Binuclear β -Diketimate Complexes of Copper(I)

Andreas Phanopoulos,^a Alice H. M. Leung,^a Shuhui Yow,^a David Palomas,^a Andrew J. P. White,^a

Klaus Hellgardt,^b Andrew Horton,^c and Mark R. Crimmin^{*a}

^aDepartment of Chemistry, Imperial College London, South Kensington, London, SW7 2AZ, U.K.

^bDepartment of Chemical Engineering, Imperial College London, South Kensington, London, SW7 2AZ, U.K.

^cPTI/DX Emerging Technologies, Shell Global Solutions International B.V, P.O. Box 38000, 1030 BN Amsterdam, The Netherlands

ABSTRACT: The reaction of a series of dinucleating bis(β -diketimate) pro-ligands with mesitylcopper in the presence and absence of mono and diphosphines has allowed the isolation of a new series of dicopper(I) complexes. Inclusion of trans-1,2-cyclohexyl (**1**), 2,6-pyridyl (**2**), and 2,2'-oxydiaryl (**3**) spacers between the β -diketimate units has been studied. The isolation of three new copper(I) phosphine complexes [**1**•Cu₂(PPh₃)₂], [**2**•Cu₂(PPh₃)₂] and [**3**•Cu₂(PPh₃)₂] is reported. While these compounds display large Cu---Cu separations of 5.4 – 7.9 Å in the solid state, solution data are consistent with a large degree of conformational freedom. Modification of the monophosphine to a diphosphine, DPPE, allowed the isolation of the novel 11-membered bimetallic macrocycle [**2**•Cu₂(DPPE)] containing both a binucleating nitrogen based ligand and a chelating diphosphine. While acetonitrile adducts of this series could also be generated in situ, under forcing conditions reaction of the 2,6-pyridyl bridged ligand with mesityl copper led to the formation [**2**•Cu₂]₂. This latter complex is a dimer of dicopper(I) units in which the bis(β -diketimate) ligand now binds four copper(I) centers through not only the expected κ^2 -N,N'-chelation but also κ^1 - and η^2 -binding of the central pyridine through orthogonal Cu–N and Cu–arene interactions. Reversible coordination of alkenes, pyridine and quinoline to the copper cluster was identified allowing the isolation and structural characterization of a further series of dinuclear complexes [**2**•Cu₂(pyridine)₂], [**2**•Cu₂(cyclopentene)₂] and [**2**•Cu₂(norbornene)₂]. Solution studies allow quantification of the reversible binding event through a van't Hoff analysis. Both solution and the solid state data suggest a weak anagostic interaction exists in the latter two alkene complexes of copper(I). The new complexes have been characterized by X-ray diffraction, multinuclear NMR spectroscopy and CHN analysis.

Introduction

Stabilisation of copper complexes by β -diketiminato ligands has led to significant advances in small molecule activation and the functionalization of inert carbon–hydrogen bonds with this element.¹⁻² This readily tunable ligand framework accommodates copper in oxidation states from +1 to +3. For example, Tolman, Cramer, Solomon, Sadighi and others have pioneered reactions of dioxygen with copper(I) complexes of this ligand class, demonstrating the formation of side-on peroxo, superoxo, and both homobimetallic and heterobimetallic di(μ -oxo) complexes formed from reaction of a either 1:1 and 2:1 ratio of Cu:O₂.³⁻¹⁵ Warren and coworkers have expanded the oxidation chemistry of copper(I) β -diketiminato complexes to include diazoalkanes, PhI=NTs, organoazides and *tert*-butylperoxide.¹⁶⁻²⁸ These stoichiometric studies are part of a broader programme, developing exciting synthetic protocols for the functionalization of carbon–hydrogen bonds in hydrocarbons. The catalytic generation of a monomeric copper nitrene intermediate and its transformation to a copper(II) amide by hydrogen atom abstraction has been proposed as a key step in the transformation of carbon–hydrogen bonds to carbon–nitrogen bonds.^{20,22-24,26} Similarly, a copper(II) alkoxide is proposed as a crucial intermediate during the oxidation of cyclohexane to *tert*-butyl-cyclohexyl ether by *tert*-butylperoxide in the presence of a copper(I) diketiminato complexes.²⁵

In more recent years, the chemistry of copper β -diketiminato has been expanded to include both dinucleating and trinucleating ligands.²⁹⁻³⁰ As part of studies toward elucidation of the rare dicopper(II) mono(oxo) functional group, Limberg and coworkers have suggested that, within a xanthene-spaced dinucleating ligand framework a dicopper mono(μ -oxo) species may be formed from reaction of a 4:1 ratio of Cu:O₂.²⁹ Murray and co-workers have reported a remarkable tricopper(I) dinitrogen complex formed within a carefully designed paracyclophane ligand.³⁰

As a first step to new dinuclear complexes containing low-coordinate copper sites within flexible and easily modified ligand frameworks, we now report synthetic approaches to a series of dicopper(I) complexes supported by dinucleating β -diketiminato ligands.³¹ Keen interest in coordination complexes containing two or more carefully orientated copper sites originates from numerous bioinorganic studies.³²⁻³³ There is potential for these complexes to act as functional

models for a number of enzymes involved in not only dioxygen transport but also the oxidation of external substrates.³⁴⁻³⁶

Experimental Details

General Experimental: All reactions were carried out in oven-dried glassware, performed under argon atmosphere and manipulated using Schlenk techniques and glove box. All solvents were dried using standard solvent drying techniques. ¹H and ¹³C NMR spectra were recorded using a Bruker AV400 spectrometer at 400 MHz in CDCl₃ unless otherwise stated, where chemical shifts were expressed in parts per million (ppm) downfield from tetramethylsilane and referenced to the residual solvent resonance. Mass spectra were recorded using a Waters LCT Premier (ES-ToF) spectrometer in positive mode. X-ray crystallography was recorded using the Agilent Xcalibur 3 E and PX Ultra A X-ray Diffraction Systems with Cu Single Wavelength Sealed Tube Source with wavelengths of 0.71 Å and 1.54 Å and at 173 K. The dinucleating ligands **1•H₂** and **2•H₂** were prepared by modification of the literature procedures (see supporting information).³⁷⁻³⁹ The copper cluster [**2•Cu₂**]₂ was prepared by the literature procedure.³¹

Synthesis of 3•H₂: To a solution of 2-(2,6-di-iso-propylphenyl)imido-2-penten-4-one (2.6 g, 9.98 mmol) in DCM (15 mL) at room temperature was added a solution of [Et₃O]BF₄ (2.1 g, 11.03 mmol) in DCM (5 mL) to produce a brown-colored solution. The reaction mixture was stirred for 6 h before the addition of Et₃N (0.2 mL, 1.43 mmol), upon which the solution turned yellow. To a solution of 2,2'-oxydianiline (1.0 g, 4.99 mmol) in Et₃N (3 mL) was added the reaction mixture and the mixture turned brown-yellow. The mixture was heated to reflux (40 °C) for 14 days. All solvents were removed *in vacuo* to give an oily-crude product. The crude was recrystallized from absolute EtOH (20 mL) and **3•H₂** was isolated as cream-colored crystals (1.20 g, 1.76 mmol, 35.2 %). ¹H (CDCl₃, 500 MHz, 298K) δ 1.00 (d, 12H, ³J_{HH} = 8.0 Hz), 1.12 (d, 12H, ³J_{HH} = 8.0 Hz), 1.65 (s, 6H), 1.92 (s, 6H), 2.94 (hept, 4H, ³J_{HH} = 8.0 Hz), 4.86 (s, 2H), 6.68 (m, 1H), 6.70 (m, 1H), 6.88 (m, 2H), 6.97 (m, 4H), 7.10 (m, 6H), 12.24 (s, 2H); ¹³C (CDCl₃, 100 MHz, 298K) δ 20.2, 20.6, 22.7, 24.1, 28.2, 94.8, 118.8, 122.9, 123.1, 124.4, 125.1, 125.3, 137.4, 140.4, 142.6, 149.4, 160.3, 162.1; Mass spec. (ToF, ES⁺): 342.23 (M²⁺), 638.47 (M⁺). Analysis Calc. for C₄₆H₅₈N₄O C, 80.89%; H, 8.56%; N, 8.20% found C, 80.81%; H, 8.62%; N, 8.20%.

