Facile assembly of a Cu_9 amido complex: a new tripodal ligand design that promotes transition metal cluster formation†

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A tripodal amido ligand with a central non-chelating phosphorus donor allows for the facile assembly of a pentane soluble organometallic copper cluster with a central copper atom surrounded by a nonplanar chain of eight copper atoms and two terminal amido–copper bonds.

The design of ligands that support transition metal clusters or organized assemblies of metals has multiple goals. Such complexes can exhibit novel reactivities based on cooperativity[1] or electron transfer between metal centres as well as unique physical properties such as luminescence[2–4] or magnetism[5] that result from interactions between metal centres. Unfortunately, the design of ligands that can support clusters or assemblies of metals with a variety of transition metals is rarely straightforward.

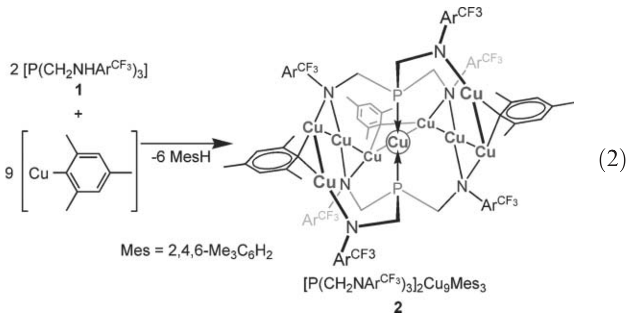
Our approach to design of such a ligand was to incorporate common donor ligands, such as amide and phosphine donors, into a ligand framework such that they could not chelate to the same metal centre. The reaction of $P(CH_2OH)_3$ with an excess of 3,5-bis(trifluoromethyl)aniline leads to the formation of $P(CH_2NHAr^{CF_3})_3$ as a spectroscopically pure white powder in an 80% yield, as shown in eqn. 1. Related compounds have previously been tested as flame retardants, but never as ligand precursors.[6]

$$P(CH_2OH)_3 + 3\ H_2NAr^{CF_3} \xrightarrow[-\ 3\ H_2O]{\text{toluene}} \underset{\mathbf{1}}{[P(CH_2NAr^{CF_3})_3]H_3} \qquad (1)$$

$$Ar^{CF_3} = C_6H_3\text{-}3,5\text{-}(CF_3)_2$$

With high-valent electropositive early transition metals, chelation by the amido donors is anticipated. In this bonding mode the phosphine lone pair is directed away from the metal chelated by the amido donors, and is available to bind a second metal; related tripodal ligands are known but lack this additional phosphine donor, and in all related amido–phosphino ligands chelation by both the amido and phosphine ligands is typically preferred.[7–14] In the alternate conformation shown as mode **A** in Fig. 1, the phosphine and amide donors all bind in the same direction. Chelation to a single metal is impossible, because the donor orbitals are nearly parallel. Such a conformation could be stabilized by, or possibly encourage, metal–metal interactions. Attachment of the phosphine donors of more than one $[P(CH_2NAr^{CF_3})_3]$ moiety to a single metal centre could potentially be used as a tool to generate larger polymetallic complexes, as shown in bonding mode **B** in Fig. 1. We decided to examine copper complexes of **1** to determine if polynuclear complexes of the low-valent late transition metals would be accessible that might exhibit interesting photophysical properties and reactivities.[15]

The reaction of 1 equiv of $[P(CH_2NAr^{CF_3})_3]H_3$ with 1 equiv of mesitylcopper was monitored at low temperature by $^{31}P\{^1H\}$ NMR spectroscopy; the major product exhibited a single phosphine environment, but the complex decomposed in solution, even when stored at −40 °C, and could not be isolated. A second small signal in the $^{31}P\{^1H\}$ NMR spectrum indicated the presence of a minor product, which was more thermally stable. Optimization of this reaction demonstrated that the production of the more thermally stable complex required 2 equiv of $P(CH_2NHAr^{CF_3})_3$ and 9 equiv of mesitylcopper, as shown in eqn. 2. The resultant solid was moderately soluble in pentane, and recrystallization at −40 °C provided $[P(CH_2NAr^{CF_3})_3]_2Cu_9(\mu\text{-}2,4,6\text{-}Me_3C_6H_2)_3$ (**2**) as bright orange crystals in a 54% yield.‡ Complex **2** is stable as a solid or in solution at −40 °C for extended periods of time. However, in solution at room temperature, the complex decomposed over the course of days, which resulted in a colour change of the solution from bright orange to dark brown.



