper center located out of the mean ring plane, but in contrast ctt-$C_{12}H_{18}$ has a conformation very similar to that seen in its copper complex. Thus, for cct- and ttt-$C_{12}H_{18}$, binding to the metal is attended by an increase in the conformational energy of the ring; this increase is a penalty that destabilizes the resulting copper complexes relative to that of ctt-**1**. We propose that the preoganization effect that favors binding of ctt-$C_{12}H_{18}$ is much smaller for nickel(0) because the metal center lies in the mean ring plane, and thus the free energies of the nickel complexes more closely track those of the unligated trienes.

These results provide interesting new insights into the thermodynamics of copper−alkene bonding.

Experimental Section

All operations were carried out under argon or vacuum unless otherwise specified. Solvents were distilled under nitrogen from sodium and benzophenone. The 1,5,9-cyclododecatriene isomers, copper(I) oxide, and triflic anhydride were obtained from Aldrich and used as received.

The IR spectra were recorded on a Nicolet Impact 410 FT-IR instrument as Nujol mulls between KBr plates. Elemental analyses were performed by the University of Illinois Microanalytical Laboratory. Electrical conductivities were measured on a YSI model 35 conductance meter, and the calibration was verified by measuring a standard (Λ = 103.5 ohm^{-1} cm^2 mol^{-1} in MeNO$_2$ for the 1:1 electrolyte Et$_4$NBr). NMR spectra were recorded on either a Varian Unity-500 spectrometer at 11.75 T (variable-temperature and ^{13}C NMR spectra), a Varian Unity Inova-500NB at 11.75 T (^{1}H NMR spectra), or a Varian Unity Inova-600 at 14.1 T (equilibrium studies and ^{63}Cu NMR spectra). NMR chemical shifts are reported in δ units with positive chemical shifts at higher frequencies relative to TMS or [Cu(MeCN)$_4$][BF$_4$]. ^{1}H and ^{13}C NMR parameters for the free trienes reported previously[55−57] are similar to our findings:

For cct-$C_{12}H_{18}$: ^{1}H NMR (C_6D_6, 25 °C): δ 5.48 (q, J_{HH} = qm 9.5 Hz, 2H, *cis*), 5.37 (eight-line pattern, 9.5 Hz, 2H, *trans*), 5.28 (qm, J_{HH} = 9.2 Hz, 2H, *cis*), 2.03 (br, 8H), 1.92 (m, 4H). $^{13}C\{^1H\}$

(60) Thompson, J. S.; Whitney, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 5488–5490.

(61) Suzuki, T.; Noble, R. D.; Koval, C. A. *Inorg. Chem.* **1997**, *36*, 136–140.

(62) Thorn-Csanyi, E.; Ruhland, K. *Macromol. Chem. Phys.* **1999**, *200*, 1662–1671.

(63) Tobisch, S. *Chem.−Eur. J.* **2003**, *9*, 1217–1232.

(64) Shishkin, O. V. Leszczynski, J. *Chem. Phys. Lett.* **1999**, *302*, 262–266. If we assume that the entropy changes associated with the three exchange reactions are zero, then the free energy changes for these reactions will be the same at room temperature as those we measured at−70 °C. Under this assumption, relative to ttt-**1**, the complexes ctt-**1** and cct-**1** have free energies at room temperature of +0.2 and 3.4 kcal mol^{-1}.

(65) Tobisch, S. *Adv. Organomet. Chem.* **2003**, *49*, 167–224.

(66) Comba, P. *Coord. Chem. Rev.* **2000**, *200−202*, 217–245.

NMR (C_6D_6, 25 °C): δ 130.9 (s, 2C) 130.8 (s, 2C), 129.2 (s, 2C), 31.4 (s, 2C), 27.8 (s, 2C), 27.7 (s, 2C).

For ctt-$C_{12}H_{18}$: ^1H NMR (C_6D_6, 25 °C): δ 5.30 (m, 2H), 5.18 (m, 2H), 5.02 (m, 2H), 2.02 (m, 8H), 1.95 (m, 4H). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 130.9 (s, 2C), 130.8 (s, 2C), 129.2 (s, 2C), 31.4 (s, 2C), 27.8 (s, 2C), 27.7 (s, 2C).

For ttt-$C_{12}H_{18}$: ^1H NMR (C_6D_6, 25 °C): δ 4.93 (s, 6H), 1.99 (s, 12H). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 132.0 (s, 6C), 33.0 (s, 6C).

