NMR Evidence for the Unprecedented Binding of a Naphthalene Group to Copper(I) in Solution

Rebecca R. Conry* and William S. Striejewske

*Department of Chemistry/216, University of Nevada, Reno, Nevada 89557*

Summary: Variable-temperature one- and two-dimensional NMR experiments with [LCu](PF$_6$) (L = N-(2-(1-naphthyl)ethyl)-1-aza-4,8-dithiacyclodecane) reveal solution binding of the pendant naphthalene group, consistent with the η^2 binding found in the solid-state structure. The free energy for the barrier to the process that involves coordination/decoordination of the naphthalene group was estimated to be 12–13 kcal/mol.

Transition-metal arene complexes are intermediates in a number of catalytic reactions, with applications in industry as well as the synthetic laboratory.[1] For isolated and structurally characterized π-arene complexes, the arene is typically benzene or a benzene derivative and is most frequently bound in an η^6 fashion; η^4, η^3, and η^2 complexes are less common.[2] Copper(I)–arene complexes are quite rare and, like most other d^{10} metal–arene complexes,[3–8] are bound in an η^2 fashion.[9,10]

We recently reported the synthesis and solid-state structure of the first copper(I)–naphthalene complex (**I**; Figure 1),[11] only the third arene complex of copper to be structurally characterized.[9,10] Subsequent variable-temperature and 2-D NMR experiments with **I** have given compelling evidence for binding of the naphthalene group in solution, which we present here. As no solution-binding data are given for the η^2-benzene ligands in the two other copper–arene complexes, this seems to represent an unprecedented observation in copper(I) chemistry.[12]

While characterizing complex **I**, we noted that the room-temperature ^{1}H NMR spectrum in CDCl$_3$ exhib-
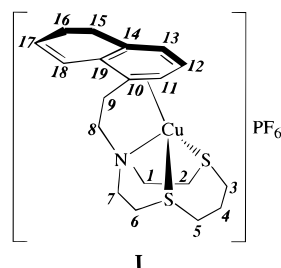
Figure 1. Drawing representing the solid-state structure of [**L**Cu](PF$_6$) (**I**),[11] showing the numbering system used for the carbon and/or proton positions discussed in the text.
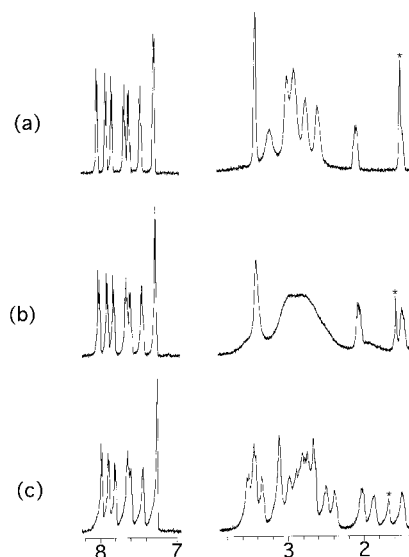
Figure 2. 500 MHz ^{1}H NMR spectra of **I** in CDCl$_3$ at (a) 50 °C, (b) 20 °C, and (c) −20 °C. The peak designated on each spectrum with an asterisk (*) is water, an impurity from the solvent.

ited only a broad envelope for most of the 18 ligand methylene protons. Assuming a fluxional process, we investigated the spectrum of **I** as a function of temperature. As the solution was cooled, the aliphatic resonances separated and sharpened into at least 15 peaks at −20 °C (Figure 2c). For temperatures above ambient, aliphatic peak separation also occurred, to eight peaks at 50 °C (Figure 2a). The coalescence temperature for the fluxional behavior appears to be near 20 °C (Figure 2b). Throughout the temperature region probed (−20 to +50 °C), the methylene resonances did not become clearly resolved or exhibit extensive coupling.[13] The aromatic proton resonances remained reasonably sharp and experienced only minor chemical shift changes

(1) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd ed.; Wiley-Interscience: New York, 1992.

