Copper(I) Complexes with a NS_2-Macrocyclic Ligand Bearing a Pendant Naphthyl Group: Structures of {*N*-[2-(1-Naphthyl)ethyl]-1-aza-4,8-dithiacyclodecane}copper(I)−Ligand, where Ligand = η^2-Naphthalene, Acetonitrile, or Triphenylphosphine

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A new macrocyclic ligand with a pendant naphthalene group, *N*-[2-(1-naphthyl)ethyl]-1-aza-4,8-dithiacyclodecane (**L**), has been synthesized and characterized. The copper(I)−acetonitrile complex [**L**Cu(CH_3CN)](PF_6) (**1**) was synthesized from **L** and [Cu(CH_3CN)$_4$](PF_6). The acetonitrile ligand from **1** was easily removed to give [**L**Cu](PF_6) (**2**). Complexes **1** and **2** have been crystallographically characterized. **1**: $C_{21}H_{28}N_2CuF_6PS_2$, triclinic, $P\bar{1}$, a = 11.1901(10) Å, b = 11.2735(12) Å, c = 12.1350(10) Å, α = 98.996(8)°, β = 117.188(6)°, γ = 105.354(7)°, Z = 2, R1 = 0.0505 (wR2 = 0.1418). **2**·0.5hexane: $C_{22}H_{31}NCuF_6PS_2$, monoclinic, $P2_1/c$, a = 15.7318(15) Å, b = 8.9164(10) Å, c = 17.205(5) Å, β = 102.431(6)°, Z = 4, R1 = 0.0587 (wR2 = 0.1545). In addition, a cocrystallized mixture of both complexes was crystallographically characterized. **1&2**·hexane: $C_{46}H_{61}N_3Cu_2F_{12}P_2S_4$, triclinic, $P\bar{1}$, a = 10.8308(9) Å, b = 12.6320(8) Å, c = 19.9412(13) Å, α = 80.445(5)°, β = 76.405(6)°, γ = 78.825(5)°, Z = 2, R1 = 0.0661 (wR2 = 0.1871). The solid-state structure of **2** features the pendant naphthalene group bound in an η^2-fashion, which is highly unusual for copper complexes. In $CDCl_3$, **2** exhibits fluxional behavior with the barrier to the process estimated, $\Delta G^{\ddagger}$ = 12−13 kcal. Variable temperature NMR spectroscopy gave compelling evidence for solution binding of the naphthalene group in **2**, apparently the first example for copper(I). The fluxional process seen for **1** is best described as interconversion of the two enantiomers via a species with an unbound naphthalene group. Consistent with the weak binding of the naphthalene group, it is readily replaced with other ligands, such as triphenylphosphine to form [**L**Cu(PPh_3)](PF_6) (**3**). Complex **3** has also been structurally characterized: $C_{37}H_{40}NCuF_6P_2S_2$, monoclinic, $P2_1/c$, a = 11.462(2) Å, b = 15.972(2) Å, c = 19.835(9) Å, β = 94.50(3)°, Z = 4, R1 = 0.0906 (wR2 = 0.1889).

Introduction

Transition metal π-complexes of benzene and benzene derivatives are well-known,[1,2] with potential industrial or laboratory synthetic applications.[3] For copper, however, arene complexes are very rare;[4,5] to our knowledge the structures of only three copper−arene complexes had been reported before 1998, (C_6H_6)$CuAlCl_4$,[6] ($CuOSO_2CF_3$)$_2C_6H_6$,[7] and [Cu($GaCl_4$)-{[*p*-$C_6H_4(CH_2)_3]_2$}].[8] All three complexes are polymeric in the solid state and exhibit an η^2-binding mode of the benzene ring to copper(I). Arene binding to the copper ion in solution was not reported for any of these complexes.[9] This lability of the arene group in solution has been exploited in a number of applications for $(CuOTf)_2$·C_6H_6. These include its use as a copper(I) starting material; as a reagent, for instance, to remove thiophenol[10] and in a copper-promoted version of the Friedel−Crafts acylation reaction;[11] and as a catalyst, such as in cyclopropanation reactions[12] as well as in a number of photochemical reactions of alkenes.[13] In addition, the benzene can be removed from the solid-state material to give a species of empirical formula CuOTf, which has been found to act as a separation catalyst for isomeric alkylaromatic compounds.[14]

In 1998, we published a preliminary account for the fourth structurally characterized copper−arene complex,[15] which featured an η^2-bound naphthalene from a new NS_2-macrocyclic ligand with a pendant naphthyl group. Several months later, π-arene interactions were reported in the solid-state structures

(1) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499−525.
(2) Maslowsky, E., Jr. *J. Chem. Educ.* **1993**, *70*, 980−984.
(3) 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.
(4) There are also accounts of chemisorbed Cu(II)−arene species formed on copper- and iron-containing aluminosilicates, for example: Pinnavaia, T. J.; Mortland, M. M. *J. Phys. Chem.* **1971**, *75*, 3957−3962. Rupert, J. P. *J. Phys. Chem.* **1973**, *77*, 784−790.
(5) There are also accounts of weak interactions in the solid state between a Cu(I) center and an arene ring, with long distances (2.7−3.0 Å) that cannot accurately be described as a full bond: (a) Rodesiler, P. F.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1974**, 599−600. (b) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1980**, *19*, 1191−1197.
(6) Turner, R. W.; Amma, E. L. *J. Am. Chem. Soc.* **1966**, *88*, 1877−1882.
(7) Dines, M. B.; Bird, P. H. *J. Chem. Soc., Chem. Commun.* **1973**, 12.
(8) Schmidbaur, H.; Bublak, W.; Huber, B.; Reber, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1089−1090.
(9) Solution arene binding, however, 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.
(10) Cohen, T.; Ruffner, R. J.; Shull, D. W.; Fogel, E. R.; Falck, J. R. *Org. Synth.* **1979**, *59*, 202−211.
(11) Kozikowski, A. P.; Ames, A. *J. Am. Chem. Soc.* **1980**, *102*, 860−862.
(12) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 3300−3310.
(13) (a) Salomon, R. G. *Tetrahedron* **1983**, *39*, 485−575. (b) Hennig, H.; Rehorek, D.; Archer, R. D. *Coord. Chem. Rev.* **1985**, *61*, 1−53. (c) Moggi, L.; Juris, A.; Sandrini, D.; Manfrin, M. F. *Rev. Chem. Intermed.* **1984**, *5*, 107−155.
(14) Dines, M. B. *Sep. Sci.* **1973**, *8*, 661−672.
(15) Striejewske, W. S.; Conry, R. R. *Chem. Commun.* **1998**, 555−556.

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of copper aryls with bulky phenyl ligands.[16] However, the unique nature of our ligand allowed arene binding in solution,[17] the first unequivocal example for copper. Herein, we describe the full details of the synthesis and characterization of this system, including the new ligand, the first copper−naphthalene complex, and a precursor complex with an acetonitrile ligand bound to the copper(I) ion instead of the naphthalene group. Preliminary reactivity studies indicate that the arene ligand is easily replaced, such as with PPh_3 to form a triphenylphosphine complex, for which complete characterization is included. The arene interaction also influences the properties of the resulting copper(I) complex, for instance making it less oxygen reactive and displaying a more positive oxidation potential than would otherwise be expected.

Experimental Section

Materials and Procedures. All reagents were used as received from Acros, Aldrich, EM, Fisher, or Spectrum, except Et_3N, which was distilled from CaH_2. Solvents for the synthesis of the copper complexes were kept air-free and dried as follows: tetrahydrofuran (THF) and Et_2O over sodium/benzophenone; CH_3CN, toluene, benzene, hexane, and CH_2Cl_2 with calcium hydride. $[Cu(CH_3CN)_4](PF_6)$[18] and 1-aza-4,8-dithiacyclodecane[19] were synthesized as described in the literature. The copper complexes were synthesized and purified using typical high vacuum and/or Schlenk techniques. R_f values are from the given solvent system on Baker-Flex silica gel IB2-F TLC plates.

Physical Measurements. Routine ^1H and ^{13}C NMR spectra were recorded on a General Electric QE 300 MHz FT-NMR spectrometer. Decoupling, heteronuclear correlation, ^{31}P, and variable temperature NMR experiments were recorded on a Varian Unity Plus 500 MHz FT-NMR spectrometer. ^1H NMR spectra were referenced to the residual proton resonance of the solvent and ^{13}C NMR spectra to a selected solvent resonance ($CDCl_3$: ^1H, δ 7.26, ^{13}C, δ 77.23. CD_3CN: ^1H, δ 1.93, ^{13}C, δ 1.39). The ^{31}P NMR spectra were referenced to 85% aqueous phosphoric acid (0.0 ppm). Some ^1H NMR data and assignments are given in tabular form in the results and discussion section, and some ^{13}C NMR data and assignments are in the Supporting Information. UV−vis spectra were taken with a Hewlett-Packard 8452A diode-array spectrophotometer; peaks are reported in nm, with ϵ in M^{-1} cm^{-1} given in parentheses. Infrared spectra (neat unless stated otherwise) were acquired on a Nicolet Protegé 460 FT-IR spectrometer; peaks are given in cm^{-1}. GC−MS data were recorded on a Hewlett-Packard model 5890 gas chromatograph (acetone solvent; HP-1 cross-linked methyl silicone gum 25 m × 0.25 mm × 0.11 μm column; He carrier gas; 80 °C for the first 3 min, then ramped at 10 °C/min up to a maximum temperature of 280 °C) coupled with a Hewlett-Packard model 5970 series mass spectrometer. FABMS were carried out by the University of California, Riverside Mass Spectrometry Facility on their VG ZAB mass spectrometer in a DCM/NBA matrix and are reported as masses for the two largest peaks within each cluster (due to the copper isotopes) followed by assignments and relative intensities for each cluster. Elemental analyses were performed by Desert Analytics (Tucson, AZ) or by NuMega Resonance Labs (San Diego, CA). Melting points were determined in open glass capillaries on a Thomas-Hoover model 6406-H melting-point apparatus and are uncorrected. Cyclic voltammetry was performed using a BAS-50W potentiostat, and all potentials are quoted relative to the saturated calomel reference electrode. A glassy carbon disk (BAS) was used as the working electrode, platinum wire as the auxiliary electrode, and $^nBu_4NPF_6$ (0.1 M) as the supporting electrolyte in THF with a sample concentration of 3.2×10^{-3} M; the reported peak potentials were from CV data taken at 1.0 V/s. The potential for the ferrocene/ferrocenium couple was determined to be 550 mV at the same conditions.

Crystallographic Studies. Suitable crystals were mounted with silicone caulk to a glass fiber on the benchtop. The data were collected with a Siemens P4 diffractometer with a graphite monochromator at ambient temperatures from 3.5 to 45° in 2θ for **1** and **3** and to 50° in 2θ for **2** and **1&2**. The structures were solved with Patterson methods (except the structure of **1&2** which was solved with direct methods) followed by subsequent cycles of least-squares refinement and calculation of difference Fourier maps. The data were refined (full-matrix least-squares on F^2) with the Siemens SHELXTL version 5.0.3 PC software package,[20] including its psi scan based semiempirical absorption correction for **1&2** and **3**. None of the structures required an extinction correction. All non-hydrogen atoms were modeled anisotropically, except solvent atoms in **2**. Hydrogens were placed at calculated distances and use a riding model where the positional and thermal parameters are derived from the carbon atom to which each hydrogen is bound, while maintaining the calculated distance and optimal angles. No peaks or holes of greater than 0.72 $e^-/Å^3$ remained in the final difference maps for the structures of **1**−**3**.