Synthesis of $[1\bullet\text{Cu}_2(\text{L}^1)_2]$: In a glovebox, to a solution of ligand $1\bullet\text{H}_2$ (400 mg, 0.67 mmol, 1 equiv.) in a 4:1 toluene:MeCN (5 mL) solvent mixture was added CuMes (269 mg, 1.47 mmol, 2.2 equiv.) the reaction mixture was transferred to a Youngs ampoule and removed from the box. The reaction mixture was heated to 50 °C for 24 h. Following cooling of the mixture to 25 °C, under a purge of inert gas solid triphenylphosphine (L^1 , 387 mg, 1.47 mmol, 2.2 equiv.) was added. The mixture was heated for a further 1 h at 50 °C, following which the volatiles were removed *in vacuo*. The ampoule was pumped back in to the glovebox and the brown residue triturated with diethyl ether (5 mL), the supernatant was carefully decanted by pipette to give a off-white solid. The solid was washed with diethyl ether (2x5 mL) following the procedure for trituration. Drying of the solid *in vacuo* gave $[1\bullet\text{Cu}_2(\text{L}^1)_2]$ ($\text{L}^1 = \text{PPh}_3$) as an off-white solid (340 mg, 0.27 mmol, 37 %). X-ray quality crystals were obtained by recrystallization from THF. ^1H NMR (C_6D_6 , 500 MHz, 298 K) δ -0.4 (m, 2H), 0.52 (d, 6H, $^3J_{\text{HH}} = 7.0$ Hz), 0.70-0.78 (m, 2H), 1.05 (d, 6H, $^3J_{\text{HH}} = 7.0$ Hz), 1.22 (d, 6H, $^3J_{\text{HH}} = 7.0$ Hz), 1.35 (d, 6H, $^3J_{\text{HH}} = 7.0$ Hz), 1.72-1.76 (m, 4H), 1.75 (s, 6H), 2.68 (2, 6H), 3.55 (hept, 2H, $^3J_{\text{HH}} = 7.0$ Hz), 3.50-3.60 (m, 2H), 3.72 (hept, 2H, $^3J_{\text{HH}} = 7.0$ Hz), 4.91 (s, 2H), 7.05-7.08 (m, 2H), 7.12-7.15 (m, 4H), 7.16-7.28 (m, 10 H); ^{13}C NMR (C_6D_6 , 125 Hz, 298 K) δ 23.5, 23.7, 24.3, 24.5, 24.7, 27.9, 28.0, 28.6, 37.7, 67.3, 95.8, 123.7, 123.8, 123.9, 128.6 (d, $J = 9.3$ Hz), 129.6, 134.4 (broad d, $J = 14.3$ Hz), 135.1 (d, $J = 39.0$ Hz), 141.4, 142.1, 151.9, 162.3, 164.4; ^{31}P NMR (C_6D_6 , 202 MHz, 298 K) δ + 0.7; Elemental Analysis Calc. for $\text{C}_{76}\text{H}_{88}\text{Cu}_2\text{P}_2\text{N}_4$ C, 73.23%; H, 7.12%; N, 4.49% found C, 73.33%; H, 7.26%; N, 4.57%.

Synthesis of $[2\bullet\text{Cu}_2(\text{L}^1)_2]$: In a glovebox, to a solution of ligand $2\bullet\text{H}_2$ (400 mg, 0.68 mmol, 1 equiv.) and triphenylphosphine (410 mg, 1.56 mmol, 2.3 equiv.) in toluene (5 mL) was added CuMes (280 mg, 1.50 mmol, 2.2 equiv.). The solution was transferred to a Youngs ampoule, removed from the box and stirred for 10 minutes during which time a yellow suspension form. The reaction mixture was heated to 50 °C for 4 days. The solvent was removed and ^1H NMR analysis of the crude showed an incomplete reaction, additional CuMes (30 mg, 0.16 mmol, 0.2 equiv.) and PPh_3 (20 mg, 0.08 mmol, 0.1 equiv.) was added and the mixture stirred for an additional 4 days at 50 °C. In a glovebox, the volatiles were removed *in vacuo* and the crude mixture triturated in diethyl ether (3 x 10 mL). The precipitate was isolated and dried to give $[2\bullet\text{Cu}_2(\text{L}^1)_2]$ ($\text{L}^1 = \text{PPh}_3$) as an off-white solid (700

mg, 0.56 mmol, 83 %). X-ray quality crystals were obtained from recrystallization of an aliquot from THF. ^1H NMR (C_6D_6 , 500 MHz, 298 K) δ 0.78 (d, 12H, $^3J_{\text{HH}} = 5.6$ Hz), 1.17 (s, 6H), 1.24 (d, 12H, $^3J_{\text{HH}} = 7.0$ Hz), 1.84 (s, 6H), 3.57 (hept, 4H, $^3J_{\text{HH}} = 7.0$ Hz), 4.89 (s, 2H), 6.05 (d, 2H, $^3J_{\text{HH}} = 8.0$ Hz), 6.48 (t, 1H, $^3J_{\text{HH}} = 8.0$ Hz), 6.94-6.97 (m, 12H), 6.99-7.02 (m, 6H), 7.06-7.07 (m, 4H), 7.12-7.14 (m, 2H), 7.23-7.27 (m, 12H); ^{13}C NMR (C_6D_6 , 125 MHz, 298 K) δ 23.4, 23.6, 23.9, 28.2, 95.8, 113.3, 123.8, 123.8, 128.8 (d, $J = 12.4$ Hz), 129.4, 133.7 (d, $J = 43.9$), 134.3 (d, $J = 25.5$ Hz), 136.3, 140.6 (q), 150.6 (q), 162.7 (q), 163.6 (q), 164.6 (q); ^{31}P NMR (C_6D_6 , 202 MHz, 298 K) δ + 3.5; Elemental Analysis Calc. for $\text{C}_{75}\text{H}_{81}\text{Cu}_2\text{P}_2\text{N}_5$ C, 72.56%; H, 6.58%; N, 5.64% found C, 72.45%; H, 6.68%; N, 5.55%.