(2) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499–525.

(3) Stanger, A.; Boese, R. *J. Organomet. Chem.* **1992**, *430*, 235–243.

(4) Stanger, A.; Vollhardt, K. P. C. *Organometallics* **1992**, *11*, 317–320.

(5) Scott, F.; Krüger, C.; Betz, P. *J. Organomet. Chem.* **1990**, *387*, 113–121.

(6) Benn, R.; Mynott, R.; Topalović, I.; Scott, F. *Organometallics* **1989**, *8*, 2299–2305.

(7) Brauer, D. J.; Krüger, C. *Inorg. Chem.* **1977**, *16*, 884–891.

(8) Griffith, E. A. H.; Amma, E. L. *J. Am. Chem. Soc.* **1974**, *96*, 5407–5413.

(9) Turner, R. W.; Amma, E. L. *J. Am. Chem. Soc.* **1966**, *88*, 1877–1882.

(10) Dines, M. B.; Bird, P. H. *J. Chem. Soc., Chem. Commun.* **1973**, 12.

(11) Striejewske, W. S.; Conry, R. R. *Chem. Commun.* **1998**, 555–556.

(12) Solution arene binding has been proposed to explain a lack of low-temperature dioxygen binding to a dinuclear copper(I) complex: Karlin, K. D.; Nasir, M. S.; Cohen, B. I.; Cruse, R. W.; Kaderli, S.; Zuberbühler, A. D. *J. Am. Chem. Soc.* **1994**, *116*, 1324–1336.
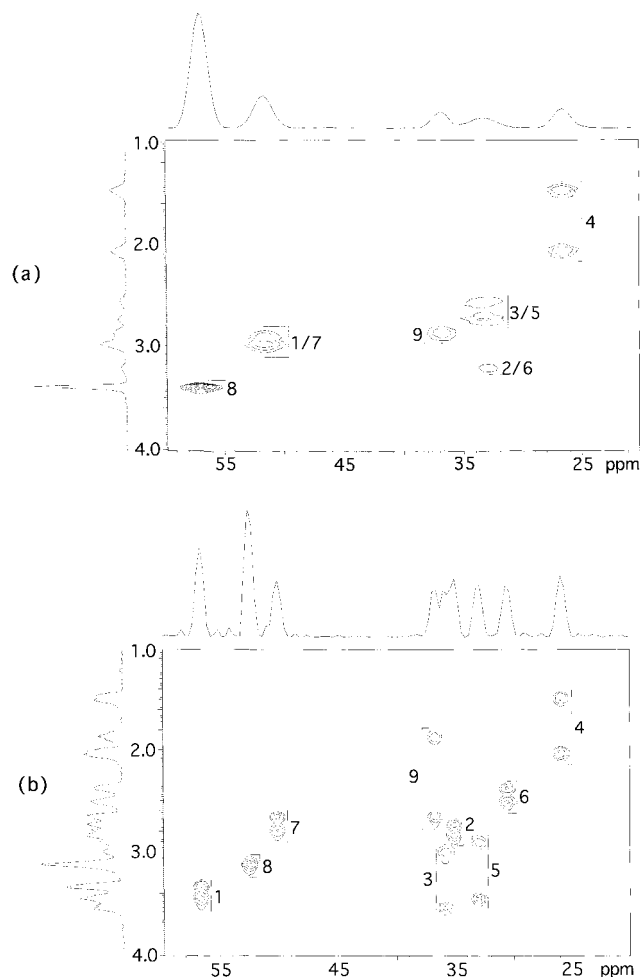
between −20 and 50 °C ($\Delta\delta \leq 0.03$ ppm) as well as versus free **L** ($\Delta\delta$ of 0.04−0.15 ppm).