The structure for compound **1** (wedge, $\pm h$, $\pm k$, $+l$ collected) contains packing disorder of the naphthalene group, in two unequally populated positions (the major position refines to 82% occupancy and is shown in the figure), related by rotation of the naphthalene group by 180°. The disorder is resolvable in the ethylene linker arm (appearing to connect, in turn, to each six-membered ring in the naphthalene group), but not in the naphthalene rings. In addition, the PF_6^- group is disordered and is modeled with two positions, which refine to 58% and 42% occupancy, respectively. For **1**, 3801 reflections were collected; 3202 independent reflections ($R_{int} = 0.0327$) were used in the refinement for 382 parameters.

The structure for compound **2** (plate, $\pm h$, $+k$, $+l$ collected) also contains disorder in an equatorial plane of the PF_6^- group, which is modeled with two positions, which refine to 59% and 41% occupancy, respectively. In addition, there is a disordered solvent molecule of uncertain identity sitting on a special position in the crystal lattice, which is crudely modeled as a cyclohexane (it is most likely some subset of isomers from the hexanes used to grow the crystals); no hydrogen atoms were placed on this fragment. For **2**, 5287 reflections were collected; 4153 independent reflections ($R_{int} = 0.0558$) were used in the refinement for 320 parameters.

The structure for cocrystallized **1&2** (block, $\pm h$, $\pm k$, $+l$ collected) appears to have packing disorder and/or thermal motion of the naphthalene group of complex **1**. In addition, the PF_6^- groups are somewhat disordered. However, neither of these disorders was modeled in the final structure. In addition, there is the same sort of disordered, ill-behaved solvent molecule of uncertain identity that was found in the structure of **2**. Again, it was crudely modeled as a cyclohexane (without hydrogen atoms) and is also most likely some mixed subset of isomers from the hexanes used to grow the crystals. For **1&2**, 10 627 reflections were collected, 9047 independent reflections ($R_{int} = 0.0228$) were used in the refinement for 623 parameters, and the range of transmission factors was 0.3771−0.3390.

The structure of **3** (plate, $\pm h$, $+k$, $+l$ collected) also has packing disorder and/or thermal motion of the naphthalene group as well as in the linker ethylene arm. Attempts to model those disorders were unsuccessful. For **3**, 5757 reflections were collected, 4733 independent reflections ($R_{int} = 0.0788$) were used in the refinement for 442 parameters, and the range of transmission factors was 0.2719−0.2450.

Synthesis of 1-Naphthylacetyl Chloride.[21,22] Benzene (75 mL) was added to 3.0 g (16 mmol) of 1-naphthylacetic acid and 3.4 g (16 mmol) of PCl_5. The resulting solution was stirred at 50 °C overnight. After the mixture was cooled to room temperature, the solvent was removed in vacuo. The resulting orange oil was vacuum distilled (bp 93 °C at $\sim 10^{-1}$ Torr) to isolate 1-naphthylacetyl chloride as a yellow oil, yield 2.53 g (12 mmol, 77%). ^1H NMR ($CDCl_3$): δ 7.90 (m, 3 H), 7.57 (m,

(16) Niemeyer, M. *Organometallics* **1998**, *17*, 4649−4656.
(17) Conry, R. R.; Striejewske, W. S. *Organometallics* **1998**, *17*, 3146−3148.
(18) Kubas, G. J. *Inorg. Synth.* **1979**, *19*, 90−92.
(19) Chandrasekhar, S.; McAuley, A. *Inorg. Chem.* **1992**, *31*, 2234−2240.
(20) Scattering factors from: *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.
(21) Sheehan, J. C.; Chapman, D. W.; Roth, R. W. *J. Am. Chem. Soc.* **1952**, *74*, 3822−3825.
(22) Pomerantz, M.; Ross, A. S. *J. Am. Chem. Soc.* **1975**, *97*, 5850−5855.

2 H), 7.47 (m, 2 H), $-C_{10}H_7$; 4.58 (s, 2 H, $-CH_2-C(O)-Cl$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 171.9 (1 C, $-C(O)-Cl$); 134.0, 131.8, 128.0, 129.3, 129.1, 128.9, 127.1, 126.3, 125.6, 123.3 (all 1 C, $-C_{10}H_7$, the last seven have bound Hs); 50.8 (1 C, $-CH_2-C(O)-Cl$). GC-MS: t_{ret} = 12.1 min; 204 (M^+, 22%), 168 (32%), 141 ($C_{10}H_7-CH_2^+$, 100%).

Synthesis of the Amide Precursor to L. The macrocycle 1-aza-4,8-dithiacyclodecane[19] (0.77 g, 4.4 mmol) was dissolved in 15 mL of freshly distilled toluene and cooled in an ice bath. Triethylamine (1.82 mL, 13.1 mmol) was added and the solution stirred for 15 min. Then 1-naphthylacetyl chloride (0.88 g, 4.3 mmol) was added dropwise. The resulting mixture was stirred overnight, allowing the ice to melt, and the solution to slowly warm to room temperature. The precipitate was filtered away in air and the toluene removed by distillation, leaving a green oil. This oil was dissolved in 60 mL of $CHCl_3$ and washed with a 10% NaOH solution. The organic layer was separated and dried ($MgSO_4$), and the solvent removed, leaving an orange-yellow oil. Further purification was carried out by vacuum filtration chromatography (F-TLC silica, 50:50 ethyl acetate/hexane as eluent, R_f = 0.5) to give the product as colorless crystals after slow evaporation of the solvent. Yield: 1.2 g (3.5 mmol, 80%). ^1H NMR ($CDCl_3$): δ 8.07 (m, 1 H), 7.87 (m, 1 H), 7.80 (d, 1 H, J = 8.3 Hz), 7.50 (m, 2 H), 7.42 (t, 1 H, J = 8.3 Hz), 7.31 (d, 1 H, J = 7.3 Hz) $-C_{10}H_7$; 4.40 (s, 2 H, $-CH_2-C(O)-N-$); 3.61 (m, 2 H, $-CH'_2-N-CH_2-$); 3.47 (m, 4 H, $-S-CH'_2-CH'_2-N-CH_2-CH_2-S-$); 3.15 (m, 2 H, $-CH'_2-CH_2-CH_2-$); 2.99 (m, 4 H, $-CH'_2-CH_2-CH_2-$ and $-S-CH'_2-CH'_2-N-CH_2-CH_2-S-$); 1.92 (m, 2 H, $-CH'_2-CH_2-CH_2-$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 173.1 (1 C, $-C(O)-N-$); 133.8, 132.2, 131.7, 128.7, 127.5, 126.7, 126.0, 125.6, 125.4, 123.9 (all 1 C, $-C_{10}H_7$, the last seven have bound Hs); 53.5, 51.2 (1 C each, $-CH_2-N-C'H_2-$); 39.0 (1 C, $-CH_2-C(O)-$); 36.2, 29.6 (1 C each, $-S-C'H_2-C'H_2-N-CH_2-CH_2-S-$); 32.8, 30.8 (1 C each, $-C'H_2-CH_2-CH_2-$); 30.0 (1 C, $-C'H_2-CH_2-CH_2-$). IR: 3046 m ν(C$-$H$_{arom}$); 2918 s ν(C$-$H$_{aliph}$); 1746 m; 1651 s ν(C=O); 1597 m; 1510 m; 1452 m; 1411 s; 1356 s; 1301 mw; 1258 m; 1232 mw; 1180 m; 1143 m; 1018 mw; 939 mw; 784 s; 734 m; 700 m. GC-MS: t_{ret} = 27.2 min; 345 (M^+, 69%), 168 (33%), 141 ($C_{10}H_7-CH_2^+$, 100%), 115 (33%).

Preparation of *N*-[2-(1-Naphthyl)ethyl]-1-aza-4,8-dithiacyclodecane, L. The amide from above, 0.17 g (0.49 mmol), was thoroughly dried and degassed in vacuo and then cooled to ice temperature. A THF solution of 2 M $BH_3{\cdot}SMe_2$ (2.50 mL, 5.0 mmol) was added slowly by syringe over about 30 min (in 0.1$-$0.2 mL portions). The resulting mixture was refluxed for 1 h and again cooled in an ice bath. Excess borane was quenched by slow dropwise addition of approximately 1 mL of 6 M HCl. The reaction mixture was opened to the air, and water (5 mL) was added to make the workup volume more manageable. After removing the THF (and SMe_2) by distillation, the aqueous layer was made basic (NaOH pellets) and extracted with 3 $\times$ 10 mL $CHCl_3$. The organic fractions were combined, dried ($MgSO_4$), and concentrated to give **L** as a clear oil (0.15 g, 0.45 mmol, 92%). ^1H NMR ($CDCl_3$): δ 8.05 (d, 1 H, J = 8.3 Hz), 7.86 (dd, 1 H, J = 7.8 Hz, 1.5 Hz), 7.72 (dd, 1 H, J = 7.3 Hz, 1.5 Hz), 7.51 (m, 2 H), 7.39 (m, 2 H), 3.30 (m, 2 H); 3.19 (m, 4 H); 2.89 (m, 4 H); 2.87 (m, 2 H); 2.73 (m, 4 H); 1.90 (m, 2 H). IR: 3044 and 3005 m ν(C$-$H$_{arom}$); 2914 and 2798 m ν(C$-$H$_{aliph}$); 1712 m; 1678 s; 1596 m; 1574 w; 1509 ms; 1452 s; 1415 ms; 1385 s; 1349 m; 1284 ms; 1256 ms; 1218 m; 1166 m; 1105 ms; 1023 m; 776 s; 735 m; 659 m. GC-MS: t_{ret} = 24.5 min; 331 (M^+, 4%), 190 ($C_7H_{14}NS_2-CH_2^+$, 100%), 141 ($C_{10}H_7-CH_2^+$, 17%). UV$-$vis (THF): 240 (3080) 270 (7400).