Synthesis of $[\mathbf{2} \cdot \text{Cu}_2(\text{L}^2)]$: In a glovebox, the ligand $\mathbf{2} \cdot \text{H}_2$ (200 mg, 0.34 mmol, 1 equiv.), DPPE (162 mg, 0.41 mmol, 1.2 equiv.) and CuMes (140 mg, 0.75 mmol, 2.2 equiv.) were weighed into separate weighing boats and then transferred to a Schlenk. Toluene (20 mL) was added and the mixture stirred at room temperature for 24 h. The solvent was removed *in vacuo* to give a sticky pale-yellow solid. The crude product was dissolved in a 3:1 mixture of diethyl ether to n-hexane (30 mL), the solution filtered and concentrated to *ca.* 5 mL upon which point an off-white solid precipitated. The solid was isolated and washed with n-hexane (2 x 10 mL) and dried *in vacuo* to give $[\mathbf{2} \cdot \text{Cu}_2(\text{L}^2)]$ ($\text{L}^2 = \text{DPPE}$) as a colourless solid (210 mg, 0.18 mmol, 55%). X-ray quality crystals were obtained from toluene. ^1H NMR (C_6D_6 , 500 MHz, 298 K) δ 0.78 (broad d, 12H), 1.18 (d, 12H, $^3J_{\text{HH}} = 7.0$ Hz), 1.87 (s, 6H), 1.95 (broad m, 4H), 2.13 (s, 6H), 3.44 (broad hept, 4H), 5.10 (s, 2H), 6.30 (d, 2H, $J = 8.0$ Hz), 6.76 (t, 1H, $J = 8.0$ Hz), 6.85-6.92 (m, 24H), 7.12-7.14 (m, 12H); ^{13}C NMR (C_6D_6 , 125 MHz, 298 K) δ 23.6, 23.7, 23.8, 28.3, 96.0, 123.7, 123.8, 128.8 (t, $J = 5.5$ Hz), 129.7, 133.2 (t, $J = 7.6$ Hz), 140.8, 150.2, 162.1, 164.0, 165.9; CH_2 and P- C_{ipso} resonance not observed; ^{31}P NMR (C_6D_6 , 162 MHz, 298 K) δ + 0.7; Elemental Analysis Calc. for $\text{C}_{65}\text{H}_{75}\text{Cu}_2\text{P}_2\text{N}_5$ C, 69.99%; H, 6.78%; N, 6.28% found C, 69.96%; H, 6.83%; N, 6.12%.

Synthesis of $[\mathbf{3} \cdot \text{Cu}_2(\text{L}^1)_2]$: In a glovebox, $\mathbf{3} \cdot \text{H}_2$ (200 mg, 0.146 mmol), CuMes (133 mg, 0.365 mmol) and PPh_3 (184 mg, 0.350 mmol) were dissolved in C_6H_6 . Mixture was heated at 80°C for 24 h. The solvent was removed *in vacuo*. Trituration of crude using Et_2O gave a precipitate which was isolated and dried *in vacuo* to give $[\mathbf{3} \cdot \text{Cu}_2(\text{L}^1)_2]$ ($\text{L}^1 = \text{PPh}_3$) as a cream-colored solid (340 mg, 0.255 mmol, 87%). ^1H (C_6D_6 , 500 MHz, 298K) δ 0.82 (d, 6H, $^3J_{\text{HH}} = 7.0$ Hz), 0.85 (d, 6H, $^3J_{\text{HH}} = 7.0$ Hz), 1.08 (d, 6H, $^3J_{\text{HH}} = 7.0$ Hz), 1.27 (d, 6H, $^3J_{\text{HH}} = 7.0$ Hz), 1.87 (s, 6H), 2.27 (s, 6H), 3.30 (hept, 2H, $^3J_{\text{HH}} = 7.0$ Hz), 3.66 (hept, 2H, $^3J_{\text{HH}} = 7.0$ Hz), 5.29 (s, 2H), 6.14 (m, 2H), 6.43 (m, 4H), 6.85-7.45 (m, 38H); ^{13}C

NMR (C_6D_6 , 125 MHz, 298K): δ 23.5, 23.7, 23.8, 24.0, 28.0, 28.1, 96.0, 118.9, 122.7, 122.8, 123.6, 123.7, 123.9, 126.1, 128.7 (d, J = 9.6 Hz), 129.4, 133.9 (d, J = 15.0 Hz), 134.3 (d, J = 34.6 Hz), 140.6(q), 140.9(q), 146.9(q), 149.9(q), 150.6(q), 163.2, 165.5; ^{31}P (C_6D_6 , 202 MHz, 298K): δ +3.9. Repeated attempts to acquire CHN analysis failed.

Synthesis of $[\mathbf{2}\cdot\text{Cu}_2(\text{L}^3)]_2$: In a glovebox, $[\mathbf{2}\cdot\text{Cu}_2]_2$ (46.5 mg, 0.0324 mmol) was suspended in diethyl ether (2.5 mL) and pyridine (39.3 μL , 0.488 mmol, 15 equiv.) added in a vial. The mixture slowly turns homogeneous with stirring over five minutes. Placing the vial in a freezer at $-35\text{ }^\circ\text{C}$ afforded orange crystals of $[\mathbf{2}\cdot\text{Cu}_2(\text{L}^3)]_2$ (L^3 = pyridine) (37.7 mg, 0.0430 mmol, 66%). ^1H NMR (C_6D_6 , 500 MHz) δ : 0.98 (d, 12H, $^3J_{\text{HH}}$ = 6.9 Hz), 1.23 (d, 12H, $^3J_{\text{HH}}$ = 7.3 Hz), 1.92 (s, 6H), 2.15 (s, 6H), 3.53 (hept, 4H, $^3J_{\text{HH}}$ = 7.0 Hz), 5.03 (s, 2H), 6.45 (d, 2H, $^3J_{\text{HH}}$ = 7.6 Hz), 6.62 (br t, 4H, $^3J_{\text{HH}}$ = 7.0 Hz), 6.89 (br t, 2H, $^3J_{\text{HH}}$ = 7.5 Hz), 7.08 (t, 1H, $^3J_{\text{HH}}$ = 7.7 Hz), 7.13–7.18 (m, 6H), 8.48 (br d, 4H, $^3J_{\text{HH}}$ = 3.5 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 126 MHz) δ : 23.4, 23.6, 23.8, 24.1, 28.1, 95.8, 111.0, 123.3, 123.6, 123.8, 128.4, 135.4, 137.1, 140.0, 148.9, 150.6, 160.8, 163.2, 163.8; FT-IR (ν/cm^{-1}): C–H stretches: 2863, 2922, 2957, 3059; others: 699, 754, 1025, 1148, 1185, 1216, 1301, 1322, 1361, 1403, 1442, 1458, 1511, 1549; Elemental Analysis Calc. for $\text{C}_{49}\text{H}_{61}\text{Cu}_2\text{N}_7$ C, 67.25%; H, 7.03%; N, 11.20% found C, 67.36%; H, 6.97%; N, 11.12%.

