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A one pot multi-component CuAAC "click" approach to bidentate and tridentate pyridyl-1,2,3-triazole ligands: Synthesis, X-ray structures and copper(II) and silver(I) complexes

James D. Crowley *, Pauline H. Bandeen, Lyall R. Hanton

Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand

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ABSTRACT

A one pot, multi-component CuAAC reaction has been developed for the generation of alkyl, benzyl or aryl substituted bi and tridentate pyridyl-1,2,3-triazole ligands from their corresponding halides, sodium azide and alkynes in excellent yields. The ligands have been fully characterized by elemental analysis, HR-ESMS, IR, ^{1}H and ^{13}C NMR and in the ferrocenyl substituted cases the structures were confirmed by X-ray crystallography. Additionally, we have examined the coordination chemistry of these ligands and found that a variety of geometrically diverse Cu(II) and Ag(I) complexes, including interesting tri and tetrasilver complexes, can be formed.

1. Introduction

Despite the central importance of ligand design and synthesis in modern coordination chemistry [1–17] there are very few modular, facile and high yielding methods for the generation of functionalised ligand scaffolds. The recently discovered Cu(I)-catalyzed 1,3-cycloaddition of organic azides with terminal alkynes [18,19] (the CuAAC reaction) offers great promise in this regard. The CuAAC methodology, a so-called 'click' [20] reaction, has been applied to functional molecule synthesis in a wide range of fields, including the biological and materials sciences, due to its reliability, mild reaction conditions and wide substrate scope [21–28]. Because the 1,4-functionalized 1,2,3-triazoles generated in the CuAAC reaction have the potential to act as N donor ligands a number of authors have examined its use in the synthesis of a range of mono [29–36], bi [33,37–44], tri [45–53] and polydentate [54–58] ligand architectures.

We have a long standing interest in the design and synthesis of functional ligand architectures [30,59–63] and became interested in exploiting the CuAAC reaction to synthesize polydentate ligands for the generation of metallosupramolecular architectures. However, retrosynthetic analysis of the desired target molecules indicated that some of the required synthons were potentially explosive low molecular weight polyazides [64]. Isolation of these types of molecules is a safety hazard and therefore ill-advised. Undeterred we set out to find a safe efficient method for the generation of polydentate 'click' chelators, herein we describe the development of such a method[1] [65,66]. We show that a one pot, multi-component CuAAC reaction can be used to generate alkyl, benzyl or aryl substituted bi and tridentate pyridyl-1,2,3-triazole ligands from their corresponding halides, sodium azide and alkynes in excellent yield. The potentially dangerous organic azides are generated *in situ* then captured by copper(I) acetylides, providing the desired pyridyl-1,2,3-triazole ligands in excellent yields. The method not only improves the synthetic efficiency for preparing previously reported bidentate and tridentate ligand architectures but also extends this family of ligands and potentially enables the rapid synthesis of functionalized ligand scaffolds. Finally, we have examined the coordination chemistry of these ligands and found that a variety of geometrically diverse Cu(II) and Ag(I) complexes, including interesting tri and tetrasilver complexes, can be formed.

2. Experimental

2.1. General

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. Dry CH_2Cl_2 and CH_3CN were obtained by passing the solvent through an activated alumina column on a PureSolvTM solvent purification system (Innovative Technologies Inc., MA). 2,6-Diethynylpyridine [67] was prepared according to the literature procedure. Petrol refers to the fraction of petroleum ether boiling in the range

* Corresponding author. Tel.: +64 34797731; fax: +64 34797906.
E-mail address: jcrowley@chemistry.otago.ac.nz (J.D. Crowley).

[1] During the preparation of this manuscript Schubert et al. has reported a similar approach, see Ref. [65] and [66].

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40–60 °C. Flash column chromatography was carried out using Kiesegel C60 (Fisher) as the stationary phase. Analytical TLC was performed on precoated silica gel plates (0.25 mm thick, 60F254, Merck, Germany) and observed under UV light. All melting points were determined using a Sanyo Gallenkamp apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 300 MHz Varian UNITY INOVA or 400 MHz Varian 400 MR spectrometer at 298 K. Chemical shifts are reported in parts per million and referenced to residual solvent. Coupling constants (J) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, quint. = quintet, q = quartet, t = triplet, d = doublet, s = singlet, br = broad. IR spectra were recorded on a Perkin–Elmer Spectrum BX FT-IR spectrometer using KBr discs. Microanalyses were performed at the Campbell Microanalytical Laboratory at the University of Otago. Electrospray mass spectra (ESMS) were collected on a Bruker micro-TOF-Q spectrometer.