(Benzene)(trifluoromethanesulfonato)copper(I). To a slurry of red Cu_2O (3.62 g, 25.3 mmol) suspended in benzene (100 mL) was added triflic anhydride (10.0 g, 35.4 mmol). The mixture was heated to reflux for 4 h and then filtered while still hot. As the yellow filtrate cooled to room temperature, a white solid crystallized out. The white solid was collected by filtration, washed with pentane (3 × 15 mL), and dried under vacuum. Yield: 5.33 g (72%). Microanalytical and IR data matched those reported by Salomon and co-workers.[42]

(1,5,9-Cyclododecatriene)(trifluoromethanesulfonato)copper(I), 1. The following procedure is suitable for all three isomers of 1,5,9-cyclododecatriene below. To a slurry of $Cu(C_6H_6)(OTf)$ (1.50 g, 5.2 mmol) in benzene (15 mL) was added 1,5,9-cyclododecatriene (0.89 g, 5.5 mmol). After 5 min, the colorless solution was diluted with pentane (30 mL), and the resulting white solid was collected by filtration, washed with pentane (3 × 15 mL), and dried under vacuum. Yield: 1.72 g (89%). Microanalytical and IR data matched those reported by Salomon and Kochi.[42] Athough all of our studies were carried out under argon, all three complexes are stable at room temperature in air for days.

For cct-**1**: ^1H NMR (C_6D_6 25 °C): δ 5.63 (br, 2H), 5.32 (br, 2H), 4.59 (br, 2H), 1.68 (br, 6H), 1.35 (br, 6H). ^1H NMR (C_7D_8 −70 °C): δ 5.85 (br, 1H), 5.64 (br, 1H), 5.58 (br, 1H), 5.55 (br, 2H), 5.31 (br, 1 H), 1.94 (br, 1H), 1.68 (br, 6H), 1.52 (br, 3H) 1.92 (br, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 126.9 (two superposed singlets, 2C), 126.4 (s, 1C), 124.3 (s, 1C), 123.6 (s, 1C), 120.8 (s, 1C), 34.4 (s, 1C), 31.4 (s, 1C), 29.0 (s, 1C), 28.2 (s, 1C), 24.3 (s, 1C), 24.1 (s, 1C). $^{13}C\{^1H\}$ NMR (C_7D_8, −78 °C): δ 126.0 (s, 1C), 125.6 (s, 1C), 124.0 (s, 1C), 123.7 (s, 1C), 123.1 (s, 1C), 121.1 (q, J_{C-F} = 320 Hz, CF_3), 119.1 (s, 1C), 34.0 (s, 1C), 31.1 (s, 1C), 28.4 (s, 1C), 28.0 (s, 1C), 23.4 (s, 1C), 23.4 (s, 1C). The ^{63}Cu NMR signal could not be observed at either room temperature or −80 °C.

For ctt-**1**: ^1H NMR (C_6D_6, 25 °C): δ 5.68 (m, 2H), 5.42 (m, 2H), 4.36 (m, 2H), 1.80 (m, 4H), 1.65 (m, 4H), 1.48 (m, 2H), 1.36 (m, 2H). ^1H NMR (C_7D_8, −70 °C): δ 5.69 (m, 2H), 5.36 (m, 2H), 4.31 (m, 2H), 1.79 (br, 4H), 1.71 (br, 4H), 1.52 (br, 2H), 1.34 (br, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 133.4 (s, 2C), 126.6 (s, 2C), 118.9 (s, 2C), 35.5 (s, 2C), 30.0 (s, 2C), 29.4 (s, 2C). $^{13}C\{^1H\}$ NMR (C_7D_8, −78 °C): δ 132.8 (s, 2C), 125.6 (s, 2C), 117.8 (s, 2C), 35.0 (s, 2C), 29.5 (s, 2C), 28.9 (s, 2C), 121.0 (q, J_{C-F} = 319 Hz, CF_3). ^{63}Cu NMR (C_6D_6, 20 °C): δ 202.9 (s, fwhm = 6000 Hz). Λ ($MeNO_2$, 25 °C): 0.0002 ohm^{-1} cm^2 mol^{-1}.

For ttt-**1**: ^1H NMR (C_6D_6, 25 °C): δ 5.11 (s, 6H), 1.69 (s, 12H). ^1H NMR (C_7D_8, −70 °C): δ 5.17 (s, 6H), 1.78 (br, 6H), 1.68 (br, 6H). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 126.6 (s, 6C), 34.9 (s, 6C). $^{13}C\{^1H\}$ NMR (C_7D_8, −78 °C): δ 125.8 (s 6C), 121.1 (q, J_{C-F} = 319 Hz, CF_3), 34.4 (s, 6C). ^{63}Cu NMR (C_6D_6, 25 °C): δ 241.2 (s, fwhm = 500 Hz).

Equilibrium Studies. In small graduated reaction flask, a selected $Cu(C_{12}H_{18})(OTf)$ isomer (0.500 g, 1.4 mmol) was combined with 3 equiv of a different free triene and the volume diluted to 5.00 mL with toluene-d_8. The relative equilibrium concentrations were established by $^{13}C\{^1H\}$ NMR spectroscopy at −70 °C, after equilibrating at this temperature for 1 h. Inversion recovery experiments showed that a delay time of 3 s was sufficient to allow for full relaxation and to obtain accurate ^{13}C NMR integrations in all three compounds.