Synthesis of $[\mathbf{2}\cdot\text{Cu}_2(\text{L}^6)]_2$: In a glovebox, $[\mathbf{2}\cdot\text{Cu}_2]_2$ (6.2 mg, 0.00432 mmol) and cyclopentene (6.11 μL , 0.0692 mmol, 16 equiv.) were dissolved in C_6D_6 (0.6 mL), showing quantitative conversion to $[\mathbf{2}\cdot\text{Cu}_2(\text{L}^6)]_2$ by ^1H NMR. The solvent and excess cyclopentene was removed *in vacuo*, and the resultant residue was dissolved in diethyl ether (1 mL), cyclopentene (6 μL) was added and the solution was placed in the freezer at $-35\text{ }^\circ\text{C}$, affording $[\mathbf{2}\cdot\text{Cu}_2(\text{L}^6)]_2$ (L^6 = cyclopentene) as yellow crystals (4.0 mg, 0.00469 mmol, 54%). ^1H NMR (C_6D_6 , 500 MHz) δ : 1.16 (d, 12H, $^3J_{\text{HH}}$ = 6.7 Hz), 1.19 (d, 12H, $^3J_{\text{HH}}$ = 7.6 Hz), 1.29–1.45 (m, 8H), 1.54–1.65 (m, 4H), 1.82 (s, 6H), 2.03 (s, 6H), 3.28 (hept, 4H, $^3J_{\text{HH}}$ = 6.8 Hz), 4.35 (s, 4H), 4.99 (s, 2H), 6.42 (d, 2H, $^3J_{\text{HH}}$ = 7.6 Hz), 7.08 (t, 1H, $^3J_{\text{HH}}$ = 7.6 Hz), 7.10–7.17 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 126 MHz) δ : 23.7, 23.9, 24.7, 24.8, 32.7, 94.7, 95.4, 113.6, 123.7, 124.6, 128.4, 138.1, 140.7, 148.7, 161.9, 164.5; Elemental Analysis Calc. for $\text{C}_{49}\text{H}_{67}\text{Cu}_2\text{N}_5$ C, 68.98%; H, 7.92%; N, 8.21% found C, 68.89%; H, 7.92%; N, 8.13%.

Synthesis of [2•Cu₂(L⁸)₂]: In a glovebox, [2•Cu₂]₂ (7.0 mg, 0.00488 mmol) and norbornene (2.0 mg, 0.0212 mmol, 4.3 equiv.) were dissolved in C₆D₆ (0.6 mL), showing quantitative conversion to [LCu₂(norbornene)₂] by ¹H NMR. The solvent and volatiles were removed *in vacuo*, and the resultant residue was dissolved in hexane (1 mL) and placed in the freezer at –35 °C, affording [2•Cu₂(L⁸)₂] (L⁸ = norbornene) as pale yellow crystals (5.8 mg, 0.00640 mmol, 66%). The crystals were found to be amenable for X-ray diffraction experiments. ¹H NMR (C₆D₆, 400 MHz) δ: 0.51–0.58 (br m, 6H), 1.04–1.06 (m, 4H), 1.17 (d, 12H, ³J_{HH} = 6.8 Hz), 1.20 (d, 12H, ³J_{HH} = 7.0 Hz), 1.27–1.40 (m, 2H), 1.82 (s, CH₃^{NacNac}), 2.07 (s, 6H), 2.26 (br s, 4H), 3.32 (hept, 4H, ³J_{HH} = 6.9 Hz), 3.93 (s, 4H), 5.01 (s, 2H), 6.52 (d, 2H, ³J_{HH} = 7.6 Hz), 7.13–7.20 (m, 7H); ¹³C{¹H} NMR (C₆D₆, 101 MHz) δ: 23.7 (s, CH₃^{NacNac}), 23.8 (s, CH₃^{NacNac}), 24.0 (s, CH₃^{iPr}), 24.7 (s, CH₃^{iPr}), 25.1 (s, CH₂^{norbornene}), 28.2 (s, CH^{iPr}), 42.5 (s, CH^{norbornene}), 43.7 (s, CH₂^{norbornene}), 94.9 (s, CH^{norbornene}), 95.6 (s, CH^{NacNac}), 113.6 (s, CH^{m-py}), 123.7, 124.6, 140.7, 162.0, 164.4, 164.9.

Results

Synthesis of Flexible Cu(I)---Cu(I) Bimetallics

In accordance with precedent,³⁷⁻³⁹ the alkylation of 2-(2,6-di-*iso*-propylphenyl)imido-2-penten-4-one with Meerwein's salt followed by condensation with a series of diamines yielded the corresponding dinucleating pro-ligands. The diamine was varied to include, *trans*-1,2-dicyclohexane diamine (**1**•H₂), 2,6-diaminopyridine (**2**•H₂), and 2,2'-oxydianiline (**3**•H₂). The products proved highly soluble in n-hexane and toluene and were purified following recrystallization from ethanol or acetone at -20 °C. In some cases multiple recrystallizations were required to remove by-products derived from [Et₃O][BF₄]. In all cases multinuclear NMR data were consistent with the pro-ligands retaining a pseudo C₂-symmetric structure in solution with chemical and magnetic equivalence of the two *N,N'*-chelates of each ligand.

Figure 1: The Crystal Structures of (a) **1**•H₂ and (b) **3**•H₂. H-atoms omitted for clarity.

While **1**•H₂ and **2**•H₂ have been reported previously, single crystal X-ray diffraction studies on these ligand systems have not. The crystal structures of one of two molecules within the unit cell of **1**•H₂ along with that of **3**•H₂ are presented in Figure 1. The data for the two molecules within the unit cell of **1**•H₂ do not vary significantly. It is noteworthy that in all cases the flexibility of the spacer, in combination with the steric demands of the 2,6-di-*iso*-propylphenyl group results in twisting of the two β -diketiminate units away from one another. This observation is consistent with single crystal X-ray diffraction studies on zinc, magnesium and calcium complexes of **2**•H₂ and related ligands in which that lack of any geometric constraint results in a flexible system and a distal relation of the two metal centers.³⁷⁻³⁹ Holland and coworkers have made similar

observations during the investigation of main group complexes of macrocyclic *bis*(diketiminate) ligands.⁴⁰

Scheme 1: Synthesis of bimetallic copper complexes by deprotonation with CuMes

Although reaction of **1**•H₂ or **2**•H₂ with 3-5 equiv. of CuO^tBu in a 10:1 mixture of C₆D₆/MeCN resulted in formation of the corresponding bimetallic Cu(I)---Cu(I) acetonitrile adducts after 24 h at 25 °C, preparations with CuMes were cleaner. Hence, CuMes was used preferentially to prepare bimetallic copper complexes by deprotonation of the aforementioned series of pro-ligands (Scheme 1).⁴¹ The reaction of 2 equiv. CuMes, 2 equiv. of a phosphine and 1 equiv. of pro-ligand in toluene gave facile access to the corresponding phosphine-ligated dicopper complexes [**2**•Cu₂(**L**¹)₂], [**2**•Cu₂(**L**²)] and [**3**•Cu₂(**L**¹)₂] (Scheme 1, method A).

Despite only minor modifications to the ligand spacer, attempts to apply this method to the *trans*-cyclohexyl bridged system did not allow the isolation of the corresponding dicopper complex **[1•Cu₂(L¹)₂]**. Rather sequential reaction of **1•H₂** with CuMes in a 4:1 mixture of toluene:MeCN resulted in the generation of **[1•Cu₂(NCMe)₂]** which could be trapped as the phosphine adduct **[1•Cu₂(L¹)₂]** following addition of 2 equiv. of PPh₃ to the reaction mixture (Scheme 1, method **B**). While our attempts to isolate and crystallize the acetonitrile adduct failed, this complex could be readily generated *in situ* (see supporting information). Monitoring reactions of **2•H₂** with 2 equiv. PPh₃ and 2 equiv. of CuMes in C₆D₆ as a function of time revealed the formation of an asymmetric intermediate characterized by three distinct resonances for the pyridyl bridge at δ = 6.07 (d, 1H, *J* = 8.0 Hz), 6.16 (d, 1H, *J* = 8.0 Hz) and 6.53 (t, 1H, *J* = 8.0 Hz) and a singlet at δ 13.80 ppm, corresponding to an unreacted –NH proton in the ¹H NMR spectrum. This latter species has been assigned as the intermediate monocopper complex which readily converts to the dicopper complex at longer reaction times.

