

Supplementary Material (ESI) for Chemical Communications
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Facile Assembly of a Cu₉ Amido Complex: A New Tripodal Ligand Design that Promotes Transition Metal Cluster Formation.

Alana L. Keen, Meghan Doster, Hua Han and Samuel A. Johnson*

Department of Chemistry & Biochemistry, University of Windsor, Windsor, ON, Canada N9B 3P4. Fax: 1 519 973 7098; Tel: 1 519 253 3000 (x3769); E-mail: sjohnson@uwindsor.ca

Supplementary Material

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Experimental

General Procedures. Unless otherwise stated, all manipulations were performed under an inert atmosphere of nitrogen using either standard Schlenk techniques or an MBraun glove box. Dry, oxygen-free solvents were employed throughout. Anhydrous pentane was purchased from Aldrich, sparged with dinitrogen, and passed through activated alumina under a positive pressure of nitrogen gas and further deoxygenated using Ridox catalyst columns.¹ Deuterated benzene was dried by heating at reflux with sodium/potassium alloy in a sealed vessel under partial pressure, then trap-to-trap distilled, and freeze-pump-thaw degassed three times. Deuterated toluene was purified in an analogous manner by heating at reflux over Na. NMR spectra were recorded on Bruker AMX (300 MHz) or Bruker AMX (500 MHz) spectrometer. All chemical shifts are reported in ppm, and all coupling constants are in Hz. For ¹⁹F{¹H} NMR spectra, trifluoroacetic acid was used as the external reference at 0.00 ppm. ¹H NMR spectra were referenced to residual protons (C₆D₅H, δ 7.15; C₇D₇H, δ 2.09) with respect to tetramethylsilane at δ 0.00. ³¹P{¹H} NMR spectra were referenced to external 85% H₃PO₄ at δ 0.0. ¹³C{¹H} spectra were referenced relative to solvent resonances (C₆D₆, δ 128.0; C₇D₈, δ 20.4). UV/Visible spectra were obtained on a Varian Carey 50

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spectrophotometer. Fluorescence spectra were obtained on a Varian Cary Eclipse fluorescence spectrophotometer. Quantum yields were obtained relative to 9,10-diphenylanthracene. Elemental analyses were performed by the Centre for Catalysis and Materials Research (CCMR), Windsor, Ontario, Canada. The compounds 1-bromo-2,4,6-trimethylbenzynes, tris(hydroxymethyl)phosphine magnesium, copper iodide, 1,4-dioxane, and 3,5-bis(trifluoromethyl)aniline were purchased from Aldrich. Mesitylcopper was prepared by the literature procedure.²

Synthesis of $[\text{P}(\text{CH}_2\text{NAr}^{\text{CF}_3})_3]\text{H}_3$ (1**).** To a solution of $\text{P}(\text{CH}_2\text{OH})_3$ (5.4g, 0.044 mol) in 60 ml of toluene, was added 3,5-bis(trifluoromethyl)aniline (50.0g, 0.22mol, 5 equiv.). The solution was heated to reflux for 45 minutes, during which time the water was collected and removed using a Dean Stark trap. The solution was then cooled to room temperature and the remaining solvent was removed under vacuum. Pentane (ca. 80 ml) was then added to dissolve any excess 3,5-bis(trifluoromethyl)aniline. The solution was filtered and **1** was collected as a fine white powder (24.1g, 80 %). ^1H NMR (C_6D_6 , 298 K, 300 MHz): δ 2.55 (dd $^3J_{\text{HH}} = 5.2$ Hz, $^2J_{\text{PH}} = 5.2$ Hz, 6H, CH_2), 3.13 (br, 3H, NH), 6.59 (s, 6H, *o*-H), 7.27 (s, 3H, *p*-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 125.8 MHz): δ 39.4 (d, $J_{\text{PC}} = 12.2$ Hz, PCH_2), 111.2 (s, *o*-C), 112.5 (s, *p*-C), 122.1 (s, *m*-C), 132.9 (q, $J = 32.9$ Hz, CF_3), 148.9 (d, $J = 5.5$ Hz, ipso-C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.5 MHz, 298 K): δ -32.6 (s). ^{19}F NMR (C_6D_6 , 298 K, 282.48 MHz): δ 14.71 (s). Anal. Calc'd for $\text{C}_{27}\text{H}_{18}\text{F}_{18}\text{N}_3\text{P}$: C, 42.82; H, 2.40; N, 5.55. Found: C, 43.00; H, 2.49; N, 5.41.