Preparation of [LCu(CH$_3$CN)](PF$_6$), 1. The ligand **L**, 0.21 g (0.6 mmol), was dissolved in 50 mL of THF and added to $[Cu(CH_3CN)_4](PF_6)$ (0.24 g, 0.6 mmol). The resulting solution was stirred overnight at room temperature and filtered and the solvent distilled away. The crude product was washed with hexane and then dried thoroughly in vacuo. The solid was dissolved in a minimum amount of CH_3CN, and Et_2O was slowly diffused in to form small pale yellow crystals. Yield: 0.22 g (0.37 mmol, 61%). ^1H NMR ($CDCl_3$ + 4 equiv of CH_3CN to **1**): δ 7.94 (d, 1 H, J = 8.3 Hz), 7.88 (d, 1 H, J = 7.3 Hz), 7.77 (d, 1 H, J = 8.8 Hz), 7.54 (m, 2 H), 7.42 (m, 1 H), 7.29 (d, 1 H), 3.35 (m, 2 H), 3.21 (m, 4 H), 3.12 (m, 4 H), 3.00 (m, 4 H), 2.77 (m, 2 H), 2.23 (m, 2 H); 2.00 (s, 3 H, $CH_3-C\equiv N$). $^{13}C\{^1H\}$ NMR ($CDCl_3$ + 4 equiv of CH_3CN to **1**): δ 116.85 ($C\equiv N$); 1.8 ($CH_3-C\equiv N$). IR: 3062 and 3009 m ν(C$-$H$_{arom}$); 2941 and 2855 ms ν(C$-$H$_{aliph}$); 2311 w [ν(C$-$C) + δ(CH$_3$)]; 2278 mw ν(C$\equiv$N); 1628 m; 1597 m; 1510 m; 1464 s; 1416 s; 1395 m; 1291 m; 1270 m; 1107 m; 1092 m; 1026 m; 843 vs (PF_6^-); 735 s; 558 s (PF_6^-). UV$-$vis (THF): 264 (4000) 274 (4100) 284 (4100). FABMS: 394/396 ([**L**Cu]$^+$). Anal. Calcd for $C_{21}H_{28}N_2CuF_6PS_2$: C, 43.41; H, 4.86; N, 4.82. Found: C, 43.73; H, 5.02; N, 5.16. Mp: 153 °C (dec).

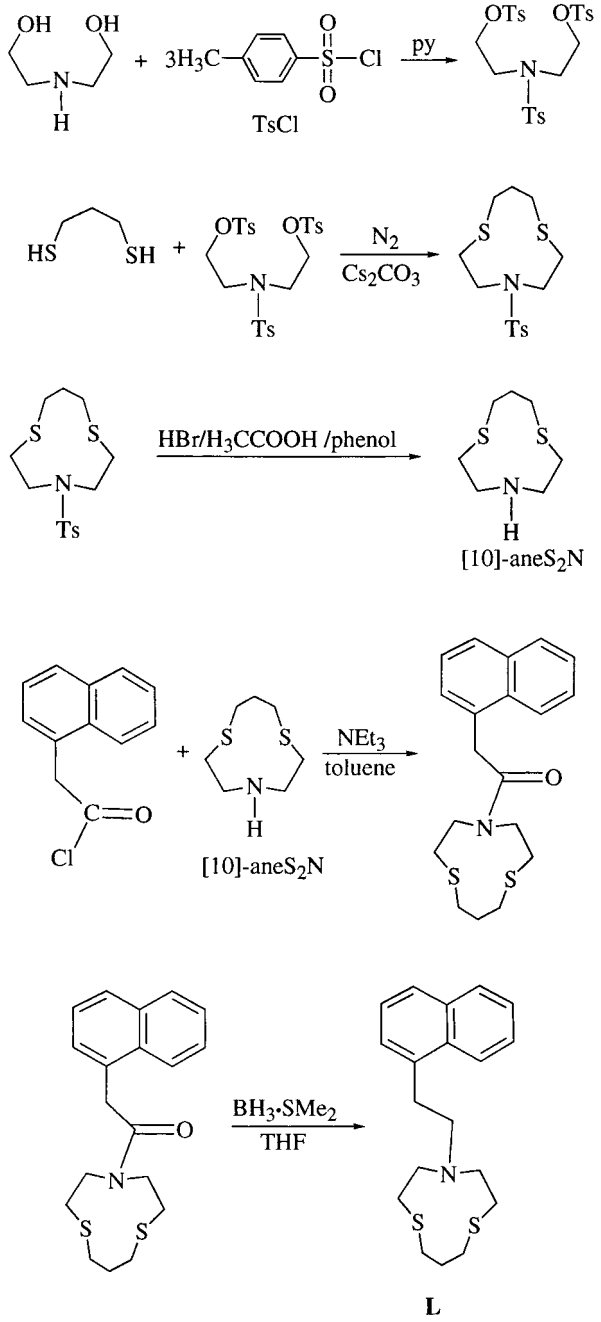
Preparation of [LCu](PF$_6$), 2. Complex **1** (0.50 g, 0.86 mmol) was dissolved in 10 mL of CH_2Cl_2 and stirred overnight. The yellow solution was filtered, and the solvent removed in vacuo. Two to three cycles of dissolution and stirring in CH_2Cl_2, followed by removal of the solvent completely removes the CH_3CN. Addition of Et_2O to a nearly saturated CH_2Cl_2 solution of **2** produced an off-white solid; slow diffusion of hexanes into the CH_2Cl_2 solution produced small nearly colorless (pale yellow) needle-shaped crystals. Yield: 0.40 g (0.74 mmol, 86%). ^1H NMR ($CDCl_3$): 8.00 (d, 1 H, J = 8.3 Hz), 7.92 (d, 1 H, J = 8.3 Hz), 7.83 (d, 1 H, J = 8.3 Hz), 7.63 (m, 2 H), 7.45 (t, 1 H, J = 7.3 Hz), 7.28 (d, 1 H, J = 7.3 Hz) $C_{10}H_7$; 3.40 (br s, 2 H), 3.2$-$2.4 (br m, 12 H), 2.10 (m, 2 H), 1.46 (m, 2 H) 9 $\times$ CH_2. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.2, 133.0, 131.8, 129.7, 129.6, 128.1, 127.7, 125.2, 125.0, 122.8 (all 1 C, $-C_{10}H_7$, the last seven have bound Hs); 56.7 (2 C, $-S-CH_2-CH_2-N-CH_2-CH_2-S-$); 51.1 (1 C, $C_{10}H_7-CH_2-CH_2-N-$); 36.2 (3 C), 32.2 (1 C), 26.1 (2 C) $-S-CH_2-CH_2-N-CH_2-CH_2-S-$, $-CH_2-CH_2-CH_2-$, $-CH_2-CH_2-CH_2-$, and $C_{10}H_7-CH_2-CH_2-N-$. IR: 3059 m ν(C$-$H$_{arom}$); 2924 and 2854 ms ν(C$-$H$_{aliph}$); 1704 m; 1629 m; 1596 m, 1586 mw; 1509 s; 1463 s; 1416 s; 1396 m; 1291 ms; 1269 ms; 1106 m; 1094 m; 1023 m; 839 vs (PF_6^-); 735 s; 558 vs (PF_6^-). UV$-$vis (THF): 276 (4400) 290 (4900). FABMS: 394/396 ([**L**Cu]$^+$). Anal. Calcd for $C_{19}H_{25}NCuF_6PS_2$: C, 42.25; H, 4.67; N, 2.59. Found: C, 41.83; H, 4.35; N, 2.55. Mp: 197 °C (dec).

Preparation of [LCu(PPh$_3$)](PF$_6$), 3. Complex **1** (74.1 mg, 0.13 mmol) and PPh_3 (32.7 mg, 0.13 mmol) were dissolved in 10 mL of THF and stirred at room temperature for 18 h. The resulting off-white precipitate was filtered, washed with 40 mL of hexane, and dried in vacuo for 3 h, yielding 61.8 mg of **3** (0.08 mmol, 61%). An analytically pure sample was prepared by recrystallization via the diffusion of C_6H_6 into a concentrated solution of **3** in CH_3CN. ^1H NMR (CD_3CN): δ 7.85 (d, 1 H, J = 8.3 Hz), 7.70 (d, 2 H, J = 8.5 Hz), 7.47 (m, 2 H), 7.40 (m, 2 H), 7.35 (d, 1 H, J = 6.5 Hz), 7.31$-$7.24 (m, 13 H), 6.83 (d, 1 H, J = 6.5 Hz), 3.36 (m, 2 H), 3.14 (m, 10 H), 2.90 (m, 2 H), 2.83 (m, 2 H), 1.80 (m, 2 H). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 134.2 (d, 6 C, $^2J_{P-C}$ = 14.8 Hz, P$-$(*ortho*-C)$_3$), 133.2 (d, 3 C, $^1J_{P-C}$ = 25 Hz, P$-$(*ipso*-C)$_3$), 131.5 (3 C, P$-$(*para*-C)$_3$), 130.1 (d, 6 C, ^3J = 9.6 Hz, P$-$(*meta*-C)$_3$). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 6.0 (PPh_3), $-$143.2 (sept, J = 706 Hz, PF_6^-). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 6.2 (PPh_3), $-$143.4 (sept, J = 711 Hz, PF_6^-). IR (KBr): 3055 and 3004 m ν(C$-$H$_{arom}$); 2940 and 2856 m ν(C$-$H$_{aliph}$); 1637 m; 1508 m; 1479 ms; 1465 m; 1436 s; 1396 m; 1293 m; 1084 s; 842 vs (PF_6^-); 794 m; 781 m; 747 ms; 696 s; 558 s (PF_6^-); 526 s; 508 ms. FABMS: 394/396 ([**L**Cu]$^+$, 100%), 656/658 ([**L**Cu(PPh$_3$)]$^+$, 37%). UV$-$vis (CH_3CN): 208 (1150) 230 (1350) 258 (1450) 298 (1450). Anal. Calcd for $C_{37}H_{40}NCuF_6P_2S_2$: C, 55.37; H, 5.03; N, 1.75. Found: C, 55.35; H, 4.90; N, 1.77. Mp: 192$-$194 °C (dec).

Results and Discussion

Synthesis and Characterization of the Ligand (L). The novel ligand **L**, *N*-[2-(1-naphthyl)ethyl]-1-aza-4,8-dithiacyclodecane, was synthesized in five steps (Scheme 1), with an overall yield of about 15%. The first three steps were required to make the parent macrocycle [10]-aneS_2N and were carried out in a manner similar to that reported by Chandrasekhar and McAuley.[19] The naphthalene arm was added by reaction of [10]-aneS_2N with 1-naphthylacetyl chloride, which was prepared from 1-naphthylacetic acid and PCl_5 in a combination of literature methods.[21,22] The resulting amide was purified by column chromatography and then, in the last step, reduced to **L** with excess borane. At room temperature, **L** exists as an oil and is soluble in nonpolar to moderately polar organic solvents, such as pentane, $CHCl_3$, CH_2Cl_2, THF, and acetone, but is

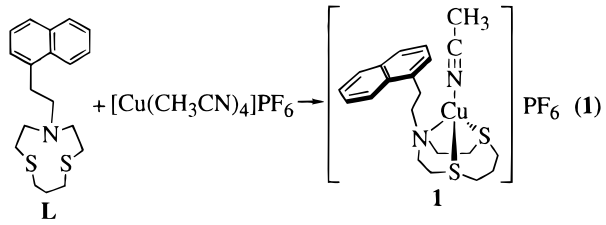
Scheme 1. Synthesis of the New Ligand (**L**)



insoluble in more polar solvents, including CH_3CN and MeOH. Full characterization of **L** has been carried out, including by ^1H and ^{13}C NMR spectroscopies, gas chromatography, and mass spectrometry.