Under more forcing conditions (54 h at 80 °C) reactions of **2•H₂** with 2 equiv. of CuMes in the presence of MeCN, 2,6-dimethylbenzonitrile or DMSO, or in the absence of a π -acidic ligand reproducibly led to the production of a red solutions and clean formation of a new species as evidenced by ¹H NMR spectroscopy. The red solid **[2•Cu₂]₂** was isolated by recrystallisation of the crude product from diethylether or THF. The dimeric structure represented in Scheme 2 has been assigned based upon multinuclear NMR, DOSY, and infrared spectroscopy, X-ray diffraction and High-res mass spectrometry.³¹

Scheme 2: Synthesis of the tetrametallic copper cluster **[2•Cu₂]₂**

While addition of 2 equiv. of Ph_3P to $[\mathbf{2}\cdot\text{Cu}_2]_2$ in C_6D_6 resulted in the non-reversible formation of $[\mathbf{2}\cdot\text{Cu}_2(\text{L}^1)_2]$ at 25 °C, this tetracopper cluster reversibly binds alkenes and pyridine ligands. Reaction of $[\mathbf{2}\cdot\text{Cu}_2]_2$ in benzene or toluene solution with hex-1-ene, cyclopentene, cyclohexene or pyridine results in the formation of an equilibrium mixture of $[\mathbf{2}\cdot\text{Cu}_2]_2$ and the cluster opened products $[\mathbf{2}\cdot\text{Cu}_2(\text{L})_2]$ (Scheme 3). The following evidence was obtained for reversible substrate binding: (i) the position of the equilibrium was found to be dependent upon the concentration of the external ligand, for example 20 equiv. of cyclohexene were required to bias the equilibrium, as drawn (scheme 3), to the product, (ii) under dynamic vacuum pyridine could be removed from $[\mathbf{2}\cdot\text{Cu}_2(\text{L}^3)_2]$ ($\text{L}^3 = \text{pyridine}$) to reform $[\mathbf{2}\cdot\text{Cu}_2]_2$, (iii) variable temperature NMR studies on $[\mathbf{2}\cdot\text{Cu}_2(\text{L})_2]$ ($\text{L}^3 = \text{pyridine}$, $\text{L}^7 = \text{cyclohexene}$) in toluene- d_8 show an expected temperature dependence upon the position of equilibrium.

The reaction of $[\mathbf{2}\cdot\text{Cu}_2]_2$ with two equiv. of norbornene proceeds with addition of the copper centre to the least hindered face of the bicycloalkane and proceeds non-reversibly. Reactions of norbornene which allow the sp^2 carbons to deviate toward sp^3 -hybridisation relieve ring-strain and are typically highly exergonic, as a result the position of the equilibrium lies significantly further toward the products than for less strained alkenes such as cyclopentene and cyclohexene. No reaction was observed between $[\mathbf{2}\cdot\text{Cu}_2]_2$ and benzothiophene, at 25 °C in hydrocarbon solvents.

Scheme 3: Reactions of tetrametallic copper cluster $[\mathbf{2}\cdot\text{Cu}_2]_2$ with alkenes and heterocycles

Solution ^1H and ^{31}P NMR Data

The ^1H NMR spectrum of $[\mathbf{3}\cdot\text{Cu}_2(\text{L}^1)_2]$ at 298K in C_6D_6 shows magnetically inequivalent *iso*-propyl groups for the flanking aromatic rings. Hence, heptet resonances at δ 3.66 (2H, $^3J_{\text{HH}} = 7.0$ Hz) and 3.30 ppm (2H, $^3J_{\text{HH}} = 7.0$ Hz) correspond to the methine proton, while the four doublet signals for the methyl protons are present at δ 1.27 (6H, $^3J_{\text{HH}} = 7.0$ Hz), 1.08 (6H, $^3J_{\text{HH}} = 7.0$ Hz), 0.85 (6H, $^3J_{\text{HH}} = 7.0$ Hz) and 0.82 (6H, $^3J_{\text{HH}} = 7.0$ Hz) ppm. Consistent with data recorded for the pro-ligand the two ‘arms’ of the dinucleating ligand are equivalent in solution as evidenced by a single methine resonance for the β -diketimate backbone at δ 5.10 ppm. Hindered rotation about the N- C_{Aryl} bonds of $[\mathbf{3}\cdot\text{Cu}_2(\text{L}^1)_2]$ readily explains the observed ^1H NMR data as under these conditions not only would each *iso*-propyl moiety contain diastereotopic Me and Me’ groups but the two sides of the aromatic flanking group should become inequivalent. While a similar scenario was recorded for $[\mathbf{1}\cdot\text{Cu}_2(\text{L}^1)_2]$ at 298K in C_6D_6 , under these conditions both $[\mathbf{2}\cdot\text{Cu}_2(\text{L}^1)_2]$ and $[\mathbf{2}\cdot\text{Cu}_2(\text{L}^2)]$ display a single broad methine resonance and two broad methyl resonances for the *iso*-propyl groups suggesting a lower energy barrier to rotation about the N- C_{Aryl} bond. In the latter two cases, ^1H NMR data are consistent with an intermediate scenario between slow-exchange and fast-exchange regimes (Figure 2a). Complexes $[\mathbf{1}\cdot\text{Cu}_2(\text{L}^1)_2]$, $[\mathbf{2}\cdot\text{Cu}_2(\text{L}^1)_2]$, $[\mathbf{2}\cdot\text{Cu}_2(\text{L}^2)]$ and $[\mathbf{3}\cdot\text{Cu}_2(\text{L}^1)_2]$ display sharp ^{31}P resonances at $\delta_{\text{P}} = +0.7, +3.5, +0.7$ and $+3.9$ ppm respectively in C_6D_6 at 298K.

Isolated samples of $[\mathbf{2}\cdot\text{Cu}_2]_2$ are soluble in benzene and toluene. ^1H NMR data recorded across the temperature range of 298 – 353 K provide a series of complex but well-resolved resonances that are consistent with a conformationally locked dicopper complex. In this case, complete desymmetrization of the ligand environments occurs in combination with the previously observed magnetic inequivalence of the *iso*-propyl units for the aromatic flanking group (Figure 2b). Both arms of the dinucleating ligand display their own set of distinct resonances, for example the two β -diketimate backbone protons are now observed at $\delta = 4.69$ and 4.92 ppm with the four methine resonances of the four *iso*-propyl groups now individually resolved as four septet resonances in the region of $\delta = 2.5 - 3.6$ ppm. Extended drying of samples of $[\mathbf{2}\cdot\text{Cu}_2]_2$ under reduced pressure resulted in the removal of all traces of toluene solvent and provided data that was inconsistent with assignment of $[\mathbf{2}\cdot\text{Cu}_2]_2$ as either a 1:1 or 2:1 copper arene complex. While the structurally

assignment ultimately relied upon the acquisition of X-ray diffraction data (*vide infra*), NOESY and DOSY spectroscopy provided additional insight to the composition of $[2\cdot\text{Cu}_2]_2$ in solution.