Single-Crystal X-ray Diffraction Studies. Single crystals of all three compounds were grown by cooling saturated solutions in 1:1 toluene−pentane, were mounted on glass fibers with Paratone-N oil (Exxon), and immediately cooled to −75 °C in a cold nitrogen gas stream on the diffractometer. The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, scan speed, and Lorentz and polarization effects. Corrections for crystal decay were unnecessary, but all three data sets were corrected for absorption. Systematically absent reflections were deleted and symmetry equivalent reflections were averaged to yield the set of unique data. The structures were solved by direct methods (SHELXTL). In the final cycle of least-squares, independent anisotropic displacement factors were refined for the non-hydrogen atoms, except where noted below. Hydrogen atoms were included in calculated positions with C−H = 0.99 and 0.95 Å for methylene and vinylic carbons, respectively; the displacement parameters for the hydrogen atoms were set equal to 1.2 times U_{eq} for the attached carbon. Successful convergence was indicated by the maximum shift/error of 0.000 for the last cycle. A final analysis of variance between observed and calculated structure factors showed no apparent errors. Final refinement parameters are given in Table 1. Further details of the data collection and refinements are given in separate sections below.

Cu(cct-$C_{12}H_{18}$)(OTf). The systematic absences were consistent only with the space group *Pbca*, and this choice was confirmed by successful refinement of the proposed model. The quantity minimized by the least-squares program was $\sum w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.087P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. The triflate group was disordered over two sites with the site occupancy factors of the major component being 0.753(7). The sulfur and carbon atoms of the disordered triflate molecules were constrained to idealized tetrahedral geometries with S−C = 1.77 ± 0.01 Å, S−O = 1.45 ± 0.01 Å, and C−F = 1.32 ± 0.01 Å. A similarity constraint was imposed on the displacement parameters of overlapping disordered atoms. The largest peak in the final Fourier difference map (0.39 e Å^{-3}) was located 1.33 Å from C9 and C10.

Cu(ctt-$C_{12}H_{18}$)(OTf). The systematic absences were consistent only with the space group $P2_1/c$, and this choice was confirmed by successful refinement of the proposed model. One reflection (2 0 2) was found to be a statistical outlier and was deleted. The quantity minimized by the least-squares program was $\sum w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.017P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. An isotropic extinction parameter was refined to a final value of $x = 1.1(3) \times 10^{-6}$, where F_c is multiplied by the factor $k[1 + F_c^2 x\lambda^3/\sin 2\theta]^{-1/4}$ with k being the overall scale factor. The largest peak in the final Fourier difference map (0.29 e Å^{-3}) was located 0.86 Å from H6.

Cu(ttt-$C_{12}H_{18}$)(OTf). The systematic absences were consistent with the space groups $Cmc2_1$, *Cmcm*, and *Ama*2. The average values of the normalized structure factors suggested that the space group was non-centrosymmetric, and the choice of $Cmc2_1$ was confirmed by subsequent successful refinement of the proposed model. One reflection (2 0 0) was partly obscured by the beamstop and was deleted. The quantity minimized by the least-squares program was $\sum w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.017P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. In the final model, all atoms except the copper atom are disordered. The carbon atoms of the cyclododecatriene ring were disordered over two sites related by the mirror plane that runs through the copper center; these atoms were assigned site occupancy factors of exactly 0.5. Chemically equivalent C−C bond distances within the ring were constrained to be equal within an esd of 0.01 Å. The atoms of the triflate anion were disordered over four sites, two of these being unique and each of these unique components being disordered across the mirror plane. The atoms within each unique component were assigned a common site occupancy factor, the sum of the SOFs adding to 0.5 (except for those atoms lying on the mirror plane, which were assigned SOFs adding to 1.0).

The site occupancy factor for the major component plus its mirror-related partner refined to 0.533(6). Chemically equivalent C−F, F···F, S−C, S−O, and O···O distances were constrained to be equal. The displacement parameters for the disordered oxygen and fluorine atoms were restrained to be near-isotropic. The largest peak in the final Fourier difference map (0.26 e Å^{-3}) was located 0.96 Å from C13. The model has the correct handedness, as shown by the absolute structure parameter of −0.02(2). No larger supercell was evident in the diffraction record, disorder was still evident even in monoclinic subgroups, and no sensible model could be devised in the centrosymmetric space group *Cmcm*.

Supporting Information Available: ^{1}H−^{1}H COSY and ^{1}H−^{13}C HMQC NMR spectra of Cu(ctt-C$_{12}$H$_{18}$)(OTf) and Cu(ttt-C$_{12}$H$_{18}$)-(OTf) and ^{1}H−^{1}H COSY of Cu(cct-C$_{12}$H$_{18}$)(OTf); X-ray crystallographic files in CIF format for all three compounds are available free of charge via the Internet at http://pubs.acs.org.

OM801078C