The ^{13}C NMR spectra of **I** at −20 and 50 °C were similar to the proton data in that the number of aliphatic peaks varied between the spectra. At 50 °C, the spectrum is consistent with the two sides of the macrocyclic ring being symmetry-related, resulting in 6 aliphatic carbon resonances (1/7, 2/6, 3/5, 4, 8, and 9). In contrast, the two sides of the macrocyclic ring become inequivalent at −20 °C, as indicated by the 9 aliphatic carbon resonances (for 1−9). The aromatic regions of the 2 spectra each had 10 resonances, as expected, and there were only slight chemical shift changes between them ($\Delta\delta$ of ≤0.5 ppm for all peaks except one with 1.4 ppm). However, two of the aromatic peaks in the ^{13}C spectra of **I** compared to **L** displayed a much larger chemical shift difference than the others (e.g., $\Delta\delta$ of 10.6 and 20.1 ppm between the −20 °C spectrum and **L**; the largest $\Delta\delta$ for the other peaks is 3.2 ppm).
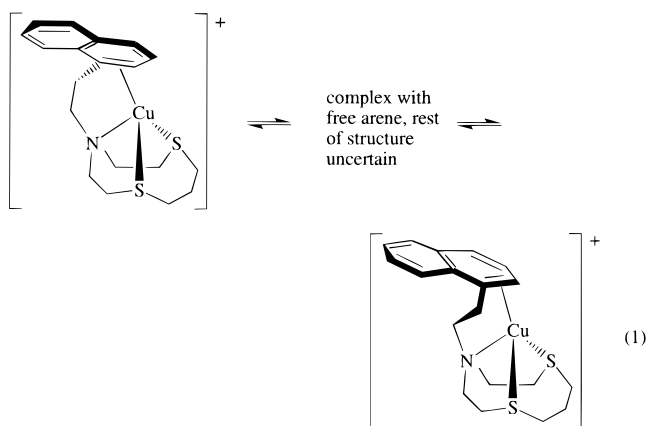
The heteronuclear correlation spectra at the two temperatures were instrumental to deciphering the proton data (aliphatic regions shown in Figure 3). The binding of the copper ion causes the macrocyclic ring methylene protons to become diastereotopic, seen as two cross-peaks to the resonance for each ring carbon atom. At −20 °C the protons on one of the two linker carbons are also clearly diastereotopic, but at 50 °C the two linker methylene protons on each carbon appear equivalent, giving one cross-peak.

From these observations, we conclude that the species at −20 °C is best described as having the naphthalene group bound to copper(I) at carbons 10 and 11, as seen in the solid-state structure.[11] The inequivalence of the two sides of the macrocyclic ring at low temperature must be due to binding of an unsymmetrical group− and the naphthyl group is the only such moiety available. The observation that the linker methylene hydrogens 9 have become diastereotopic clearly supports this hypothesis. The diastereotopic nature of the protons 9 is well-resolved because of the close proximity to the bound unsymmetrical group. The lack of a resolvable chemical shift difference for the two protons 8 is reasonable because the difference in environment experienced by the two hydrogens would be predicted to be small, as these protons are farther removed from the naphthyl group and are adjacent to the symmetrical macrocyclic ring. The behavior of the aromatic resonances for the copper-coordinated positions 10 and 11 in the spectra of **I** versus that of **L** is similar to that observed for Cu(I)−alkene complexes, which exhibit small shifts in the proton spectra (e.g., ∼0−0.8 ppm upfield or slightly downfield)[14] and larger shifts in the carbon spectra (e.g., ∼8−30 ppm upfield) upon coordination.[14]

The data at 50 °C are most consistent with the interpretation that **I** is involved in an exchange process involving dissociation/reassociation of the naphthyl group and interconversion of the two enantiomers of the compound (eq 1). This will regenerate the apparent

(13) Even at −80 °C in CD$_2$Cl$_2$ the spectrum was not more resolved than the one at −20 °C in CDCl$_3$. At higher temperatures, for instance at 85 °C in C$_2$D$_2$Cl$_4$ solvent, the complex begins to decompose.
(14) Baum, T. H.; Larson, C. E.; May, G. *J. Organomet. Chem.* **1992**, *425*, 189−200 and references therein.