Figure 2: (a) ^1H and ^{13}C NMR data for $[2\cdot\text{Cu}_2(\text{L}^1)_2]$, (b) ^1H and ^{13}C NMR data for $[2\cdot\text{Cu}_2]_2$, (c) a model of $[2\cdot\text{Cu}_2]_2$ with dotted lines representing the interatomic relationships that give rise to the observed NOE interactions.

In C_6D_6 solution strong NOE cross peaks are observed between the both *para*- and *meta*-hydrogens of the pyridine spacer of $[2\cdot\text{Cu}_2]_2$ with both the methine and methyl resonances of four of the individually resolved *iso*-propyl groups (Figure 3c). The observation is consistent with a conformational rigidity not apparent for the phosphine and acetonitrile ligated members of the series and can be explained by a folding of one of the aromatic groups of the β -diketiminate ligand over the top of the pyridyl spacer. No such signal enhancement was observed in a NOESY spectrum of $[3\cdot\text{Cu}_2(\text{L}^1)_2]$. A DOSY experiment revealed a hydrodynamic radius of 7.11 Å for $[2\cdot\text{Cu}_2]_2$ at 298K, a value larger than that of the free ligand $2\cdot\text{H}_2$ (5.25 Å) and suggestive of the formation of a higher nuclearity species in solution.

Variable temperature NMR studies on $[2\cdot\text{Cu}_2(\text{L})_2]$ ($\text{L}^3 = \text{pyridine}$, $\text{L}^7 = \text{cyclohexene}$) across the 193 to 353 K in toluene- d_8 show a series of reversible changes consistent with the equilibrium represented in equation 1:

As the temperature is increased the equilibrium is forced toward the reactants (eq. 1). For example, at 333 K a 4:1 mixture of cyclohexene and $[2\bullet\text{Cu}_2]_2$ demonstrates a series of resonances that can be assigned to the free alkene and the tetracopper cluster, the latter characterised by the high-field resonances of the desymmetrised and η^2 -coordinated pyridine motif between $\delta = 5.5$ and 6.2 ppm. As the reaction mixture is cooled to 273 K the formation of $[2\bullet\text{Cu}_2(\text{L}^7)_2]$ becomes apparent due to new signals consistent with a symmetrized binucleating ligand and the upfield shift of the copper-coordinated alkene resonances observed at $\delta = 4.40$ ppm. A van't Hoff analysis on the 4:1 mixture of cyclohexene and $[2\bullet\text{Cu}_2]_2$ (28 mM : 7 mM) in toluene- d_8 gave a linear slope between 273 and 313 K with corresponding values of $\Delta H = -8.3 \text{ kcal mol}^{-1}$, $\Delta S = -7.8 \text{ cal K}^{-1} \text{ mol}^{-1}$ and $\Delta G_{298\text{K}} = -6.0 \text{ kcal mol}^{-1}$ (Figure 3 & 4). As such the reaction as drawn (eq. 1) is exergonic with the alkene binding being exothermic. As the temperature is raised the negative entropy of reaction, associated with the decreased disorder of products, means that the equilibrium favours the reactants. Similar data were recorded for a mixture of pyridine and $[2\bullet\text{Cu}_2]_2$ across 193 -353 K. In the latter case the equilibrium lies further toward the product (Eq. 1).

Figure 3: Variable Temperature ^1H NMR data for $2\text{-Cu}_2(\text{L}^7)_2$ across 278 – 333 K

Figure 4: Variable Temperature ^1H NMR data for $2\cdot\text{Cu}_2(\text{L}^7)_2$ van't Hoff Analysis (273 – 313 K)

The solid state structures of $[2\cdot\text{Cu}_2(\text{L})_2]$ (L^6 = cyclopentene, L^8 = norbornene) show a puckering of the hydrocarbon ligand to position a hydrogen atom over the top of the trigonal planar copper centre (*vide infra*). While in the case of norbornene this geometry is unavoidable based on the stereochemistry, for cyclopentene the envelope conformer could flex toward or away from the metal and chooses the latter in both copper environments within the solid state structure. Consideration of these data along with the ^1H NMR resonances for the hydrocarbon ligands (Figure 5) suggests that an anagostic interaction may be present in $[2\cdot\text{Cu}_2(\text{L}^8)_2]$. Anagostic interactions, a broad terminology incorporating $\text{M}\cdots\text{H}-\text{C}$ geometries that are not agnostic and are primarily characterised as electrostatic, are typically characterised by obtuse $\text{M}\cdots\text{H}-\text{C}$ angles ($\sim 110\text{--}170^\circ$), long $\text{M}\cdots\text{H}$ distances ($\sim 2.3 - 2.9 \text{ \AA}$) and a downfield shift of the resonance of the proton engaged with the metal.⁴² The case for an anagostic interaction is perhaps best represented by comparison of the proton resonances of the bridgehead methylene of the norbornene ligand in $[2\cdot\text{Cu}_2(\text{L}^8)_2]$ (L^8 = norbornene, Figure 5), the assignment of H_a and H_b is supported by the observation of a $^4J_{\text{H-H}}$ ω -coupling between H_c and H_b .

Figure 5: Selected ^1H NMR data for $[\mathbf{2}\cdot\text{Cu}_2(\text{L}^8)_2]$. Data in ppm.

X-ray Diffraction Data

Single crystal X-ray diffraction experiments have been conducted on the entire series of new phosphine, pyridine and alkene ligated dicopper complexes and the tetracopper cluster $[\mathbf{2}\cdot\text{Cu}_2]_2$.³¹ The results of these experiments are presented in Figure 6 and 7 and in Table 1 and 2. Comparison of the structures of $[\mathbf{1}\cdot\text{Cu}_2(\text{L}^1)_2]$, $[\mathbf{2}\cdot\text{Cu}_2(\text{L}^1)_2]$, $[\mathbf{2}\cdot\text{Cu}_2(\text{L}^2)]$ and $[\mathbf{3}\cdot\text{Cu}_2(\text{L}^1)_2]$ ($\text{L}^1 = \text{PPh}_3$, $\text{L}^2 = \text{DPPE}$) reveals that in most cases the two arms of the dinucleating ligand rotate out of planarity. The conformational freedom in the 2,6-pyridyl and 2,2'-oxydiaryl spacers do not constrain the geometry of the metal centers or force them into a proximal environment in the solid state, moreover the *trans*-dicyclohexyl spacer displays the expected 1,2-diequatorial relation of the copper binding sites forcing an almost perfect anti-planar relation between the two β -diketiminato ligands. The Cu---Cu separation ranges from 5.4 to 7.9 Å. The inclusion of DPPE tethers together the two copper sites and results in the formation of an unusual 11-membered bimetallic macrocycle incorporating both N-based and P-based ligands. While DPPE brings the two copper centers into closer proximity than that observed in the triphenylphosphine analogue $[\mathbf{2}\cdot\text{Cu}_2(\text{L}^1)_2]$ and aligns the diketiminato ligand frameworks, the Cu---Cu separation of 6.0 Å is still large. Through comparison of the solid state structures of a series of dicopper complexes, Limberg and co-workers have previously commented on the likely perturbation of the coordination environment and increase of the Cu---Cu separation by the inclusion of bulky triphenylphosphine ligands on Cu(I) within dinucleating frameworks.²⁹

Figure 6: The crystal structures of (a) $[1 \cdot \text{Cu}_2(\text{L}^1)_2]$, (b) $[2 \cdot \text{Cu}_2(\text{L}^1)_2]$ (c) $[3 \cdot \text{Cu}_2(\text{L}^1)_2]$ and (d) $[2 \cdot \text{Cu}_2(\text{L}^2)]$. H-atoms and phenyl groups of the phosphine ligands omitted for clarity.