Safety note: Sodium azide is very toxic and appropriate precautions should be taken. As low molecular weight organic azides are potential explosives, care must be taken during their handling [64]. Generally, when the total number of carbon (C) plus oxygen (O) atoms is less than the total numbers of nitrogen atoms (N) by a ratio of three, i.e., (C + O)/N < 3, the compound is considered as an explosive hazard. A standard PVC blast shield was used when necessary. Additionally, copper azides and acetylides are explosive when dry, and their traces should be removed before the CuAAC reaction products are dried. This is achieved by pouring the crude reaction mixture into 100 mL of aqueous EDTA/NH_4OH (1 M).

2.2. Experimental procedures

2.2.1. Ligand synthesis

*2.2.1.1. 2-(1-Benzyl-1H-1,2,3-triazol-4-yl)pyridine (**1a**).* To a stirred solution of 2-ethynylpyridine (0.62 g, 6.0 mmol, 1 equiv.) in DMF/H_2O (15 mL, 4:1) was added NaN_3 (0.42 g, 6.6 mmol, 1.1 equiv.), Na_2CO_3 (0.65 g, 6.0 mmol, 1 equiv.), $CuSO_4{\cdot}5H_2O$ (0.30 g, 1.20 mmol, 0.2 equiv.) and ascorbic acid (1.06 g, 6.0 mmol, 1.0 equiv.). Benzyl bromide (1.07 g, 6.3 mmol, 1.05 equiv.) was added and the reaction mixture was stirred at room temperature for 20 h. Upon completion (monitored by TLC or LC-MS), the crude mixture was poured into 100 mL of aqueous EDTA/NH_4OH (1 M). The off-white precipitate was isolated by filtration and washed with dilute aqueous EDTA/NH_4OH (10 mL, 1 M) and H_2O (10 mL) and vacuum dried. The solid was redissolved in CH_2Cl_2 (100 mL) and the organic phase was washed with H_2O (100 mL) and brine (100 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure giving **1a** as a white solid. If necessary the product can be further purified by chromatography (CH_2Cl_2 then 20% acetone in CH_2Cl_2). Yield: 1.3 g, 92%. Mp 115–116 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.56 (ddd, J = 4.9, J = 1.8, J = 1.0, 1H, H_a), 8.21 (d, J = 8.5, 1H, H_d), 8.18 (s, 1H, H_e), 7.83 (td, J = 7.8, 1.7, 1H, H_c), 7.40–7.31 (m, 5H, $H_{g,h,i}$), 7.27–7.25 (m, 1H, H_b), 5.61 (s, 2H, H_f). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.2, 149.2, 148.6, 137.0, 134.3, 129.2, 128.9, 128.3, 122.7, 122.0, 120.3, 54.4; I. R. (KBr): υ (cm^{-1}) 3102, 3090, 3066, 2924, 1603, 1595, 1421, 1345, 1224, 1150, 1072, 1045, 995, 786, 727. HRESI-MS (MeOH): m/z = 237.1138 $[M+H]^+$ (calc. for $C_{14}H_{13}N_4$ 237.1140 $[M+H]^+$), 259.0967 $[M+Na]^+$ (calc. for $C_{14}H_{12}N_4Na$ 259.0959 $[M+Na]^+$; *Anal.* Calc. for $C_{14}H_{12}N_4$: C, 71.17; H, 5.12; N, 23.71. Found: C, 70.77; H, 5.06; N, 23.77%.

*2.2.1.2. 2-(1-Ferrocenylmethyl-1H-1,2,3-triazol-4-yl)pyridine (**1b**).* To a stirred solution of 2-ethynylpyridine (0.21 g, 2.0 mmol, 1 equiv.) in DMF/H_2O (15 mL, 4:1) was added NaN_3 (0.15 g, 2.5 mmol, 1.25 equiv.), Na_2CO_3 (0.21 g, 2.0 mmol, 1 equiv.), $CuSO_4{\cdot}5H_2O$ (0.20 g, 0.8 mmol, 0.4 equiv.) and ascorbic acid (0.35 g, 2.0 mmol, 1.0 equiv.). (Ferrocenylmethyl)trimethylammonium iodide (0.79 g, 2.0 mmol, 1.02 equiv.) was added and the reaction mixture was heated to 95 °C for 20 h. The resulting suspension was poured into 100 mL of aqueous EDTA/NH_4OH (1 M). The orange precipitate was isolated by filtration and washed with dilute EDTA/NH_4OH (10 mL) and H_2O (10 mL) then vacuum dried. The solid was redissolved in CH_2Cl_2 (100 mL) and the organic phase was washed with H_2O (100 mL) and brine (100 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure giving **1b** as an orange solid. If necessary the product can be further purified by chromatography (CH_2Cl_2 then 20% acetone in CH_2Cl_2). Yield: 0.58 g, 85%. Mp 174–175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.55 (ddd, J = 0.9, J = 1.7, J = 4.8, 1H, H_a), 8.23–8.11 (m, 1H, H_d), 8.05 (s, 1H, H_e), 7.76 (td, J = 1.8, J = 7.8, 1H, H_c), 7.21 (ddd, J = 1.2, J = 4.9, J = 7.5, 1H, H_b), 5.37 (s, 2H, H_f), 4.31 (t, J = 1.8, 2H, H_g), 4.23 (t, J = 1.8, 2H, H_h), 4.21 (s, 5H, H_i); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.4, 149.4, 148.3, 137.0, 134.2, 122.8, 121.4, 120.2, 80.5, 69.2, 69.1, 68.9, 50.3; I.R. (KBr): υ (cm^{-1}) 3105, 3096, 3075, 2925, 1603, 1595, 1543, 1426, 1405, 1333, 1260, 1234, 1223, 1191, 1075, 1050, 996, 980, 928, 853, 824, 785, 743, 729; HRESI-MS (CH_2Cl_2/MeOH): m/z = 367.0614 $[M+Na]^+$ (calc. for $C_{18}H_{16}FeN_4Na$ 367.0617 $[M+Na]^+$); *Anal.* Calc. for $C_{18}H_{16}FeN_4$: C, 62.81; H, 4.69; N, 16.28. Found: C, 62.76; H, 4.86; N, 16.30%.