Synthesis of $[\text{P}(\text{CH}_2\text{NAr}^{\text{CF}_3})_3]_2\text{Cu}_9(\mu\text{-2,4,6-Me}_3\text{C}_6\text{H}_2)_3$ (2**):** To a stirred solution of CuMes (1.09g, 6 mmol, 4.5 equiv.) in 20 ml of toluene was added a solution of $[\text{P}(\text{CH}_2\text{NAr}^{\text{CF}_3})_3]\text{H}_3$ (1.00g, 1.3 mmol, 1 equiv.) in 20 ml of toluene. The solution was stirred for 5 minutes over which time the

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colour of the solution turned from pale yellow to orange. The solvent was then removed under vacuum. The residue was extracted with 60 ml of pentane and filtered through Celite. The volume of pentane was then reduced to 30 mL. $[\text{P}(\text{CH}_2\text{NAr}^{\text{CF}_3})_3]_2\text{Cu}_9(\mu\text{-}2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_3$ crystallized from pentane as a pale orange solid at $-40\text{ }^\circ\text{C}$ to in a 54% yield. Redissolving the solid into pentane at lesser concentrations allowed for isolation of X-ray quality crystals of the product. ^1H NMR (C_7D_8 , 243 K, 300 MHz) assigned using ^1H - ^1H COSY and NOESY and identified by the crystal structure atom labels: δ 1.75 (s, 3H, CH_3 , Mes-p-C71), 2.01 (s, 6H, CH_3 , Mes-p-C62), 2.20 (s, 6H, CH_3 , Mes-o-C63), 2.41 (s, 6H, CH_3 , Mes-o-C70), 2.63 (s, 6H, CH_3 , Mes-o-C61), 3.24 (overlapping, 4H, $\text{CH}_2\text{-H3a/H2a}$), 3.51 (d, 2H, $^2J_{\text{HH}} = 13.5\text{ Hz}$, $\text{CH}_2\text{-1a}$), 3.63 (d, 2H, $^2J_{\text{HH}} = 13.5\text{ Hz}$, $\text{CH}_2\text{-1b}$), 3.78 (d, 2H, $^2J_{\text{HH}} = 12.5\text{ Hz}$, $\text{CH}_2\text{-3b}$), 4.10 (d, 2H, $^2J_{\text{HH}} = 12.5\text{ Hz}$, $\text{CH}_2\text{-2b}$), 6.15 (s, 2H, terminal N-o-H), 6.24 (s, 2H, Mes-m-H59), 6.30 (s, 2H, Mes-m-H66), 6.56 (s, 2H, Mes-m-H57), 6.90 (s, 2H, terminal N-o-H), 7.26 and 7.27 (s, 3H total, bridging N-p-H and terminal N-p-H), 7.30 (overlapping s, 8H total, bridging N-o-H), 7.44 (s, 2H, bridging N-p-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 300 K, 121.54 MHz): 9.23(s). ^{19}F NMR (C_7D_8 , 228 K, 282.48 MHz): δ 14.78 (s, 6F), 14.80 (s, 6F), 15.20 (br s, 12 F, non-terminal aryl CF_3), 15.30 (s, 6F), 15.42 (s, 6F). Anal. Calc'd for $\text{C}_{81}\text{H}_{66}\text{Cu}_9\text{F}_{36}\text{N}_6\text{P}_2$: C, 39.85; H, 2.73; N, 3.44. Found: C, 39.98; H, 2.50; N, 3.40. UV/VIS: $\epsilon=33980.3\text{ L mol}^{-1}\text{ cm}^{-1}$. $\lambda_{\text{max}} = 373\text{ nm}$. $\lambda_{\text{emit}} = 418\text{ nm}$.