Table 1: Selected bond angles ($^\circ$) and bond lengths ($\text{\AA}$) in dicopper phosphine complexes

	$[1 \cdot \text{Cu}_2(\text{L}^1)_2]$	$[2 \cdot \text{Cu}_2(\text{L}^1)_2]$	$[3 \cdot \text{Cu}_2(\text{L}^1)_2]$	$[2 \cdot \text{Cu}_2(\text{L}^2)]$
Cu---Cu	5.4	6.3	7.9	6.0
Cu–N _{Dipp}	1.9686(17)	1.9597(17)	1.946(2)	1.9394(15)
	1.9662(17)	1.9562 (18)	1.959(2)	1.9710(14)
Cu–N _{Spacer}	1.9734(16)	1.9589(17)	1.950(2)	1.9578(16)
	1.9748(17)	1.9627(18)	1.965(2)	1.9678(16)
Cu–P	2.1965(6)	2.1777(6)	2.1556(7)	2.1620(5)
	2.1934(6)	2.1713(6)	2.1747(7)	2.1698(5)
N–Cu–N (bite angle)	99.03(7)	97.14(7)	97.43(9)	97.79(7)
	99.93(7)	97.72(7)	97.00(9)	96.41(6)

The Cu–P and Cu–N bond lengths and N–Cu–N bite angles of the series described above may be compared to the two known monomeric copper(I) phosphine complexes supported by β -diketimate ligands. The range of Cu–N and Cu–P bond distances recorded for $[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NCMe})_2\text{CH}\}\text{Cu}(\text{PPh}_3)]$ and *s,s*- $[(\text{PhCHMeNCMe})_2\text{CH}\}\text{Cu}(\text{PPh}_3)]$ are 1.9465(17)- 1.983(1) and 2.1664(8)-2.195(1) Å respectively.^{9,43-44} These values compare well with the data presented in Table 2. The N–Cu–N bite angles of **[1•Cu₂(L¹)₂]** are slightly more obtuse than the rest of the series and may reflect the steric pressure exerted by congestion of the ligand sphere by the two-atom, rather than three-atom, spacing group.

Consistent with the complex solution NMR data and large hydrodynamic radius, **[2•Cu₂]₂** displays a conformationally locked structure in the solid-state, we have reported this structure previously³¹ and provided a more detailed discussion of the data here. Each ligand unit coordinates to four, copper centers through not only the two expected *N,N'*-chelates of the β -diketimate ligands but also coordination to the central pyridine nitrogen and an η^2 -interaction with π -system of the pyridine.³¹ Each ligand acts as a κ^5, η^2 -coordinator. In combination the binding interactions bring together two **2•Cu₂** motifs into the dimeric structure **[2•Cu₂]₂**. Two distinct coordination environments are observed for Cu, both bound by a *N,N'*-chelate of the β -diketimate but one coordinated to pyridine and the other the arene. The pyridine units are aligned in an anti-configuration to accommodate the combination of edge on (nitrogen) and face-on (π -system) coordination modes.³¹

Table 2: Selected Bond Angles ($^{\circ}$) and Bond Lengths ($\text{\AA}$) in $[2\cdot\text{Cu}_2]_2$

$[2\cdot\text{Cu}_2]_2$	
Cu–C _{arene}	2.220(3), 2.137(3), 2.214(3), 2.125(3)
Cu–N _{Dipp}	1.942(3), 1.930(3), 1.923(3), 1.970(3)
Cu–N _{spacer}	1.923(3), 2.051(3), 1.919(3), 2.054(3)
Cu–N _{pyridine}	1.968(2), 1.964(3)
N–Cu–N (bite angle)	99.93(11), 96.37(11)

Figure 7: The crystal structure of (a) $[2\cdot\text{Cu}_2(\text{L}^3)_2]$, (b) $[2\cdot\text{Cu}_2(\text{L}^6)_2]$ and (c) $[2\cdot\text{Cu}_2(\text{L}^8)_2]$. H-atoms omitted for clarity.

Figure 8: Comparison of the coordination mode for the alkene in (a) $[2\cdot\text{Cu}_2(\text{L}^6)_2]$ and (b) $[2\cdot\text{Cu}_2(\text{L}^8)_2]$. Selected atoms only.

Table 3: Selected bond angles (°) and bond lengths (Å) in dicopper alkene and pyridine complexes

	[2•Cu₂(L³)₂]	[2•Cu₂(L⁶)]	[2•Cu₂(L⁸)₂]
Cu---Cu	4.8	6.3	6.5
Cu–N _{Dipp}	1.956(4)	1.933(2) 1.9434(18)	1.9265(19) 1.931(2)
Cu–N _{Spacer}	1.961(4)	1.9248(19) 1.9349(18)	1.929(2) 1.932(2)
Cu–L (N or C)	1.968(4)	2.019(2), 2.010(2), 2.030(2), 2.019(2)	2.023(3), 2.005(3), 2.027(3), 1.997(3)
N–Cu–N (bite angle)	97.10(17)	98.42(8) 98.23(8)	98.00(9) 98.61(9)

The Cu---Cu separations within the series of structures presented in Figure 7 & 8 and Table 3 are consistent with the previously described phosphine adducts. The pyridine analogue shows the shortest Cu---Cu separation of 4.8 Å. Copper–nitrogen bond lengths and the N–Cu–N bite angle within the *bis*(diketiminate) chelates in **[2•Cu₂(L)₂]** range between 1.9265(19) to 1.9748(17) Å and 97.10(17) to 98.00(9)° respectively and are consistent across the whole series of complexes. In **[2•Cu₂(L)₂]** (L⁶ = cyclopentene, L⁸ = norbornene) the alkene coordinates through the expected η²-mode to copper. While in the case of norbornene the copper approaches the alkene on the least hindered face of the [2.2.1]-bicycle, in both cases a close contact between a C–H bond of the hydrocarbon and the copper centre is observed (2.55-2.87 Å). Consideration of both X-ray diffraction data and the ¹H NMR data (*vide supra*) on these complexes suggests that the interaction may be classified as anagostic.

Conclusions

In summary we have reported the preparation of a new series of dicopper (I) complexes supported by dinucleating diketiminate ligands by deprotonation of the pro-ligand with either copper tert-butoxide or mesityl copper. Inclusion of 2,6-pyridyl, trans-1,2-cyclohexyl and 2,2'-oxydiaryl spacers between the β -diketiminate units has been studied and a series of phosphine and diphosphine, pyridine and alkene ligated complexes isolated and structurally characterized. In the absence of a co-ligand the pyridyl bridged system forms an unusual dimer of dicopper(I) complexes in which each ligand binds four copper centers through a combination of κ^2 -diketiminate, κ^1 -pyridine and η^2 -pyridine binding sites. The oxidation of these dicopper(I) complexes and their application in carbon-hydrogen bond functionalization is the subject of ongoing studies.