*2.2.1.3. 2-(1-Octyl-1H-1,2,3-triazol-4-yl)pyridine (**1c**).* To a stirred solution of 2-ethynylpyridine (0.62 g, 6.0 mmol, 1 equiv.) in DMF/H_2O (15 mL, 4:1) was added NaN_3 (0.47 g, 7.2 mmol, 1.2 equiv.), Na_2CO_3 (0.65 g, 6.0 mmol, 1 equiv.), $CuSO_4{\cdot}5H_2O$ (0.30 g, 1.2 mmol, 0.2 equiv.) and ascorbic acid (1.05 g, 6.0 mmol, 1.0 equiv.). 1-Bromooctane (1.27 g, 6.6 mmol, 1.1 equiv.) was added and the reaction mixture was stirred at 95 °C for 20 h. The suspension was then partitioned between aqueous NH_4OH/EDTA (1 M, 100 mL) and CH_2Cl_2 (100 mL) and the layers separated. The organic phase was washed with H_2O (100 mL) and brine (100 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Chromatography (CH_2Cl_2 then 10% acetone in CH_2Cl_2) gave **1c** as a white solid. Yield: 0.71 g, 88%. Mp 67–68 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.52–8.50 (m, 1H, H_a), 8.12 (d, J = 8.0, 1H, H_d), 8.07 (s, 1H, H_e), 7.71 (td, J = 1.8, J = 7.8, 1H, H_c), 7.16 (ddd, J = 1.1, J = 4.9, J = 7.5, 1H, H_b), 4.35 (t, J = 7.2, 2H, H_f), 1.88 (p, J = 7.3, 2H, H_g), 1.24 (m, 10H, $H_{h\text{-}l}$), 0.80 (t, J = 6.7, 3H, H_m); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.7, 149.6, 148.6, 137.1, 123.0, 122.9, 120.4, 50.8, 31.9, 30.5, 29.3, 29.2, 26.7, 22.8, 14.3; I.R. (KBr): υ (cm^{-1}) 3120, 3050, 2928, 1605, 1594, 1421, 1377, 1345, 1299, 1227, 1149, 1080, 1047, 996, 851, 798, 751; HRESI-MS (CH_2Cl_2/MeOH): m/z = 281.1755 $[M+Na]^+$ (calc. for $C_{15}H_{22}N_4Na$ 281.1742 $[M+Na]^+$); *Anal.* Calc. for $C_{15}H_{22}N_4{\cdot}(0.66H_2O)$: C, 66.66; H, 8.70; N, 20.73. Found: C, 66.77; H, 8.34; N, 20.82%.