(2)

The solid-state structure of **2** was determined by X-ray crystallography, and a simplified ORTEP depiction is shown in Fig. 2.§ The structure demonstrates that two ligand fragments encapsulate a Cu_9 core. At the centre of the cluster, Cu(1) is bound

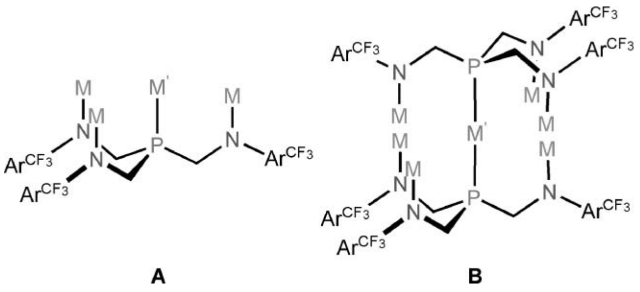


Fig. 1 Two possible binding modes of the $P(CH_2NAr^{CF_3})_3$ ligand that could lead to polynuclear complexes.

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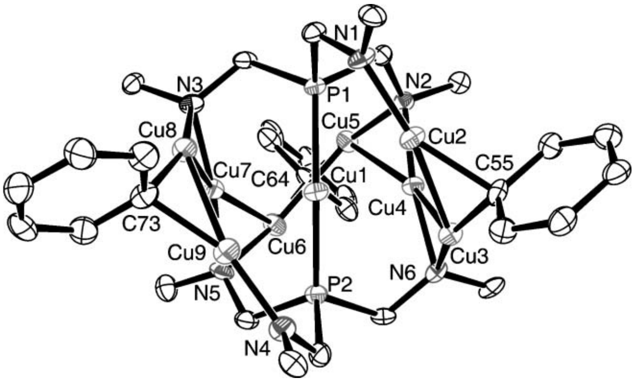

Fig. 2 ORTEP depiction of the solid-state structure of **2**, with 50% probability ellipsoids. Hydrogen atoms are omitted. Only the ipso carbons of the 3,5-bis(trifluoromethyl)phenyl substituents are shown. The 1,3,5 methyl substituents of the mesityl groups and short contacts between the central and outer copper atoms are omitted for clarity.

to the phosphine donors of 2 $P(CH_2NAr^{CF_3})_3$ moieties, and no anionic ligands. The remaining 8 Cu atoms nearly completely encircle Cu(1) and are bound to the amido donors of the ligands held together by Cu(1) and three mesityl groups. These 8 Cu atoms at the periphery of the complex are bonded in a nonplanar zig-zag chain *via* d^{10}–d^{10} bonding interactions,[16–20] with Cu–Cu bond distances ranging from 2.4657(13) to 2.5125(13) Å. If the central Cu is considered as Cu(I), the peripheral Cu_8 fragment must bear a delocalized negative charge. The Cu–Cu–Cu angles in the zig-zig chain tend to be close to either 90° or 180°, with Cu(2)–Cu(3)–Cu(4), Cu(3)–Cu(4)–Cu(5) and Cu(4)–Cu(5)–Cu(6) angles of 94.65(4), 161.53(5), and 94.38(4)° respectively. The complex has no crystallographic symmetry, but approximate C_2 symmetry. The N(1)–Cu(2) and the N(4)–Cu(9) bonds are rare examples of terminal amido–copper bonds.[21,22] The terminal-amido–ipso-carbon bonds are slightly shorter than the related bridging-amido–ipso-carbon bonds; the terminal-amido–ipso-carbon N(1)–C(4) and N(4)–C(31) distances are 1.372(9) and 1.385(9) Å, respectively, whereas the bridging-amido–ipso-carbon bonds are on average 0.043 Å longer. Such shortening of terminal-amido–ipso-carbon bonds has been observed before in electron-rich amido complexes, including a related Cu complex with a slightly shorter N–C bond length of 1.354(9) Å.[21] This shortened bond length can be attributed to increased delocalization of the amido lone pair into the aromatic ring, due to its destabilization *via* antibonding interactions with occupied metal d-orbitals.[23] Such destabilizing interactions typically render late transition metal amides highly nucleophilic and basic.[24–26] In complex **2**, the π-systems of the aromatic rings associated with the terminal amides are aligned appropriately to overlap with the lone pair of electrons on the terminal-amido moieties.