The approach, adding coordinating or otherwise reactive pendant groups to macrocyclic ligands, has previously been utilized by a number of researchers.[23] The parent [10]-aneS_2N macrocyclic ligand has only appeared in the one report, which details its synthesis, along with two octahedral Ni(II) and Ni(III) bis([10]-aneS_2N) complexes as well as the "ear-muff" ligand derivative where two of the [10]-aneS_2N macrocycles are joined with an ethylene bridge.[19,24]

Synthesis of [LCu(CH$_3$CN)](PF$_6$), 1. The ligand **L** was coordinated to copper(I) via a stoichiometric reaction with $[Cu(CH_3CN)_4](PF_6)$[18] in THF (eq 1). The final yield of the product, the copper(I)−acetonitrile complex of **L**, [**L**Cu(CH_3-CN)]PF_6 (**1**), was typically about 60%. Crystals of **1** are pale yellow in color and are soluble in polar organic solvents, such as CH_3CN, $CHCl_3$, CH_2Cl_2, and THF, and are insoluble in Et_2O and hydrocarbon solvents. Compound **1** is stable to air both in the solid state as well as in CH_3CN solution for at least a couple of days.



Characterization of 1. Complex **1** has been characterized by ^1H and ^{13}C NMR (discussed in a separate section below), IR, and UV−vis spectroscopies, mass spectrometry, elemental analysis, and X-ray crystallography. Two fairly weak peaks are observed in the IR spectrum of **1**, at 2311 and 2278 cm^{-1}, in the region nitrile stretches are expected to occur. The 2278 cm^{-1} band can be assigned to the nitrile stretch, which has shifted to higher wavenumbers versus free CH_3CN (2255 cm^{-1}), which occurs upon coordination. The nitrile stretch observed for **1** is inside the typical range given for all metal−acetonitrile complexes (2270−2300 cm^{-1})[25] and compares favorably with some other Cu−$NCCH_3$ complexes,[26−32] with values in the 2260−2280 cm^{-1} range. The peak observed in the IR spectrum at 2311 cm^{-1} is assigned as the combination band (ν[C−C] + $\delta[CH_3]$) which is seen for CH_3CN complexes.[25]

The solid-state structure of **1** was determined by X-ray crystallography (crystallographic data, Table 1). The copper ion is four-coordinate (Figure 1a), bound to the three macrocyclic ring heteroatoms as well as the nitrogen from the CH_3CN ligand.

(23) Some recent examples: (a) Adam, K. R.; Lindoy, L. F.; Skelton, B. W.; Smith, S. V.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1994**, 3361−3367. (b) Beissel, T.; Bürger, K. S.; Voigt, G.; Weighardt, K.; Butzlaff, C.; Trautwein, A. X. *Inorg. Chem.* **1993**, *32*, 124−126. (c) Bu, X. H.; Zhang, Z. H.; Cao, X. C.; Ma, S. Y.; Chen, Y. T. *Polyhedron* **1997**, *16*, 3525−3532. (d) De Santis, G.; Fabbrizzi, L.; Licchelli, M.; Mangano, C.; Sacchi, D. *Inorg. Chem.* **1995**, *34*, 3581−3582. (e) Funkemeier, D.; Mattes, R. *J. Chem. Soc., Dalton Trans.* **1993**, 1313−1319. (f) Kim, W. D.; Hrncir, D. C.; Kiefer, G. E.; Sherry, A. D. *Inorg. Chem.* **1995**, *34*, 2225−2232. (g) McLachlan, G. A.; Fallon, G. D.; Martin, R. L.; Spiccia, L. *Inorg. Chem.* **1995**, *34*, 254−261. (h) Parker, D.; Williams, J. A. G. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1305−1314. (i) Schmid, C. L.; Neuburger, M.; Zehnder, M.; Kaden, T. A.; Bujno, K.; Bilewicz, R. *Helv. Chim Acta* **1997**, *80*, 241−252. (j) Shionoya, M.; Ikeda, T.; Kimura, E.; Shiro, M. *J. Am. Chem. Soc.* **1994**, *116*, 3848−3859. (k) Turonek, M. L.; Moore, P.; Clase, H. J.; Alcock, N. W. *J. Chem. Soc., Dalton Trans.* **1995**, 3659−3666. (l) Villanueva, N. D.; Chiang, M. Y.; Bocarsly, J. R. *Inorg. Chem.* **1998**, *37*, 685−692. (m) Whittle, B.; Batten, S. R.; Jeffery, J. C.; Rees, L. H.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1996**, 4249−4255. (n) Zhu, S.; Chen, W.; Lin, H.; Yin, X.; Kou, F.; Lin, M.; Chen, Y. *Polyhedron* **1997**, *16*, 3285−3291.
(24) Danks, J. P.; Champness, N. R.; Schröder, M. *Coord. Chem. Rev.* **1998**, *174*, 417−468.
(25) Endres, H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1987; Vol. 2, pp 261−267.
(26) Conry, R. R.; Ji, G.; Tipton, A. A. *Inorg. Chem.* **1999**, *38*, 906−913.
(27) Lastra, E.; Gamasa, M. P.; Gimeno, J.; Lanfranchi, M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1989**, 1499−1506.
(28) Karlin, K. D.; Hayes, J. C.; Hutchinson, J. P.; Zubieta, J. *Inorg. Chim. Acta* **1983**, *78*, L45−L46.
(29) Csöregh, I.; Kierkegaard, P.; Norrestam, R. *Acta Crystallogr., Sect. B* **1975**, *31*, 314−317.
(30) Black, J. R.; Levason, W.; Webster, M. *Acta Crystallogr., Sect. C* **1995**, *51*, 623−625.
(31) Díez, J.; Gamasa, M. P.; Gimeno, J.; Tiripicchio, A.; Camellini, M. T. *J. Chem. Soc., Dalton Trans.* **1987**, 1275−1278.
(32) Massaux, M.; Bernard, M. J.; Le Bihan, M.-T. *Acta Crystallogr., Sect. B* **1971**, *27*, 2419−2424.

Table 1. Selected Crystallographic Data for the Structures of **1**−**3**

parameter	**1**	**2**·0.5hexane	**1&2**·hexane	**3**
chemical formula	$C_{21}H_{28}N_2CuF_6PS_2$	$C_{22}H_{31}NCuF_6PS_2$	$C_{46}H_{61}N_3Cu_2F_{12}P_2S_4$	$C_{37}H_{40}NCuF_6P_2S_2$
formula wt	581.08	582.11	1201.24	802.30
temperature (K)	293	300	299	298
λ	0.71073 Å (Mo Kα)	0.71073 Å (Mo Kα)	0.71073 Å (Mo Kα)	0.71073 Å (Mo Kα)
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	11.1901(10)	15.7318(15)	10.8308(9)	11.462(2)
b (Å)	11.2735(12)	8.9164(10)	12.6320(8)	15.972(2)
c (Å)	12.1350(10)	17.205(5)	19.9412(13)	19.835(9)
α (deg)	98.996(8)	90	80.445(5)	90
β (deg)	117.188(6)	102.431(6)	76.405(6)	94.50(3)
γ (deg)	105.354(7)	90	78.825(5)	90
V (Å^3)	1242.6(2)	2356.8(4)	2580.7(3)	3620.0(18)
Z	2	4	2	4
calcd ρ (g/cm^3)	1.553	1.641	1.546	1.472
cryst dimens (mm)	0.85 × 0.80 × 0.15	0.85 × 0.40 × 0.06	0.74 × 0.34 × 0.26	0.50 × 0.20 × 0.02
μ (mm^{-1})	1.169	1.231	1.128	0.867
R1[a]	0.0505	0.0587	0.0661	0.0906
wR2	0.1418	0.1545	0.1871	0.1889

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ (observed data, $I > 2\sigma(I)$). [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ (all data).

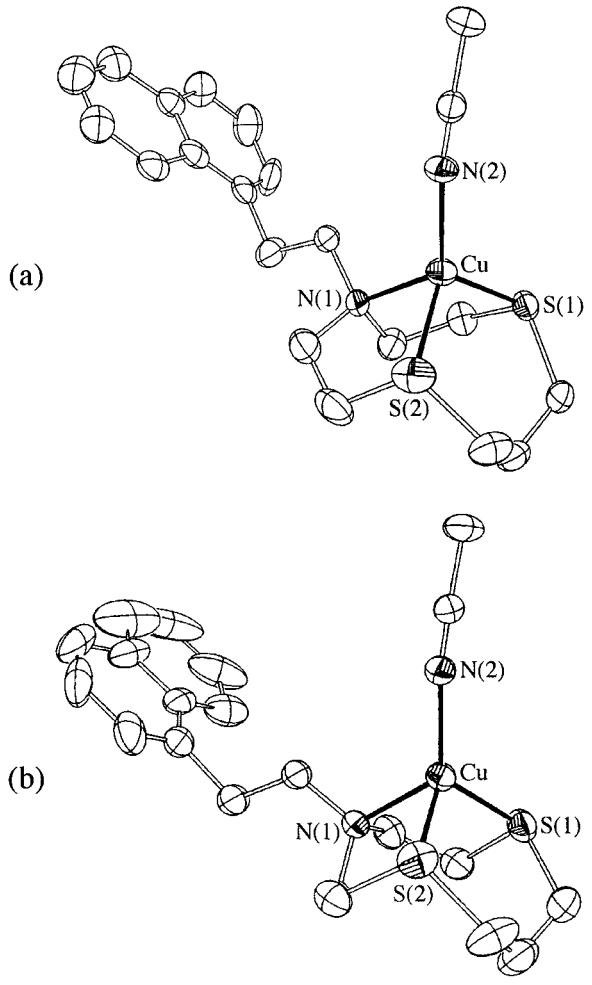


Figure 1. Thermal ellipsoid plots of the solid-state structures of [**L**Cu(CH_3CN)]$^+$ at the 25% probability level (hydrogens omitted for clarity): (a) from the crystal just containing **1**; (b) from the crystal containing cocrystallized **1&2**.

The geometry about the copper center is distorted tetrahedral as is common for Cu(I), with angles ranging from 90.3 to 121.7° (selected bond distances and angles, Table 2). The copper−sulfur distances are nearly identical, at 2.2687(14) and 2.260(2) Å, while the copper−nitrogen distances are different as they should be, at 2.167(4) Å for the macrocyclic nitrogen atom and 1.923(4) Å for the nitrile nitrogen, respectively. The naphthalene is essentially planar as expected; if a plane is calculated using all 10 carbon positions, the mean deviation from that plane is 0.027 Å, with the largest deviation of 0.054 Å belonging to C(16), one of the carbons in the ring not directly linked to the macrocycle.

The positive-ion FAB mass spectrum of **1** shows only a peak corresponding to [**L**Cu]$^+$, suggesting weak binding to the CH_3CN ligand. This weak binding is also observed in solution; we have been able to take advantage of this facile loss of the CH_3CN ligand to isolate [**L**Cu]$^+$, as discussed in the next section.