References

1. C. J. Cramer, W. B. Tolman, *Acc. Chem. Res.* **2007**, *40*, 601.
2. R. T. Gephart III, T. H. Warren, *Organometallics* **2012**, *31*, 7728.
3. D. J. E. Spencer, A. M. Reynolds, P. L. Holland, B. A. Jazdzewski, C. Duboc-Toia, L. Le Pape, S. Yokota, Y. Tachi, S. Itoh, W. N. Tolman, *Inorg. Chem.* **2002**, *41*, 6307.
4. D. J. E. Spencer, N. W. Aboelella, A. M. Reynolds, P. L. Holland, W. B. Tolman, *J. Am. Chem. Soc.* **2002**, *124*, 2108.
5. N. W. Aboelella, E. A. Lewis, A. M. Reynolds, W. W. Brennessel, C. J. Cramer, W. B. Tolman, *J. Am. Chem. Soc.* **2002**, *124*, 10660.
6. N. W. Aboelella, S. V. Kryatov, B. F. Gherman, W. W. Brennessel, V. G. Young, Jr, R. Sarangi, V. Rybak-Akimova, K. O. Hodgson, B. Hedman, E. I. Solomon, C. J. Cramer, W. B. Tolman, *J. Am. Chem. Soc.* **2004**, *126*, 16896.
7. A. M. Reynolds, B. F. Gherman, C. J. Cramer, W. B. Tolman, *Inorg. Chem.* **2005**, *44*, 6989.
8. A. M. Reynolds, E. A. Lewis, N. W. Aboelella, W. B. Tolman, *Chem. Commun.* **2005**, *15*, 2014.
9. J. T. York, V. G. Young, Jr, W. B. Tolman, *Inorg. Chem.* **2006**, *45*, 4191.
10. R. Sarangi, N. Aboelella, K. Fujisawa, W. B. Tolman, B. Hedman, K. O. Hodgson, E. I. Solomon, *J. Am. Chem. Soc.* **2006**, *128*, 8286.

11. L. M. R. Hill, B. F. Gherman, N. W. Aboelella, C. J. Cramer, W. B. Tolman, *Dalton. Trans.* **2006**, 4944-4953.
12. D. E. Heppner, B. F. Gherman, W. B. Tolman, C. J. Cramer, *Dalton Trans.* **2006**, 4773.
13. N. W. Aboelella, B. F. Gherman, L. M. R. Hill, J. T. York, N. Holm, V. G. Young, Jr., C. J. Cramer, W. B. Tolman, *J. Am. Chem. Soc.* **2006**, *128*, 3445.
14. D. S. Laitar, C. J. N. Mathison, W. M. Davis, J. P. Sadighi, *Inorg. Chem.* **2003**, *42*, 7354.
15. C. Shimokawa, J. Teraoka, Y. Tachi, S. Itoh, *J. Inorg. Biochem.* **2006**, *100*, 1118.
16. X. Dai, T. H. Warren, *Chem. Commun.* **2001**, 1998.
17. X. Dai, T. H. Warren, *J. Am. Chem. Soc.* **2004**, *126*, 10085.
18. L. D. Amisial, X. Dai, R. A. Kinney, A. Krishnaswamy, T. H. Warren, *Inorg. Chem.* **2004**, *43*, 6537.
19. Y. M. Badiei, T. H. Warren, *J. Organomet. Chem.* **2005**, *690*, 5989.
20. Y. M. Badiei, A. Krishnaswamy, M. M. Melzer, T. H. Warren, *J. Am. Chem. Soc.* **2006**, *128*, 15056.
21. J. A. Tang, B. D. Ellis, T. H. Warren, J. V. Hanna, C. L. B. Macdonald, R. W. Schurko, *J. Am. Chem. Soc.* **2007**, *129*, 13049.
22. Y. M. Badiei, A. Dinescu, X. Dai, R. M. Palomino, F. W. Heinemann, T. R. Cundari, T. H. Warren, *Angew. Chem., Int. Ed.* **2008**, *47*, 9961.
23. S. Wiese, Y. M. Badiei, R. T. Gephhardt, S. Mossin, M. S. Varonka, M. M. Melzer, K. Meyer, T. R. Cundari, T. H. Warren, *Angew. Chem., Int. Ed.* **2010**, *49*, 8850.
24. R. T. Gephhardt III, D. L. Huang, M. J. B. Aguila, G. Schmidt, A. Shahu, T. H. Warren, *Angew. Chem., Int. Ed.* **2012**, *51*, 6488.
25. R. T. Gephart III, C. L. McMullin, N. G. Sapiezynski, E. S. Jang, M. J. B. Aguila, T. R. Cundari, T. H. Warren, *J. Am. Chem. Soc.* **2012**, *134*, 17350.
26. M. J. B. Aguila, Y. M. Badiei, T. H. Warren, *J. Am. Chem. Soc.* **2013**, *135*, 9399.
27. E. S. Jang, C. L. McMullin, M. Käß, K. Meyer, T. Cundari, T. H. Warren, *J. Am. Chem. Soc.* **2014**, *136*, 10930.
28. N. C. Tomson, K. D. Williams, X. Dai, S. Sproules, S. DeBeer, T. H. Warren, K. Wieghardt, *Chem. Sci.* **2015**, *6*, 2474.
29. P. Haack, C. Limberg, K. Ray, B. Braun, U. Kuhlmann, P. Hildebrandt, C. Herwig, *Inorg. Chem.* **2011**, *50*, 2133.

30. L. J. Murray, W. W. Weare, J. Shearer, A. D. Mitchell, K. A. Abboud, *J. Am. Chem. Soc.* **2014**, *136*, 13502.
31. For a preliminary communication detailing the synthesis of $[2\bullet\text{Cu}_2]_2$ see: A. Phanopoulos, M. Warren, A. J. P. White, A. Horton, M. R. Crimmin, *manuscript submitted for publication*.
32. Karlin & Zubieta, *Copper Coordination Chemistry Biochemical and Inorganic Perspectives*, Adenine Press, **1983**.
33. S. J. Lippard, J. M. Berg, *Principles of Bioinorganic Chemistry*, University Science Books, **1994**, Chapter 11, 283-347.
34. Z. Tyeklar, K. D. Karlin, *Acc. Chem. Res.* **1989**, *22*, 241.
35. C. J. Cramer, W. B. Tolman, *Acc. Chem. Res.* **2007**, *40*, 601.
36. E. I. Solomon, J. W. Ginsbach, D. E. Heppner, M. T. Kieber-Emmons, C. H. Kjaergaard, P. J. Smeets, L. Tian, J. S. Woertink, *Faraday Discuss.* **2011**, *148*, 11.
37. J. Spielmann, S. Harder, *Dalton Trans.* **2011**, *40*, 8314.
38. J. Spielmann, D. F.-J. Piesik, S. Harder, *Chem. Eur. J.* **2010**, *16*, 8307.
39. D. F. Piesik, S. Range, S. Harder, *Organometallics*, **2008**, 6178.
40. J. Vela, L. Zhu, C. J. Flaschenriem, W. W. Brennessel, R. J. Lachicotte, P. L. Holland, *Organometallics* **2007**, *26*, 3416.
41. M. Stollenz, F. Meyer, *Organometallics* **2012**, *31*, 7708.
42. M. Brookhart, M. L. Green, G. Parkin, *PNAS* **2007**, *104*, 6908.
43. P. O. Oguadinma and F. Schaper, *Organometallics*, **2009**, *28*, 4089.
44. P. O. Oguadinma and F. Schaper, *Organometallics*, **2009**, *28*, 6721.
45. M. Niemeyer, *Organometallics* **1998**, *17*, 4649.