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COMMUNICATION

Complexes of Cu(I) supported by a tris(ketimine) tripod⁺

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Arylation of tris(2-benzylnitrile)amine with PhLi, followed by aqueous work-up, results in the formation of a tripodal tris(ketimine) scaffold, $N(ArCNHPh)_3$. $N(ArCNHPh)_3$ readily coordinates a number of Cu^I salts, generating complexes that exhibit trigonal pyramidal geometries in the solid-state.

Tridentate and tetradentate ligands with C_3 symmetry have received a great deal of attention in the last two decades.¹⁻³ One attribute of these ligands is the ability to enforce a single site of reactivity when coordinated to a metal centre, a desirable property for small molecule activation and atom transfer chemistry. Notable examples of C_3 enforcing scaffolds include HIPTN₃N,⁴ (SiP^{iPr}₃),^{5,6} [B(PhP^{iPr}₂)₃],^{7,8} [PhBP^{iPr}₃],^{9,10} [PhB(^{*t*}BuIm)₃];^{11,12} and [TIMEN^R].¹³ The first example, HIPTN₃N supports a Mo complex capable of catalytic N_2 reduction; (SiP^{iPr}_3) , $[B(PhP^{iPr}_{2})_{3}]$, $[PhBP^{iPr}_{3}]$, and $[PhB('BuIm)_{3}]$ support Fe complexes relevant to small molecule activation and atom transfer reactions; and [TIMEN^R] has been shown to support Cu^{I,13,14} Tripods have also been utilized to model bioinorganic copper chemistry. For example, the ethyl and methyl linked (tris-pyridine)amine ligands TEPA $(N[CH_2CH_2-2-py]_3)^{15-18}$ and TMPA $(N[CH_2-2-py]_3)^{15-18}$ $py]_3)^{19,20}$ have been utilized to form Cu^I model complexes of the multicopper enzymes tyrosinase²¹ and hemocyanin.²²

Within the broader class of tripodal ligands, those based upon tris(arylamine) functionality are particularly attractive as they are readily synthesised and are highly modular, allowing for the construction of a wide variety of derivatives. These scaffolds have a demonstrated ability to support a number of transition metal ions, including Ni^{II},²³ Mn^{II},²⁴ Fe,²⁵ Cu^I,²⁵ Co^{II},²⁶ and Cr^{III},²⁴ Notably, tripods constructed upon the tris(arylamine) framework exhibit a more rigid structure than their alkylamine counterparts.^{23,27} Furthermore, chelating *o*-arylamine units have the potential to act as redox active ligands.^{28–30}

Our laboratory has previously reported the isolation of several homoleptic first row transition metal complexes supported by the bis-*tert*-butylketimide anion. The isolation of $M^{IV}(N = C'Bu_2)_4$ (M = Mn, Fe) demonstrates the ability of the ketimide ligand to support high valent transition metals in unusual geometries.^{31,32} We reasoned that a multidentate ketimide ligand would also be a

strong σ and π donor, facilitating the stabilisation of high valencies and promoting novel reactivity. Herein we report the synthesis of a tridentate tris(ketimine) tripod, the coordination chemistry of the neutral tripod with a series of Cu^I salts, and the electrochemistry of the tris(ketimine) tripod and its CuOTf adduct.

Arylation of tris(2-benzylnitrile)amine³³ with 3 equiv of PhLi results in the formation of an orange suspension (Scheme 1). Characterisation of the presumptive tris(lithium) ketimide proved elusive due to its sparse solubility in diethyl ether, THF, and pyridine. Consequently, methanolysis was utilized to access the protio tris(ketimine) scaffold N(ArCNHPh)₃ (1) in 80% yield. This material crystallizes in the monoclinic space group C2/c from a concentrated solution of ethyl acetate (Fig. S1†). Its solid-state structure reveals C–N bond distances of 1.2748(18)–1.2788(19) Å for the three ketimine functionalities, consistent with double bond character, while the apical nitrogen lies 2.6576 (17) Å out of the plane defined by the three ketimine nitrogens. Finally, the ¹H NMR spectrum of 1 in CD₂Cl₂ reveals three-fold symmetry in solution (Fig. S6†), and is consistent with the solid-state structure.