Figure 3. Aliphatic regions of the 500 MHz HMQC spectra of **I** in CDCl$_3$ with assignments. ^{13}C data are on the *x* axes, and ^{1}H data are on the *y* axes. Spectrum (a) is at 50 °C. A cross-peak for one proton in position 2/6 is not seen at this contour level (and does not appear until the spectrum becomes cluttered), as the carbon resonance for that position is fairly broad and thus shortens the cross-peak height. Spectrum (b) is at −20 °C. The two sides of the ring are arbitrarily assigned.

symmetry relationship between the two sides of the macrocyclic ring. However, the spectra at 50 °C are not adequately explained only by the rapid interconversion of the two enantiomers, as the chemical shifts for the same positions at 50 °C are not an average of those at −20 °C (e.g., protons 9 appear at 2.68 and 1.87 ppm at −20 °C and at 2.89 ppm at 50 °C). Therefore, there

must be another species contributing to the spectra—most likely a complex with an unbound naphthyl group (for which the geometry about the copper(I) center cannot be discerned from the NMR data). The direction of the ^{1}H NMR shift for protons 9 is consistent with this postulation, as those protons are seen at ≥ 3.3 ppm in free **L** as well as in the acetonitrile-ligated complex [**L**Cu(CH$_3$CN)]PF$_6$, which has an acetonitrile ligand and an unbound arene.[11] The fact that the two carbon resonances due to the bound carbon atoms do not shift substantially toward those for free **L** suggests that at 50 °C the naphthalene-bound species remains an important contributor to the spectrum.

Using the coalescence temperature of 20 °C[15] or peak separation analysis[16] to estimate the $\Delta G^{\ddagger}$ associated with the fluxional process gives a value of 12−13 kcal/mol.[17] Arene complexes of other metals have been found to participate in a nondissociative 1,2-shift mechanism, with barriers determined to be ≤ 11 or near 20 kcal/mol for those bound in an η^2 or η^4 fashion, respectively.[18] In addition, naphthalene and anthracene complexes are known to undergo intramolecular migration of the coordinated metal between ligand rings, with barriers of 12−15 kcal/mol for η^2 complexes[4,5] and 25−33 kcal/mol for η^6 complexes.[19−22] In at least one case, intermolecular exchange of an η^6-naphthalene ligand for an η^6-benzene ligand occurs, with an activation energy of 22.5 kcal/mol.[23] However, the presence of the tether arm in our molecule and the significant shifting of only two aromatic carbon resonances suggest that these typical arene fluxional processes are not likely operative here. Also, nondissociative processes would fail to remove the resolvable diastereotopic character for the one linker methylene group.

We are continuing to explore the properties of this interesting complex, such as probing its reactivity, to further understand the nature of this unique compound.

Supporting Information Available: Text giving further experimental details and figures giving spectra of **I** that were discussed but not shown here (5 pages). Ordering information is given on any current masthead page.

OM980131X

(15) For the 500 MHz NMR spectrometer used to acquire the data.
(16) Sandström, J. *Dynamic NMR Spectroscopy*; Academic: San Francisco, 1982.
(17) Paudler, W. W. *Nuclear Magnetic Resonance*; Wiley: New York, 1981.
(18) Mann, B. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 3, pp 89−171.
(19) Kündig, E. P.; Desobry, V.; Grivet, C.; Rudolph, B.; Spichiger, S. *Organometallics* **1987**, *6*, 1173−1180.

(20) Oprunenko, Yu. F.; Malugina, S. G.; Ustynyuk, Yu. A.; Ustynyuk, N. A.; Kravtsov, D. N. *J. Organomet. Chem.* **1988**, *338*, 357−368.
(21) Kirss, R. U.; Treichel, P. M., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 853−855.
(22) Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396−3411 and references therein.
(23) Kündig, E. P.; Perret, C.; Spichiger, S.; Bernardinelli, G. *J. Organomet. Chem.* **1985**, *286*, 183−200.