Synthesis of [LCu](PF$_6$), 2. The acetonitrile ligand from **1** could be removed, to synthesize [**L**Cu](PF_6) (**2**), by first adding CO to a CH_2Cl_2 solution of **1** at room temperature, followed by removal of the solvent and CO in vacuo (eq 2). The strategy of replacing the acetonitrile ligand in **1** with a CO ligand takes synthetic advantage of the weak copper−carbonyl bond generally found for Cu^I−CO complexes.[33] The intermediate carbonyl complex displayed a ν(C≡O) at 2101 cm^{-1}, which is within the range for terminal Cu^I−CO complexes reported through 1987 (2055−2180 cm^{-1}).[33]

$$[\mathbf{L}Cu(CH_3CN)]PF_6 \xrightarrow[-\,CH_3CN]{+\,CO,\ CH_2Cl_2} [\mathbf{L}Cu(CO)]PF_6 \qquad \mathbf{1}$$

$$\xrightarrow[(vacuum)]{-\,CO,\ CH_2Cl_2} [\mathbf{L}Cu]PF_6 \qquad \mathbf{2} \qquad (2)$$

The addition of CO in the synthesis of **2** from **1** was found not to be necessary. The acetonitrile ligand in **1** could also be removed by several cycles of stirring **1** in CH_2Cl_2 at room temperature, followed by removal of the solvent in vacuo (eq 3). Similar results were obtained by repeatedly stirring **1** in CH_2Cl_2, concentrating the solution, and precipitating the product with hexane or Et_2O. The typical isolated yield for these syntheses of **2** was 85%. Recrystallization of **2** was accomplished by slow diffusion of hexanes into a saturated CH_2Cl_2 solution of **2**. Crystals of **2** are almost colorless and have comparable solubility to **1**. Surprisingly, **2** is reasonably stable to air. In fact, a CH_2Cl_2 solution of **1** was unreactive toward an atmosphere of O_2, added and maintained at −78 °C for several

(33) Hathaway, B. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1987; Vol. 5, pp 533−774.

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Structures of **1**−**3**

bond distances	**1**	**2**	**1** in **1&2**	**2** in **1&2**	**3**
Cu−S(1)	2.2687(14)	2.268(2)	2.282(2)	2.254(2)	2.325(4)
Cu−S(2)	2.260(2)	2.233(2)	2.264(2)	2.255(2)	2.307(4)
Cu−N(1)	2.167(4)	2.146(5)	2.155(5)	2.139(5)	2.107(10)
Cu−P					2.189(4)
Cu−N(2)	1.923(4)		1.927(6)		
Cu−C(10)		2.414(6)		2.288(6)	
Cu−C(11)		2.129(6)		2.150(6)	
Cu−center of C(10)−C(11)		2.168		2.109	
C(10)−C(11)	1.343(11)	1.384(9)	1.356(13)	1.389(9)	1.43(4)
ave naph C−C	1.381	1.388	1.380	1.394	1.38
nitrile C−N(2)	1.119(6)		1.115(7)		
bond angles	**1**	**2**	**1** in **1&2**	**2** in **1&2**	**3**
S(1)−Cu−S(2)	109.04(6)	111.08(7)	119.96(8)	110.52(10)	105.9(2)
S(1)−Cu−N(1)	90.26(11)	90.5(2)	90.1(2)	91.3(2)	91.5(4)
S(2)−Cu−N(1)	90.76(12)	91.89(14)	90.1(2)	91.7(2)	90.3(3)
S(1)−Cu−P					112.5(2)
S(2)−Cu−P					118.0(2)
N(1)−Cu−P					133.5(4)
S(1)−Cu−N(2)	119.32(14)		117.7(2)		
S(2)−Cu−N(2)	121.73(14)		123.6(2)		
N(1)−Cu−N(2)	118.0(2)		117.1(2)		
S(1)−Cu−center of C(10)−C(11)		122.6		124.9	
S(2)−Cu−center of C(10)−C(11)		126.1		123.5	
N(1)−Cu−center of C(10)−C(11)		92.7		96.6	
Cu−N(2)−C nitrile	171.0(4)		171.3(6)		
N(2)−C−C nitrile	179.1(6)		177.9(7)		

hours, followed by warming to ambient temperatures for 2 weeks!

$$\underset{\mathbf{1}}{[\mathbf{L}Cu(CH_3CN)]PF_6} \xrightarrow{+\,CH_2Cl_2} \xrightarrow[(vacuum)]{-\,CH_3CN,\,CH_2Cl_2} \underset{\mathbf{2}}{[\mathbf{L}Cu]PF_6} \quad (3)$$

Characterization of 2. Complex **2** has been characterized by ^{1}H and ^{13}C NMR (discussed below in a separate section), IR, and UV−vis spectroscopies, FABMS, elemental analysis, and X-ray crystallography. Loss of the acetonitrile ligand was confirmed by the absence of peaks in the nitrile region of the IR spectrum as well as the corresponding resonance(s) in the ^{1}H and ^{13}C NMR spectra. The IR and ^{19}F NMR spectra show no evidence for PF_6^- binding in the solid state and solution, respectively. Close comparison of the IR spectra of **L** and **2** in the region where C═C stretches tend to occur show two bands are present in both spectra, at 1596 and 1509 cm^{-1}. In addition, there is a third band that is apparently shifted from 1574 for **L** to 1586 cm^{-1} for **2** that we tentatively assign as a C═C stretch. The 12 wavenumber shift for complex **2** versus **1** and **L** seems reasonable for weak copper−arene binding. Coordination of an alkene to copper(I) is known to shift the C═C stretch from 15 to 170 cm^{-1} versus the free alkene.[34]

The structure of **2** in the solid state, from the crystal structure (crystallographic data, Table 1), reveals that the copper ion remains four-coordinate, by binding the three macrocyclic ring heteroatoms and also by η^2-coordination of the pendant naphthyl group (Figure 2a). The geometry about the copper center is best described as distorted tetrahedral, with bond angles ranging from 90.5° to 126.1° (calculated using the center of the coordinated carbon atoms from the naphthyl group, see Table 2). The copper−naphthalene bond involves the aromatic ring joined to the ethylene linker group, at the position including the carbon atom bound to the linker as well as the adjacent carbon atom. The binding to the naphthalene is unsymmetrical, with Cu−C distances of 2.414(6) and 2.129(6) Å, with the longer distance to C(10), which is bound to the linking group. While the copper to macrocyclic ring nitrogen distance is essentially unchanged as compared to **1**, the distances to the sulfur atoms are no longer identical to each other, but vary only by 0.03 Å. The C(10)−C(11) distance (between the bound carbons) appears to change very little upon coordination (comparing **2** to **1**). The naphthalene is essentially planar; if a plane is calculated using all 10 carbon positions, the mean deviation from that plane is 0.026 Å, with the largest deviation of 0.065 Å belonging to C(11). If the plane is only calculated for the eight carbon atoms not bound to copper, the average deviation is 0.015 Å and the largest deviation is 0.107 for C(11), with no other deviation being greater than 0.035 Å (C(10) is only 0.018 Å from the plane).

Substitution Reactions of the Arene Ligand in 2: Synthesis and Characterization of [LCu(PPh$_3$)]PF$_6$, 3. The arene interaction in **2** could be disrupted by the addition of neutral ligands, such as nitriles, alkenes, and phosphines (eq 4), as indicated by NMR spectroscopy. Thus, the addition of 1 equiv of PPh_3 to **2** in THF leads to formation of [**L**Cu(PPh_3)]PF_6 (**3**) in good yields, and when excess acetonitrile and **2** are combined, **1** is regenerated. Complex **3** can also be synthesized from **1** (see Experimental Section). As is typical for most Cu^I−PPh_3 complexes, **3** is reasonably air stable both in solution and as a solid. Some differences in solubility for **3** were seen as compared to **1** and **2**; **3** is essentially insoluble in THF and $CHCl_3$ and is much less soluble in CH_2Cl_2. Complex **3** is quite soluble in CH_3CN and is insoluble in Et_2O and hydrocarbon solvents, consistent with the ionic nature of the compound. Complex **3** has been fully characterized, including by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, FABMS, elemental analysis, and X-ray crystal-

(34) (a) Engelhardt, L. M.; Healy, P. C.; Kildea, J. D.; White, A. H. *Aust. J. Chem.* **1989**, *42*, 185−199. (b) Van Den Hende, J. H.; Baird, W. C., Jr. *J. Am. Chem. Soc.* **1963**, *85*, 1009−1010. (c) Munakata, M.; Kitagawa, S.; Shimono, H.; Masuda, H. *Inorg. Chem.* **1991**, *30*, 2610−2614. (d) Håkansson, M.; Wettström, K.; Jagner, S. *J. Organomet. Chem.* **1991**, *421*, 347−356. (e) Cook, B. W.; Miller, R. G. J.; Todd, P. F. *J. Organomet. Chem.* **1969**, *19*, 421−430. (f) Leedham, T. J.; Powell, D. B.; Scott, J. G. V. *Spectrochim. Acta* **1973**, *29A*, 559−565.

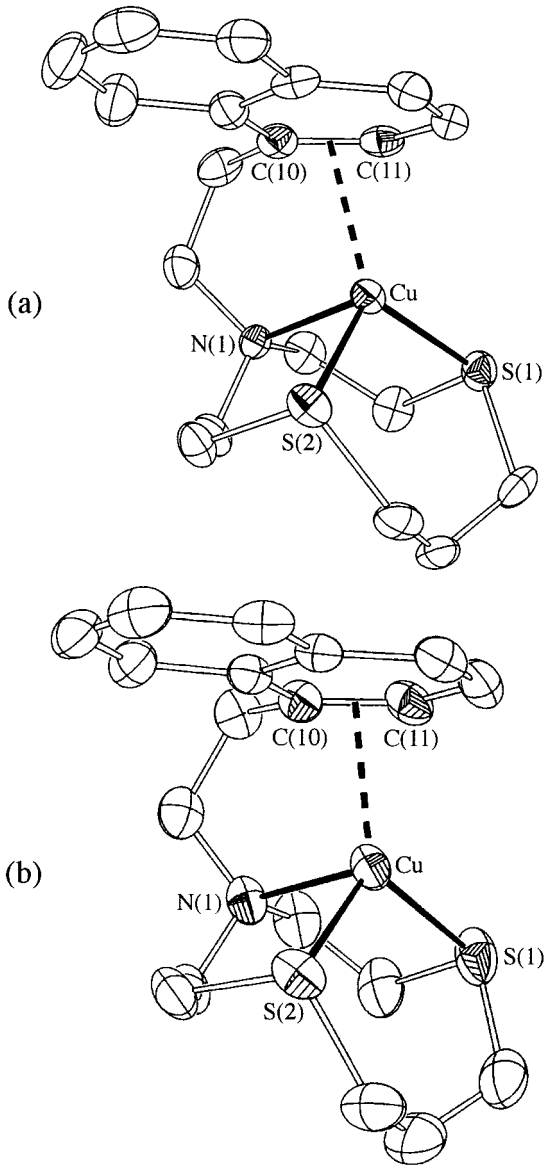
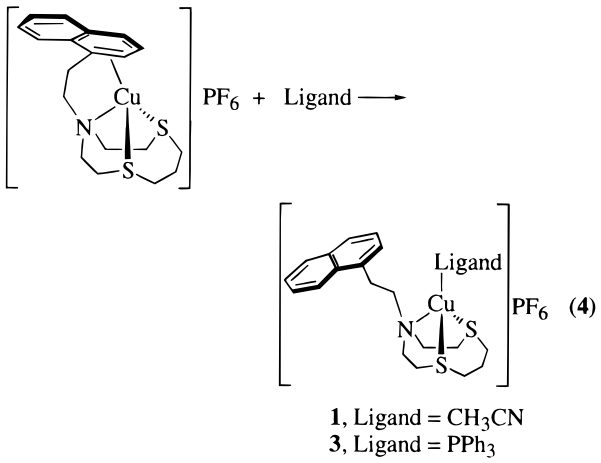