Characterization of a series of Cu^I halide and pseudohalide coordination complexes was undertaken in order to provide proof of concept that the tris(ketimine) scaffold could coordinate a metal ion. Thus, addition of 1 equiv of CuCl to a stirring THF solution of N(ArCNHPh)₃ results in the immediate formation of an orange solution, which upon removal of solvent in vacuo vields an orange solid (Scheme 2). The ¹H NMR spectrum of this material (THF-d₈) reveals the presence of a new diamagnetic complex, in addition to free N(ArCNHPh)₃ in a 1:1 ratio (Fig. S8[†]). Addition of 2 equiv of CuCl to a CH₂Cl₂ solution of 1 yields the same orange solid, according to ¹H NMR spectroscopy, along with complete consumption of the free scaffold (Fig. S9[†]). Surprisingly, single crystal X-ray diffraction of the orange material reveals the formation of a cation-anion pair, namely [N(ArCNHPh)₃Cu][CuCl₂]·C₇H₈ (2·C₇H₈) (Fig. 1). In the solid state, the [CuCl₂]⁻ anion lies in close contact with the [N(ArCNHPh)₃Cu]⁺ cation. However, the Cu1–Cu2 distance is 2.8847(8) Å, greater than the sum of the covalent radii.³⁴ The



Scheme 1 Synthesis of the tris(ketimine) scaffold 1.

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[†]Electronic supplementary information (ESI) available: Experimental details. CIF files for **1**, **2**, **3**, **4**, and **5**. CCDC 863473–863477. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30101f



Scheme 2 Synthesis of Cu^I complexes supported by a tris(ketimine) tripod.



Fig. 1 Solid-state structure of $[N(ArCNHPh)_3Cu][CuCl_2] \cdot C_7H_8$ (2·C₇H₈) Hydrogen atoms and toluene solvate omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1–N7 = 1.9697(14), Cu1– N27 = 1.9302(13), Cu1–N47 = 1.9252(13), Cu1–N1 = 2.6341(14), Cu2–Cl1 = 2.0999(6), Cu2–Cl2 = 2.0993(6), Cu1–Cu2 = 2.8847(8), Cu1–N1 = 2.6341(14), N7–Cu1–N27 = 109.61(5), N7–Cu1–N47 = 115.05(6), N27–Cu1–N47 = 129.00(5).

Cu1 nucleus exhibits a distorted trigonal pyramidal coordination environment with N–Cu–N bond angles of 109.61(5)°, 115.05 (6)°, and 129.00(5)°. The Cu1–N_{eq} distances range from 1.9252 (13) Å–1.9697(14) Å, consistent with previously reported Cu¹–N(H)==CR₂ bond lengths.³⁵ In comparison, the Cu–N_{eq} bond distances of [(TEPA)Cu]BPh₄ ¹⁵ (2.022(5) Å–2.012(5) Å) are slightly longer. Additionally, Cu1 sits 0.2814(7) Å above the plane defined by the three ketimine nitrogens, while the Cu–N_{axial} bond distance is long (2.6341(14) Å). Interestingly, the apical nitrogen lies 2.3519(15) Å below the plane defined by the same three nitrogens, a contraction of approximately 0.30 Å *versus* the free ligand. This contraction results from a twisting of the diphenylketimine arms away from the Cu–N_{axial} vector, which is apparently required to accommodate the Cu ion.

Addition of 1 equiv of CuI to a stirring CD_2Cl_2 solution of 1 also results in the formation of a cation–anion pair, namely $[N(ArCNHPh)_3Cu]_2[CuI_3]$ (3) (Scheme 2), (see ESI[†] for full characterization details). Thus, to circumvent the unwanted formation of a multi-metallic copper complex, the reaction of 1 with $[Cu(MeCN)_4][OTf]$ was explored, with the hope that the weaker Lewis base $[OTf]^-$ would be less amenable to copper halide counterion formation. Addition of 1 equiv of $[Cu(MeCN)_4][OTf]$ to a stirring solution of $N(ArCNHPh)_3$ in CH_2Cl_2 results in formation of $[N(ArCNHPh)_3Cu][OTf]$ (4), which is isolable as a orange solid in 80% yield. Its ¹H NMR spectrum in C_6D_6 is consistent with a 3-fold symmetric structure,



Fig. 2 Solid-state structure of $[N(ArCNHPh)_3Cu][OTf]$ (4). Hydrogen atoms and CH_2Cl_2 solvates omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1-N7 = 1.9736(17), Cu1-N27 = 1.9427(17), Cu1-N47 = 1.9343(17), Cu1-N1 = 2.5876(15), Cu1-O1 = 2.5554(16), N7-Cu1-N27 = 113.35(7), N7-Cu1-N47 = 118.43(7), N27-Cu1-N47 = 123.66(7).

while ¹⁹F NMR spectroscopy reveals a single resonance at -78.80 ppm (Fig. S16†). Single crystal X-ray diffraction reveals a complex with the formulation [N(ArCNHPh)₃Cu]-[OTf]·1.5CH₂Cl₂ (**4**·1.5CH₂Cl₂) (Fig. 2). The Cu1 nucleus in **4** exhibits a distorted trigonal pyramidal coordination environment with N–Cu–N bond angles of 113.35(7)°, 118.43(7)°, and 123.66(7)°. The Cu1–N_{eq} distances range from 1.9343(17) Å–1.9736(17) Å, while the Cu1–N_{axial} distance is 2.5867(15) Å, consistent with those found in **2** and **3**. Cu1 resides 0.2419(9) Å out of the plane defined by the three ketimine nitrogens, while the Cu1–O1 bond distance is 2.5554(16) Å, indicating a weakly coordinating [OTf]⁻ anion.