The Cu–Cu distances are summarized in Fig. 3. Aside from coordination to the two phosphine donors, the central Cu(1) appears to have relatively short interaction with 6 of the 8 Cu centres that encircle it (all except Cu(5) and Cu(6)); however, all of these interactions are approximately 10 to 15% longer than the Cu–Cu interactions in the 8-membered chain. For clarity these short contacts are not drawn in the ORTEP depiction in Fig. 2. The Cu(1)–Cu(5) and Cu(1)–Cu(6) distances of 3.8634(12) and 3.8667(12) Å preclude any significant interactions between these pairs of metals.

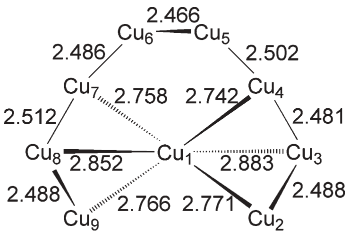

Fig. 3 Summary of Cu–Cu distances in **2**. Bond lengths shown in Å; standard deviations are 0.0012–0.0013 Å.

Low-temperature ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectroscopy in toluene verifies that the C_2 structure observed in the solid-state is maintained in solution. A combination of 1-D homonuclear decoupling experiments at 273 K, and 2-D ^1H–^1H COSY and EXSY/NOESY NMR data obtained at 228 K was used to fully assign the ^1H NMR resonances; surprisingly, long-range couplings between aromatic protons were readily observed in the low temperature ^1H–^1H COSY spectrum, whereas the 2-bond couplings of the ligand methylene protons were more easily assigned with the aid of 1-D homonuclear decoupling experiments.

Two fluxional processes were observed by variable-temperature NMR spectroscopy over the temperature range of 213–303 K. One of the ligand 3,5-$(CF_3)_2C_6H_3$ substituents experiences a moderate barrier to rotation about the N–C bond, as observed by coalescence of a pair of ortho protons in the ^1H NMR spectra and a pair of CF_3 environments in the ^{19}F NMR spectra. The activation energy for this barrier to rotation was calculated to be 24 kJ/mol; we assign this as the 3,5-$(CF_3)_2C_6H_3$ substituent on the terminal amide, which should have slight N–C_{ipso} double bond character due to delocalization of its lone pair onto the aromatic ring.

The second fluxional process was observed near room temperature, where all of the resonances in the ^1H NMR of **2** were exchange broadened. The complex appears to be achieving higher apparent symmetry. At higher temperatures the rate of decomposition of **2** becomes significant, which prevented a fast-exchange spectrum from being obtained. The room-temperature ^1H NMR spectrum was not affected by the concentration of **2**, which is evidence against an intermolecular exchange process. Unfortunately, at 228 K, the EXSY/NOESY spectrum provided little information regarding chemical exchange, because the cross peaks due to nuclear Overhauser effects had the same phase as the exchange cross peaks, as expected for a sizeable molecule with a large rotational correlation time. ^1H spin-saturation transfer experiments performed at 273 K demonstrated that all ligand arms are exchanged in the fluxional process responsible for the broadening of the resonances in the ^1H NMR spectrum at room temperature. The mesityl substituent environments are also exchanged. Such a fluxional process appears to require a breaking of some of the Cu–Cu bonding interactions; however, inadequate evidence is available from the ^1H NMR data to provide a detailed mechanism. A dissociative mechanism in which mesityl copper is lost from **2** was ruled out by adding mesitylcopper to a solution of **2**. The lack of line broadening in the mesitylcopper resonances of the room temperature ^1H NMR, combined with the results of ^1H NMR spin-saturation transfer experiments, indicates that any chemical exchange process involving mesitylcopper is too slow to account for the fluxional behaviour observed near room temperature.