Figure 2. Thermal ellipsoid plots of the solid-state structures of $[\mathbf{L}Cu]^+$ at the 25% probability level (hydrogens omitted for clarity): (a) from the crystal just containing **2**; (b) from the crystal containing cocrystallized **1&2**.



lography (crystallographic data, Table 1). For **3**, the ^{31}P NMR resonance for PPh_3 appears at +6.0 ppm in CD_3CN (+6.2 ppm in CD_2Cl_2), which is shifted 12 ppm downfield from free PPh_3 and is within the $\Delta\delta$ of 15 ppm seen for most Cu(I)−PPh_3 complexes.[26,35]

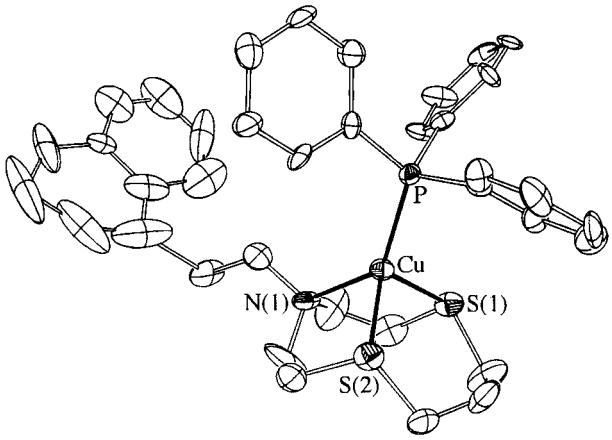


Figure 3. Thermal ellipsoid plot of the solid-state structure of $[\mathbf{L}Cu(PPh_3]^+$ at the 25% probability level (hydrogens omitted for clarity).

Single crystals of **3** could be grown by the slow diffusion of C_6H_6 into CH_3CN or from the evaporation of CH_2Cl_2. The solid-state structure (Figure 3) consists of a distorted tetrahedral copper(I) ion, bound to the macrocycle as well as the phosphine. The angles about the copper average to 108.6° but range from 90.3(3) to 133.5(4)° (Table 2). As for **1**, the naphthalene is located well away from the copper center.

Issues Dealing with the Weak Binding of the Acetonitrile Ligand in 1. It was anticipated that the CO ligand would be much more easily lost than the acetonitrile ligand. Thus, it was surprising, at first, that **1** loses its acetonitrile ligand so readily. Although it is not unusual for Cu(I)−$NCCH_3$ complexes to be utilized in acetonitrile-replacing reactions, for instance, the common use of $[Cu(CH_3CN)_4]^+$ as a starting material, these reactions usually depend on a suitable incoming coordinating group. Thus, the loss of the acetonitrile of **1** is facilitated, at least in part, by the coordination of the naphthyl group. Additional evidence for this hypothesis comes from the observation that the copper(I)−acetonitrile complex of the macrocyclic ligand without the pendant ethylnaphthyl group, [{*N*-methyl-1-aza-4,8-dithiacyclodecane}$Cu(CH_3CN)]PF_6$, does not lose its acetonitrile ligand when subjected to the multiple cycles of stirring/removing CH_2Cl_2 that remove the acetonitrile ligand from **1**.[36]

The observed facile loss of the acetonitrile ligand also raised the question of whether the resonances in the NMR spectra of dissolved complex **1** were representative of **1** (with its bound acetonitrile) or, instead, more closely corresponded to a rapidly exchanging mixture of **1** and the product from loss of the acetonitrile ligand ($[\mathbf{L}Cu]^+$ or **2**). To probe this question, we acquired ^1H NMR spectra with increasing stoichiometries of added acetonitrile, up to ∼130 equiv of added CH_3CN to **2** (or to Cu^+). We found that the ^1H chemical shifts of not only the acetonitrile but also of the ligand hydrogens were sensitive to the concentration of CH_3CN. In all of the spectra, only one set of peaks was observed for the acetonitrile and ligand resonances, indicating fast exchange on the NMR time scale. The resonances that were the most sensitive to the acetonitrile concentration shift the most dramatically upon the addition of the first 5 equiv of acetonitrile and then the magnitude of the shift diminishes

(35) Anderson, Q. T.; Erkizia, E.; Conry, R. R. *Organometallics* **1998**, *17*, 4917−4920.
(36) Conry, R. R.; Striejewske, W. S.; Caffaratti, A. R. Unpublished results.

rapidly. Thus, to make the ^1H and ^{13}C NMR data more representative of **1**, rather than an interconverting mixture of **1** and **2**, we added 4 equiv of acetonitrile to the solution of **1** (for a total of 5 equiv of CH_3CN per Cu^+) before acquiring spectra. The data from the titration experiment of **2** with CH_3CN could be used to crudely estimate the room-temperature equilibrium constant for the binding of acetonitrile to **2** (**2** + $CH_3CN \rightleftarrows$ **1**) to be in the 10^2 range.

Crystal Structure of Cocrystallized 1&2. Another consequence of the equilibrium between complexes **1** and **2** is that, given the right conditions, the two complexes cocrystallize. Thus, we have also determined the crystal structure of the two complexes together (crystallographic data for cocrystallized **1&2**, Table 1) as well as separate (discussed above). The complexes pack such that each complex occupies a discrete site within the unit cell; there is no crystallographic evidence for disorder of the two complexes in the occupancy of the sites. The two copper-containing cations from the crystal containing both **1** and **2** are shown in Figures 1b and 2b, respectively.

For complex **1**, there are mostly minor variations in the distances and angles for the structure of **1** alone versus the one cocrystallized with **2** (Table 2). The biggest differences include a 10° widening of the S(1)−Cu−S(2) angle in the cocrystallized structure and the orientation of the naphthyl group. There is obviously significant thermal motion of the naphthalene in **1** in the mixed structure, essentially amounting to pivoting about the linker arm (attempts to model this disorder with two positions were unsuccessful).

For complex **2**, there are also mostly minor variations in the distances and angles between the two structures (Table 2). However, in the cocrystallized sample, the naphthyl group appears to have less of a tilt away from the copper center, resulting in diminished asymmetry to the two bound carbon atoms and a shorter copper to center of the bound C−C bond distance. The naphthalene in **1** from the cocrystallized sample is also essentially planar; if a plane is calculated using all 10 carbon positions, the mean deviation from that plane is 0.016 Å, with the largest deviation of 0.031 Å belonging to C(10). If the plane is only calculated for the eight carbon atoms not bound to copper, the average deviation is 0.013 Å and the largest deviation is 0.043 for C(10), with no other deviation being greater than 0.028 Å (C(11) is only 0.009 Å from the plane). The naphthalene in **2** in the cocrystallized sample is quite planar; for a plane calculated using all 10 carbon positions, the mean deviation from that plane is 0.009 Å, with the largest deviation of −0.016 Å belonging to C(10).

Binding of the Macrocycle in the Solid State (Complexes 1−3). Copper(I)−thioether complexes are fairly common, especially with macrocyclic ligands;[37−43] tertiary amine complexes of copper(I) are also quite frequently found. Mixed N/S-ligated copper complexes are typically studied as models for the blue copper proteins.[37,38,40] A partial literature survey of these types of complexes quickly establishes that the $Cu-S_{thioether}$ and $Cu-N_{tertiary\ amine}$ distances in both structures of complexes **1** and **2** are unexceptional, with copper(I) four-coordinate thioether complexes having Cu−S distances in the 2.19−2.41 Å range[44−46] and copper(I) four-coordinate tertiary amine complexes displaying Cu−N distances between 1.88 and 2.32 Å.[28,44,46−51]

Binding of the Acetonitrile and Triphenylphosphine Ligands in the Solid State (Complexes 1 and 3). The structural parameters for the CH_3CN and PPh_3 ligands in **1** and **3** are also unexceptional. Thus, the nitrile C−N distance has shortened in **1** versus free acetonitrile[25] to nearly identical values in the two structures. The acetonitrile ligand is essentially linear, as is typical for copper−acetonitrile complexes.[26−32,52,53] The copper−nitrile angle is within the usual range for transition metal complexes[25] and some other $Cu-NCCH_3$ complexes.[26−32,49,52−54] The $Cu-N_{acetonitrile}$ distances in both structures of **1** are identical to one another and fall within the range seen for some other four-coordinate copper(I)−acetonitrile complexes.[26−32,44,52−54] The Cu−P distance in **3** falls well within the range seen for some other four-coordinate, copper(I), mono-PPh_3 structures.[26,35,49,55−66]

Binding of the Naphthalene Group in the Solid State (Complex 2). Isolated and structurally characterized π-arene complexes are reasonably common for other transition metals; the arene is typically bound in an η^6-fashion; η^4-, η^3-, and η^2-complexes are less common.[1] All structurally characterized copper(I)−arene complexes are bound in an η^2-fashion.[6−8,15,16] Naphthalene complexes of other metals are known,[67] including