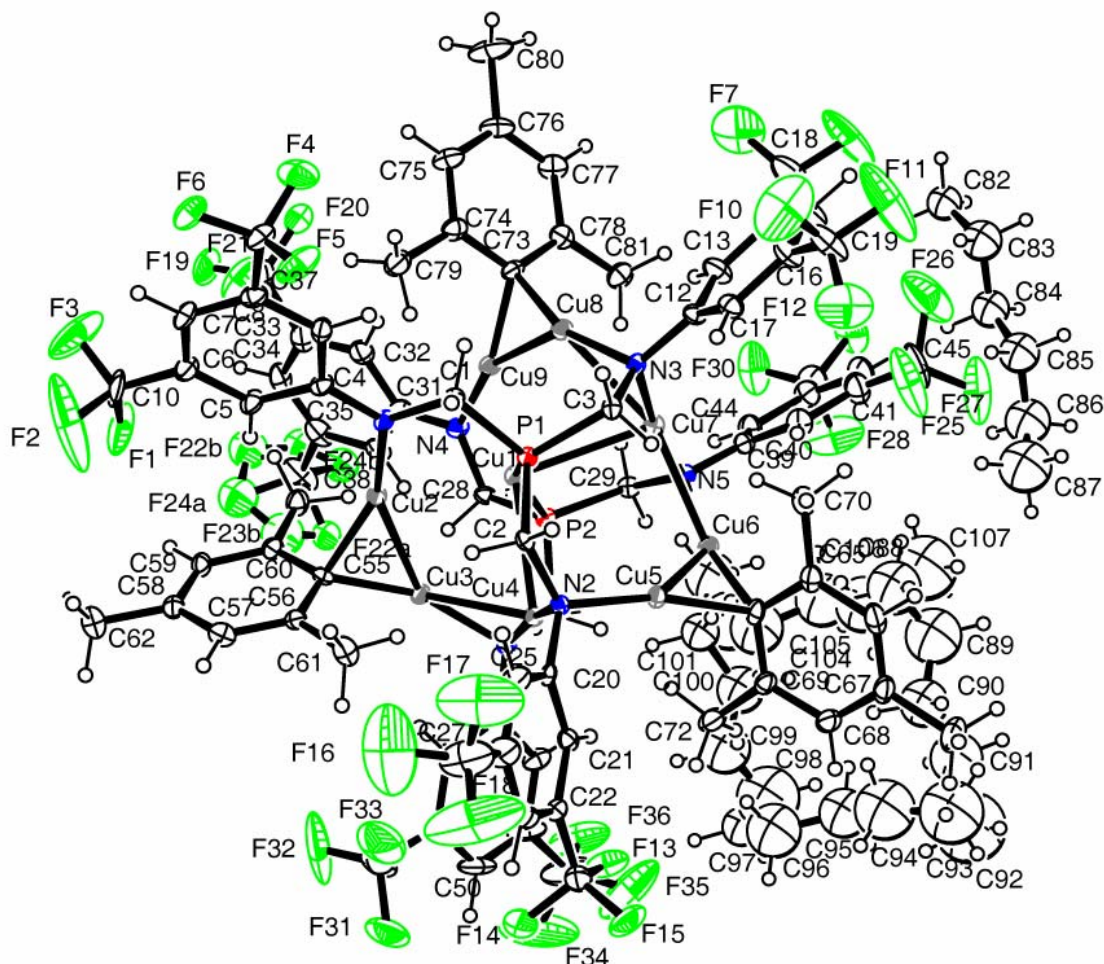
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X-ray Crystallography. The X-ray structure of **2** was obtained at low temperature, with the crystal covered in Paratone and placed rapidly into the cold N₂ stream of the Kryo-Flex low-temperature device. The crystals were prone to rapid desolvation, and shatter at room temperature as soon as they are removed from pentane. The data were collected using the SMART³ software on a Bruker APEX CCD diffractometer using a graphite monochromator with Mo K α radiation ($\lambda = 0.71073$ Å). A hemisphere of data was collected using a counting time of 30 s per frame. Details of crystal data, data collection, and structure refinement are listed in Table 1, atomic coordinates are provided in Table 2, selected metrical parameters are compiled in Table 3, and anisotropic displacement parameters are in Table 4. Data reductions were performed using the SAINT⁴ software, and the data were corrected for absorption using SADABS.⁵ The structure was solved by direct methods using SIR97⁶ and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms, except for disordered fragments, using SHELXL-97⁷ and the WinGX⁸ software package, and thermal ellipsoid plots were produced using ORTEP32.⁹ The structure of **2** features one cocrystallized pentane molecules whose terminal carbon were disordered to give the appearance of a six carbon chain. The terminal CH₃ groups (C82 and C87) were given half-site occupancy; however, a hydrogen atom is omitted in this treatment of the disorder. Thus 4 hydrogen atoms per unit cell are absent from the model. The two remaining pentane molecules were modeled as disordered over two sites with 50% occupancy, to give the appearance of a square (C88-C92, C93-C97, C98-C102, C103-C107). All the disordered pentane molecules were forced to have equivalent C-C distances and the atoms were treated anisotropically. The CF₃ groups of the ligand fragment suffer from varying degrees of rotational disorder, despite the low temperature the data set was collected at. One was treated as disordered over two sites, with 50 % occupancy of each site (F22a/b, F23a/b and F24a/b). This disordered CF₃ group was

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constrained to have equivalent C-F distances, and the fluorines were treated isotropically. The largest residual electron density (1.27) is associated with the two-fold disordered CF₃ group and is within 0.89 Å of F22a and 1.369 Å of C38. Some of the remaining CF₃ groups feature some large prolate anisotropic thermal ellipsoids indicative of rotational disorder; however, attempts to find more effective models for their disorder proved futile.

Figure 1. Fully labelled ORTEP Depiction of **2**.



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