The absorption spectrum for **1** displays an absorbance (λ_{max}) at 373 nm, and the emission spectrum displays a maximum at 418 nm. The luminescence occurred with a quantum yield (Φ) of 0.27 in toluene at 298 K, relative to 9,10-diphenylanthracene (Φ = 0.90). This value is slightly lower than the recently reported copper amide dimer of Peters.[15] This reduced luminescence is not surprising, considering the increased flexibility of **2**, and the relatively lesser steric bulk of the supporting ligand.

Although a few examples of amido complexes of Cu(I) are known,[27–35] the ease by which **2** assembles, and its structural integrity in solution are remarkable. Most copper amido complexes adopt dinuclear, trinuclear or tetranuclear structures. Closely related tripodal silane ligands, which lack the central phosphine in **1** have also been observed to form anticipated trinuclear copper complexes with bridging amido ligands.[36] Usually, bulky ligands and careful synthetic methodology are required to synthesize terminal copper–amido bonds.[21] We are currently investigating the reactivity of this complex, to determine if the terminal amido ligands display the strong nucleophilicity and basicity common to electron-rich late-transition metals, and the ability of this ligand to provide polymetallic complexes with other transition metals.

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Notes and references

‡ Characterization data for $[P(CH_2NAr^{CF_3})_3]H_3$ (**1**): ^{1}H NMR (C_6D_6, 298 K, 300 MHz): δ 2.55 (dd, $^3J_{HH}$ = 5.2 Hz, $^2J_{PH}$ = 5.2 Hz, 6H, C*H*$_2$), 3.13 (br, 3H, N*H*), 6.59 (s, 6H, *o-H*), 7.27 (s, 3H, *p-H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 125.8 MHz): δ 39.4 (d, J_{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). $^{31}P\{^1H\}$ 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 $C_{27}H_{18}F_{18}N_3P$: C, 42.82; H, 2.40; N, 5.55. Found: C, 43.00; H, 2.49; N, 5.41.

Characterization data for $[P(CH_2NAr^{CF_3})_3]_2Cu_9(\mu\text{-}2,4,6\text{-}Me_3C_6H_2)_3$ (**2**): ^{1}H 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, C*H*$_3$, Mes-*p*-C71), 2.01 (s, 6H, C*H*$_3$, Mes-*p*-C62), 2.20 (s, 6H, C*H*$_3$, Mes-*o*-C63), 2.41 (s, 6H, C*H*$_3$, Mes-*o*-C70), 2.63 (s, 6H, C*H*$_3$, Mes-*o*-C61), 3.24 (overlapping, 4H, C*H*$_2$-H3a/H2a), 3.51 (d, 2H, $^2J_{HH}$ = 13.5 Hz, C*H*$_2$-1a), 3.63 (d, 2H, $^2J_{HH}$ = 13.5 Hz, C*H*$_2$-1b), 3.78 (d, 2H, $^2J_{HH}$ = 12.5 Hz, C*H*$_2$-3b), 4.10 (d, 2H, $^2J_{HH}$ = 12.5 Hz, C*H*$_2$-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). $^{31}P\{^1H\}$ 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 C*F*$_3$), 15.30 (s, 6F), 15.42 (s, 6F). Anal. Calc'd for $C_{81}H_{66}Cu_9F_{36}N_6P_2$: C, 39.85; H, 2.73; N, 3.44. Found: C, 39.98; H, 2.50; N, 3.40. UV/VIS: ε = 33980 L mol^{-1} cm^{-1}. λ_{max} = 373 nm. λ_{emit} = 418 nm.

§ A suitable single crystal of **2** was covered with paratone and mounted in the 143 K N_2 stream of a Bruker AXS P4/SMART 1000 CCD diffractometer equipped with a Mo Kα radiation (λ = 0.71073 Å) source. The structure was solved using full matrix least squares on F^2. Crystal data for **2**: $C_{96}H_{99}Cu_9F_{36}N_6P_2$, monoclinic, *a* = 20.5700(30), *b* = 21.1510(30), *c* = 28.4010(30) Å, α = 90.000(0)°, β = 119.442(8)°, γ = 90.000(0)°, *V* = 10761(2) Å^3, *Z* = 4, D_{calcd} = 1.638 g cm^{-3}. A total of 101105 reflections were collected of which 18926 were unique; wR_2 = 0.167, *R* = 0.075. CCDC 292735. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517531c

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