(37) Kitajima, N. *Adv. Inorg. Chem.* **1992**, *39*, 1−77.
(38) McKee, V. *Adv. Inorg. Chem.* **1993**, *40*, 323−410.
(39) Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329−436.
(40) Reid, G.; Schröder, M. *Chem. Soc. Rev.* **1990**, *19*, 239−269.
(41) Cooper, S. R. *Acc. Chem. Res.* **1988**, *21*, 141−146.
(42) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365−414.
(43) Blake, A. J.; Schröder, M. *Adv. Inorg. Chem.* **1990**, *35*, 1−80.
(44) Atkinson, N.; Blake, A. J.; Drew, M. G. B.; Forsyth, G.; Lavery, A. J.; Reid, G.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1989**, 984−986.
(45) (a) Hartman, J. R.; Cooper, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 1202−1208. (b) Diaddario, L. L., Jr.; Dockal, E. R.; Glick, M. D.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1985**, *24*, 356−363. (c) Chen, L.; Thompson, L. K.; Tandon, S., S.; Bridson, J. N. *Inorg. Chem.* **1993**, *32*, 4063−4068. (d) Martin, J. W. L.; Organ, G. J.; Wainwright, K. P.; Weerasuria, K. D. V.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1987**, *26*, 2963−2968. (e) Nanda, K. K.; Addison, A. W.; Butcher, R. J.; McDevitt, M. R.; Rao, T. N.; Sinn, E. *Inorg. Chem.* **1997**, *36*, 134−135. (f) Flanagan, S.; Dong, J.; Haller, K.; Wang, S.; Scheidt, W. R.; Scott, R. A.; Webb, T. R.; Stanbury, D. M.; Wilson, L. J. *J. Am. Chem. Soc.* **1997**, *119*, 8857−8868. (g) Wainwright, K. P.; Patalinghug, W.; Skelton, B. W.; White, A. H.; Healy, P. C. *J. Chem. Soc., Dalton Trans.* **1988**, 2301−2305. (h) Küppers, H.-J.; Wieghardt, K.; Tsay, Y.-H.; Krüger, C.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 575−576. (i) Clarkson, J. A.; Yagbasan, R.; Blower, P. J.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1244−1245.
(46) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1−S83.
(47) Karlin, K. D.; Hayes, J. C.; Hutchinson, J. P.; Hyde, J. R.; Zubieta, J. *Inorg. Chim. Acta* **1982**, *64*, L219−L220.
(48) Halfen, J. A.; Young, V. G., Jr.; Tolman, W. B. *J. Am. Chem. Soc.* **1996**, *118*, 10920−10921.
(49) Tyeklár, Z.; Jacobson, R. R.; Wei, N.; Murthy, N. N.; Zubieta, J.; Karlin, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 2677−2689.
(50) Wei, N.; Murthy, N. N.; Tyeklár, Z.; Karlin, K. D. *Inorg. Chem.* **1994**, *33*, 1177−1183.
(51) Pattrick, G.; Hancock, R. D. *Inorg. Chem.* **1991**, *30*, 1419−1422.
(52) Blake, A. J.; Gould, R. O.; Holder, A. J.; Lavery, A. J.; Schröder, M. *Polyhedron* **1990**, *9*, 2919−2924.
(53) Lynch, W. E.; Kurtz, D. M., Jr.; Wang, S.; Scott, R. A. *J. Am. Chem. Soc.* **1994**, *116*, 11030−11038.
(54) Li, D.; Yip, H.-K.; Che, C.-M.; Zhou, Z.-Y.; Mak, T. C. W.; Liu, S.-T. *J. Chem. Soc., Dalton Trans.* **1992**, 2445−2449.
(55) Cotton, F. A.; Takats, J. *J. Am. Chem. Soc.* **1970**, *92*, 2353−2358.
(56) Hanusa, T. P.; Ulibarri, T. A.; Evans, W. J. *Acta Crystallogr., Sect. C* **1985**, *41*, 1036−1038.
(57) Lang, J.; Tatsumi, K.; Yu, K. *Polyhedron* **1996**, *15*, 2127−2130.
(58) Teixidor, F.; Viñas, C.; Abad, M. M.; Lopez, M.; Casabó, J. *Organometallics* **1993**, *12*, 3766−3768.
(59) Lu, J.; Crisci, G.; Niu, T.; Jacobson, A. J. *Inorg. Chem.* **1997**, *36*, 5140−5141.
(60) Healy, P. C.; Whittaker, A. K.; Kildea, J. D.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1991**, *44*, 729−736.
(61) Nianyong, Z.; Jianhui, W.; Xintao, W. *Acta Crystallogr., Sect. C* **1991**, *47*, 856−858.
(62) Barron, P. F.; Engelhardt, L. M.; Healy, P. C.; Kildea, J. D.; White, A. H. *Inorg. Chem.* **1988**, *27*, 1829−1834.

η^2-complexes,[68] η^4-complexes,[69] and η^6-complexes;[70] typically the naphthalene ring system is fairly planar in the structurally characterized η^2- and η^6-complexes and deviates substantially from planarity in the η^4-complexes.

The distance between C(10) and C(11) is not significantly different between the structures in which the naphthyl group is coordinated and those in which it is not. In addition, the planarity of the naphthalene system is essentially maintained in all the structures of **1** and **2**, plus the deviations from planarity are not substantially greater in the structures of **2** compared to **1**. This is consistent with weak binding of the arene in **2**. Essentially the same properties are observed in the other copper−arene complexes;[6−8,16] no discernible lengthening of the C−C distance or disturbance of the planarity of the benzene rings occurred.

(63) Wei, N.; Murthy, N. N.; Chen, Q.; Zubieta, J.; Karlin, K. D. *Inorg. Chem.* **1994**, *33*, 1953−1965.

(64) Karlin, K. D.; Cruse, R. W.; Gultneh, Y.; Farooq, A.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1987**, *109*, 2668−2679.

(65) Karlin, K. D.; Ghosh, P.; Cruse, R. W.; Farooq, A.; Gultneh, Y.; Jacobson, R. R.; Blackburn, N. J.; Strange, R. W.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 6769−6780.

(66) Green, B. E.; Kennard, C. H. L.; Smith, G.; James, B. D.; White, A. H. *Acta Crystallogr., Sect. C* **1984**, *40*, 426−428.

(67) Jonas, K. *Pure Appl. Chem.* **1990**, *62*, 1169−1174.

(68) (a) Hall Griffith, E. A.; Amma, E. L. *J. Am. Chem. Soc.* **1974**, *96*, 743−749. (b) Benn, R.; Mynott, R.; Topalović, I.; Scott, F. *Organometallics* **1989**, *8*, 2299−2305. (c) Scott, F.; Krüger, C.; Betz, P. *J. Organomet. Chem.* **1990**, *387*, 113−121. (d) Winemiller, M. D.; Kelsch, B. A.; Sabat, M.; Harman, W. D. *Organometallics* **1997**, *16*, 3672−3678.

(69) (a) Albright, J. O.; Brown, L. D.; Datta, S.; Kouba, J. K.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1977**, *99*, 5518−5519. (b) Albright, J. O.; Datta, S.; Dezube, B.; Kouba, J. K.; Marynick, D. S.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1979**, *101*, 611−619. (c) Hull, J. W., Jr.; Gladfelter, W. L. *Organometallics* **1984**, *3*, 605−613. (d) Crabtree, R. H.; Parnell, C. P. *Organometallics* **1984**, *3*, 1727−1731. (e) Schäufele, H.; Hu, D.; Pritzkow, H.; Zenneck, U. *Organometallics* **1989**, *8*, 396−401. (f) Thompson, R. L.; Lee, S.; Rheingold, A. L.; Cooper, N. J. *Organometallics* **1991**, *10*, 1657−1659. (g) Ellis, J. E.; Blackburn, D. W.; Yuen, P.; Jang, M. *J. Am. Chem. Soc.* **1993**, *115*, 11616−11617. (h) Müller, J.; Gaede, P. E.; Hirsch, C.; Qiao, K. *J. Organomet. Chem.* **1994**, *472*, 329−335.

(70) (a) Kunz, V.; Nowacki, W. *Helv. Chim. Acta* **1967**, *50*, 1052−1059. (b) Kündig, E. P.; Perret, C.; Spichiger, S.; Bernardinelli, G. *J. Organomet. Chem.* **1985**, *286*, 183−200. (c) Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A* **1968**, 1866−1870. (d) Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* **1970**, *92*, 716−717. (e) Dötz, K. H.; Dietz, R.; von Imhof, A.; Lorenz, H.; Huttner, G. *Chem. Ber.* **1976**, *109*, 2033−2038. (f) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654−1661. (g) Kündig, E. P.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1980**, 991−995. (h) Elschenbroich, C.; Möckel, R.; Massa, W.; Birkhahn, M.; Zenneck, U. *Chem. Ber.* **1982**, *115*, 334−345. (i) Hull, J. W., Jr.; Gladfelter, W. L. *Organometallics* **1982**, *1*, 264−274. (j) Kirss, R. U.; Treichel, P. M., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 853−855. (k) Kündig, E. P.; Desobry, V.; Grivet, C.; Rudolph, B.; Spichiger, S. *Organometallics* **1987**, *6*, 1173−1180. (l) Oprunenko, Yu F.; Malugina, S. G.; Ustynyuk, Yu A.; Ustynyuk, N. A.; Kravtsov, D. N. *J. Organomet. Chem.* **1988**, *338*, 357−368. (m) Müller, P.; Bernardinelli, G.; Jacquier, Y. *Helv. Chim. Acta* **1988**, *71*, 1328−1330. (n) Crocker, M.; Green, M.; Howard, J. A. K.; Norman, N. C.; Thomas, D. M. *J. Chem. Soc., Dalton Trans.* **1990**, 2299−2301. (o) Phan Do Thi, N.; Spichiger, S.; Paglia, P.; Bernardinelli, G.; Kündig, E. P.; Timms, P. L. *Helv. Chim. Acta* **1992**, *75*, 2593−2607. (p) Pertici, P.; Ballantini, V.; Salvadori, P.; Bennett, M. A. *Organometallics* **1995**, *14*, 2565−2569. (q) Zhang, S.; Shen, J. K.; Basolo, F.; Ju, T. D.; Lang, R. F.; Kiss, G.; Hoff, C. D. *Organometallics* **1994**, *13*, 3692−3702. (r) Sun, S.; Yeung, L. K.; Sweigart, D. A.; Lee, T.-Y.; Lee, S. S.; Chung, Y. K.; Switzer, S. R.; Pike, R. D. *Organometallics* **1995**, *14*, 2613−2615. (s) Freedman, D. A.; Magneson, D. J.; Mann, K. R. *Inorg. Chem.* **1995**, *34*, 2617−2624. (t) Bennett, M. A.; Neumann, H.; Thomas, M.; Wang, X.-q.; Pertici, P.; Salvadori, P.; Vitulli, G. *Organometallics* **1991**, *10*, 3237−3245. (u) McNair, A. M.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 2519−2527. (v) Pomije, M. K.; Kurth, C. J.; Ellis, J. E.; Barybin, M. V. *Organometallics* **1997**, *16*, 3582−3587.

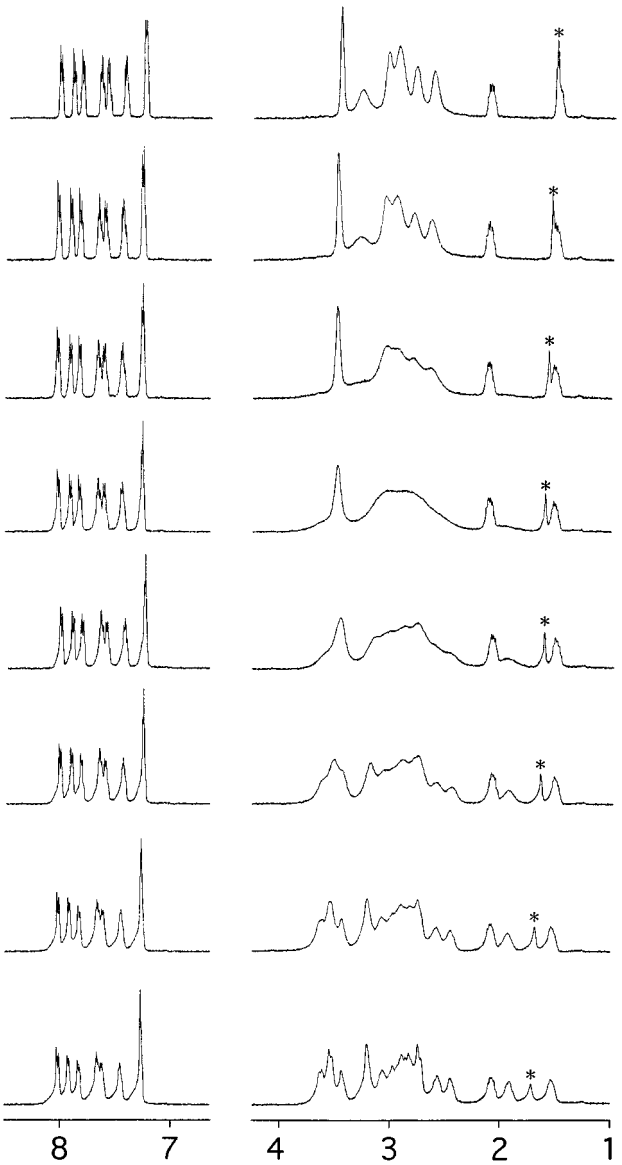


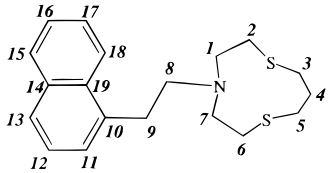
Figure 4. Proton spectra (500 MHz) for a $CDCl_3$ solution of **2** at 10 °C intervals from −20 °C on the bottom to +50 °C at the top. A water impurity is marked in each spectrum with an asterisk.