Similarly, addition of 1 equiv of $[Cu(MeCN)_4][PF_6]$ to a stirring solution of 1 in CH₂Cl₂ results in the immediate formation of $[N(ArCNHPh)_3Cu][PF_6]$ (5), which is isolable as an orange solid in good yield. Its ¹H NMR spectrum is similar to that of 4, while its ¹⁹F NMR spectrum reveals a doublet centered at -73.45 ppm, consistent with the presence of the $[PF_6]^-$ anion (Fig. S19†). Single crystal X-ray diffraction reveals a complex with the formulation $[N(ArCNHPh)_3Cu][PF_6]\cdot 4CH_2Cl_2$ (5·4CH₂Cl₂) (Fig. S5†). Unlike complex 4, there is no interaction between Cu1 and the counterion in 5. Accordingly, the Cu1 nucleus exhibits a distorted trigonal planar coordination environment, and its Cu1–N_{eq} distances range from 1.923(2) Å–1.966(2) Å.

To evaluate the electron donating ability of the tris(ketimine) scaffold we attempted to prepare a Cu(1)-carbonyl complex containing this ligand.^{25,36} Bubbling CO through a CH₂Cl₂ solution of **5** results in the appearance of a v_{CO} stretch at 2086 cm⁻¹, assignable to [N(ArCNHPh)₃CuCO][PF₆] (**6**) (Fig. S23†). This value is similar to that reported for the tris(arylamine) Cu(1) complex [(N(*o*-PhNMe₂)₃)CuCO][PF₆] ($v_{CO} = 2088 \text{ cm}^{-1}$, nujol),²⁵ but higher than those reported for [(Me₆tren)CuCO]-[PF₆] ($v_{CO} = 2077 \text{ cm}^{-1}$, nujol).³⁷ Therefore, it appears that **1** is not as

donating as the Me₆tren and TMPA ligands, a trend which can be attributed to the rigidity of the tris(arylamine) backbone.²⁵ However, this comparison is complicated by the ability of Me₆tren and TMPA to undergo $\kappa^4 - \kappa^3$ isomerizations,^{25,37} which results in large changes to the observed CO stretch. Attempts to isolate **6** have proven difficult, as the coordinated CO ligand is readily removed by applying a vacuum to the CH₂Cl₂ solution (Fig. S23†).

Finally, the solution phase redox properties of 1 and 4 were explored by cyclic voltammetry. The cyclic voltammogram of 1 (0.25 V s^{-1}) reveals two irreversible oxidation features at 0.83 V and 1.03 V (vs. Fc^+/Fc). These remain irreversible even at elevated scan rates (1.0 V s⁻¹) and presumably document the oxidation of 1, which consistent with the proposed redox activity of the tris(arylamine) framework.^{28–30} Their irreversibility suggests that the arylamine skeleton in 1 is unstable and rearranges upon oxidation. Consistent with this hypothesis, a new feature appears in the CV trace of 1 at -1.35 V after first scanning to positive potentials (past the two oxidation features). This new feature is irreversible, even at elevated scan rates (1.0 V s^{-1}) . The cyclic voltammogram of 4 (0.25 V s^{-1}) reveals a quasi-reversible oxidation feature centered at 0.28 V (vs. Fc⁺-Fc), assignable to the Cu^I-Cu^{II} redox couple (Fig. S21[†]). We also probed the reactivity of 4 with O₂. Upon addition of O₂ the resonances associated with 4 were broadened, however no new products were observed suggesting that no reaction occurred (Fig. S25⁺).

In summary, we have synthesized a C_3 symmetric tris(ketimine) tripod, N(ArCNHPh)₃, by arylation of tris(2-benzylnitrile)amine. This ligand readily coordinates to the Cu¹ ion, demonstrating that the rigid tripod architecture is able to accommodate a metal ion. Efforts towards the installation of other transition metals ions into the neutral binding pocket of **1** are ongoing. We are also attempting the synthesis of tris(ketimide) metal complexes by the deprotonation of **1** in the presence of metal salts.

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