The Cu−C distances in **2** are comparable to those reported for the other Cu(I)−η^2-benzene complexes,[6−8,16] which range from 2.07 to 2.30 Å. Most Cu(I)−(RHC═CHR) and Cu(I)−π-Cp complexes also have Cu−C distances within that range,[35] averaged at 2.079(33) and 2.211(18) Å, respectively.[46] The binding in all of the copper−arene complexes is unsymmetrical, with differences in the pairs of Cu−C distances of 0.03 to 0.18 Å for the other structures[6−8,16] and almost 0.3 Å in **2** alone and 0.13 Å in **2** in **1&2**. At least some of the asymmetry in **2** alone can be attributed to packing forces. It is also reasonable to suggest that the linker arm may cause some of the unsymmetrical binding; however, it is not necessarily a contributing factor.

NMR Spectroscopic Studies on L and 1−3. In contrast to the ^{1}H NMR spectra of **L** and **1** at room temperature in $CDCl_3$ (and **3** in CD_3CN), which are reasonably sharp and resolved, the aliphatic region in the ^{1}H NMR spectrum of **2** was dominated by a broad peak for most of the aliphatic protons. When the solution of **2** was warmed or cooled, the resulting ^{1}H NMR spectra (Figure 4) revealed that **2** undergoes a fluxional process, with a coalescence temperature near 20 °C.

Table 3. ^{1}H NMR Assignments for the Ligand Aliphatic (Above) and Aromatic (Below) Resonances of **L** and **1**−**3**

assignment	**L**	**1**	**2** (50 °C)	**2** (−20 °C)	**3**
#1	2.87	3.05, 2.96	2.98, 2.89	3.46, 3.36	3.06, 3.21
#2	2.73	3.05	3.40, 3.21	2.82, 2.76	3.36, 3.21
#3	3.19	2.96, 2.70	2.74, 2.58	3.53, 2.99	3.06, 2.83
#4	1.90	2.22, 1.69	2.07, 1.49	2.04, 1.51	2.32, 1.80
#5	same as 3	same as 3	same as 3	3.46, 2.90	same as 3
#6	same as 2	same as 2	same as 2	2.57, 2.40	same as 2
#7	same as 1	same as 1	same as 1	2.79, 2.68	same as 1
#8	2.91	3.22	3.40	3.13	2.90
#9	3.30	3.33	2.89	2.68, 1.87	3.21

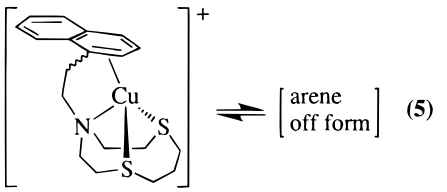


assignment	1-methyl-naphthalene	**L**	**1**	**2** (50 °C)	**2** (−20 °C)	**3**
#11	7.26	7.39	7.32	7.27	7.26	6.83
#12	7.33	7.39	7.42	7.44	7.45	7.28
#13	7.66	7.72	7.77	7.82	7.81	7.71
#15	7.80	7.86	7.92	7.90	7.90	7.85
#16	7.43	7.51	7.52	7.60	7.63	7.47
#17	7.47	7.51	7.58	7.66	7.63	7.40
#18	7.95	8.05	7.95	8.01	8.00	7.71

^{13}C NMR spectra were acquired for **L**, **1**, and **3** at room temperature and for **2** not only at ambient temperature (see Experimental Section) but also at the two easily accessible temperature extremes in $CDCl_3$, −20 and 50 °C. To help understand what was occurring with the variable temperature NMR experiments, we assigned the peaks in the ^{1}H and ^{13}C NMR spectra of **L**, **1**, and **3** at ambient temperature plus **2** at −20 and 50 °C (^{1}H NMR data, Table 3; ^{13}C NMR data and a discussion of how assignments were made, Supporting Information). The assignments for the two sides of the macrocylic ring (e.g., 1 and 7, 2 and 6, and 3 and 5) at −20 °C were made arbitrarily.

The spectra for complexes **1** and **3**, the ligand **L**, and **2** at 50 °C exhibited apparent mirror symmetry for the macrocyclic ring; for **2** at −20 °C, the two sides of the macrocyclic ring were no longer equivalent. A similar lack of symmetry was seen in the spectra for the amide precursor to **L** because of the restricted rotation of the amide bond. These NMR data for **2** at −20 °C provide unequivocal evidence for naphthalene binding in solution.[17] Since the two sides of the macrocyclic ring are clearly different, the presence of an asymmetrical group is indicated, and the only such moiety in the system is the naphthyl group. In addition, the linker methylene hydrogens 9 are diastereotopic, attributable to the restricted rotation of the naphthalene group, that can only be due to Cu(I)−arene binding. Also, the large chemical shift difference of only the two aromatic carbon peaks assigned to C(10) and C(11) in **2** versus **1**, **3**, and **L** is consistent with binding in solution as seen in the solid-state structure of **2**. The proton resonances of the aromatic group in **2** are relatively insensitive to binding. The fact that at 50 °C the two carbon resonances due to the bound carbon atoms C(10) and C(11) do not significantly shift toward those for free **L** suggests that the naphthalene-bound species is a major contributor to that spectrum.

From the VT-NMR data, an estimation for $\Delta G^{\ddagger}$ of 12−13 kcal/mol for the barrier associated with the fluxional process was made.[17] At 50 °C, a process in the solution spectra of **2** is occurring that regenerates the apparent symmetry relationship between the two sides of the macrocyclic ring and removes the resolvable diastereotopic character for the linker methylene group 9. The most logical process to suggest is simply fast interconversion of the two enantiomers of **2**. However, with that explanation, it is difficult to account for all of the features of the spectra at 50 °C, most notably that 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). Although temperature-induced changes in the ^{1}H NMR chemical shifts are to be expected, the magnitude seen herein (>0.5 ppm) is unusually large. Therefore, the best explanation is that there is another species contributing to the spectra. The most reasonable postulation for this other species is a complex with an unbound naphthyl group, which is a likely intermediate in the interconversion of the two enantiomers anyway. Indeed, the chemical shift of the protons 9 in the free **L** as well as in **1** both occur at higher values, 3.30 and 3.33, respectively, consistent with the direction of the shift seen for protons 9 for **2** at 50 °C. Thus, the best explanation for the fluxional process involves the exchange of the two enantiomers of **2** and an unbound complex (eq 5). Complex **2** must be a lower energy species than the unbound form and thus is favored at lower temperatures. However, the substantial shift of protons 9 at 50 °C suggests that at that temperature the concentration of the unbound complex may be significant.



(5)

2

The barrier measured for **2** contains as a major component the energy required to break the copper(I)−η^2-naphthalene bond. The 12−13 kcal/mol represents a weak bond at best, considering the extreme where the only contributor to this barrier is the bond dissociation energy. Thus, it is much lower than other measured bond energies, such as 37(2) kcal/mol for the Cr−CO bond in $Cr(CO)_6$, 25(2) kcal/mol for the Ni−CO bond in $Ni(CO)_4$, and 38(5) kcal/mol for the nickel−ethylene bond in $[CpNi(C_2H_4)]^+$.[71] Such a weak copper−arene interaction is consistent with the paucity of stable copper−arene complexes and the observation of solution binding only in a chelating system, such as provided by the unique ligand **L**.

The pendant naphthyl group definitely has an influence on the solution chemistry of **2**. For example, preliminary CV data for **2** contain an oxidation at about +1.0 V versus SCE in THF (the process is irreversible up to the 3 V/s probed in the experiment). This oxidation is a couple of hundred millivolts more positive that one would normally predict for a mixed S/N ligand on Cu(I).[72−75] The more positive oxidation potential for

(71) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science: Mill Valley, CA, 1987.
(72) Sakaguchi, U.; Addison, A. W. *J. Chem. Soc., Dalton Trans.* **1979**, 600−608.
(73) Dockal, E. R.; Jones, T. E.; Sokol, W. F.; Engerer, R. J.; Rorabacher, D. B.; Ochrymowycz, L. A. *J. Am. Chem. Soc.* **1976**, *98*, 4322−4324.
(74) Bernardo, M. M.; Heeg, M. J.; Schroeder, R. R.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1992**, *31*, 191−198.
(75) Haanstra, W. G.; Cabral, M. F.; de O. Cabral, J.; Driessen, W. L.; Reedijk, J. *Inorg. Chem.* **1992**, *31*, 3150−3151.

2 is likely an influence of arene binding stabilizing the Cu(I) ion and/or destabilizing the Cu(II) ion. Consistent with that observation, under the same experimental conditions, the addition of 4 equiv of CH_3CN to the solution shifts the oxidation to +0.6 V. It follows then that the stability of **2** to O_2 in solution is at least partially due to arene binding, causing **2** to be more difficult to oxidize. However, the CV data for **2** are fairly complex and still under investigation; at 1.0 V/s, the ill-defined oxidation at about +1.0 V must be carried out before the first reduction peak (at −0.2 V) appears. In addition, at this scan rate, there is a second reduction peak at −2.0 V that upon being traversed causes the appearance of four oxidation peaks. Slower scan rates cause even more complicated cyclic voltammograms.

Conclusions

The novel ligand **L** and three copper(I) complexes of that ligand (**1**−**3**) have been synthesized and characterized. The presence of the pendant naphthalene group has resulted in arene binding in the solid state, giving a rare arene complex of copper, which is also the first structurally characterized naphthalene and mononuclear copper−arene complex. In addition, the unique ligand allowed for the first unequivocal evidence for copper(I)−arene binding in solution. This binding clearly influences the solution chemistry, as seen in the enhanced stability of **2** toward oxygen. However, the upper limit for the bond dissociation energy of the Cu−η^2-arene bond in **2** of 12−13 kcal/mol, as determined by solution NMR spectroscopic measurements, indicates a weak Cu−arene bonding interaction. The weak binding of both the arene and acetonitrile ligands in this system has allowed their facile replacement with other ligands, such as with PPh_3 to form **3**.

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Supporting Information Available: Table of ^{13}C NMR data for **L** and complexes **1**−**3** and discussion of how assignments were made. X-ray crystallographic files in CIF format for the structure determinations of **1**−**3** and cocrystallized **1&2**. This information is available free of charge via the Internet at http://pubs.acs.org.

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