*2.2.1.4. 2-(1-Phenyl-1H-1,2,3-triazol-4-yl)pyridine (**1d**).* To a stirred argon degassed solution of iodobenzene (0.41 g, 2.2 mmol, 1.1 equiv.) in EtOH/H_2O (10 mL, 7:3) was added NaN_3 (0.16 g, 2.4 mmol, 1.2 equiv.), CuI (0.08 g, 0.4 mmol, 0.2 equiv.), N,N′-Dimethylethylenediamine (0.05 g, 0.6 mmol, 0.3 equiv.) and sodium ascorbate (0.20 g, 1.0 mmol, 0.5 equiv.). The reaction was then heated to reflux under an argon atmosphere for 2 h. After this time had elapsed the reaction mixture was cooled to room temperature and 2-ethynylpyridine (0.21 g, 2.0 mmol, 1 equiv.), $CuSO_4{\cdot}5H_2O$ (0.10 g, 0.2 mmol, 0.2 equiv.) and sodium ascorbate (0.20 g, 1.0 mmol, 0.5 equiv.) were added to the reaction mixture and the resulting suspension was stirred at room temperature for 20 h. The reaction mixture was then poured into aqueous NH_4OH/EDTA (1 M, 100 mL). The resulting precipitate was isolated by filtration and washed well with NH_4OH/EDTA (10 mL) and H_2O (10 mL) then vacuum dried. Chromatography (CH_2Cl_2 then 19:1 CH_2Cl_2/acetone) gave **1d** as a white solid. Yield: 0.39 g, 89%. Mp 90–91 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.63 (ddd, J = 0.9, J = 1.7, J = 4.9, 1H, H_a), 8.61 (s, 1H, H_e), 8.26 (m, 1H, H_d), 7.85–7.80 (m,

3H, $H_{c,f}$), 7.59–7.52 (m, 2H, H_g), 7.46–7.43 (m, 1H, H_h), 7.27 (m, 1H, H_b); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.0, 149.5, 149.0, 137.2, 137.0, 129.9, 128.9, 123.1, 120.5, 120.4, 119.9; I. R. (KBr): υ (cm^{-1}) 3117, 3049, 2925, 1599, 1592, 1567, 1543, 1411, 1353, 1273, 1237, 1146, 1090, 1073, 1036, 993, 842, 794, 758; HRESI-MS (CH_2Cl_2/MeOH): m/z = 245.0813 $[M+Na]^+$ (calc. for $C_{13}H_{10}N_4Na$ 245.0798 $[M+Na]^+$); *Anal.* Calc. for $C_{13}H_{10}N_4$: C, 70.26; H, 4.54; N, 25.21. Found: C, 70.21; H, 4.73; N, 24.93%.

*2.2.1.5. 2,6-Bis(1-benzyl-1H-1,2,3-triazol-4-yl)pyridine (**2a**).* To a stirred solution of 2,6-diethynylpyridine (0.38 g, 3 mmol, 1 equiv.) in DMF/H_2O (15 mL, 4:1) was added NaN_3 (0.41 g, 6.2 mmol, 2.1 equiv.), Na_2CO_3 (0.63 g, 3.0 mmol, 1.0 equiv.), $CuSO_4{\cdot}5H_2O$ (0.15 g, 0.6 mmol, 0.2 equiv.), and ascorbic acid (0.42 g, 3.0 mmol, 1 equiv.). Benzyl bromide (1.02 g, 6.1 mmol, 2.05 equiv.) was added and the reaction mixture was stirred at room temperature for 20 h. The suspension was then partitioned between aqueous NH_4OH/EDTA (1 M, 100 mL) and CH_2Cl_2 (100 mL) and the layers separated. The organic phase was washed with H_2O (100 mL) and brine (100 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Chromatography (CH_2Cl_2 then 2% acetone in CH_2Cl_2) gave **2a** as a white solid. Yield: 1.06 g, 90%. Mp 196–198 °C; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.09 (d, J = 7.7, 2H, H_b), 8.04 (s, 2H, H_c), 7.85 (t, J = 7.7, 1H, H_a), 7.45–7.28 (m, 10H, $H_{e,f,g}$), 5.59 (s, 4H, H_d); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.9, 148.8, 137.8, 134.6, 129.2, 128.8, 128.1, 122.0, 119.5, 54.3; I. R. (KBr): υ (cm^{-1}) 3105, 3056, 2946, 1603, 1595, 1421, 1345, 1224, 1150, 1072, 1045, 995, 786, 727. HRESI-MS (MeOH): m/z = 394.1704 $[M+H]^+$ (calc. for $C_{23}H_{20}N_7$ 394.1780 $[M+H]^+$), 416.1604 $[M+Na]^+$ (calc. for $C_{23}H_{19}N_7Na$ 416.1600 $[M+Na]^+$; *Anal.* Calc. for $C_{23}H_{19}N_7$: C, 70.21; H, 4.87; N, 24.92. Found: C, 70.34; H, 4.79; N, 25.20%.

*2.2.1.6. 2,6-Bis(1-ferrocenylmethyl-1H-1,2,3-triazol-4-yl)pyridine (**2b**).* To a stirred solution of (ferrocenylmethyl)trimethylammonium iodide (1.08 g, 2.8 mmol, 2.1 equiv.) in DMF/H_2O (15 mL, 4:1) was added NaN_3 (0.19 g, 2.9 mmol, 2.2 equiv.) and the reaction mixture was stirred at 95 °C for 16 h. The reaction mixture was cooled to room temperature and $CuSO_4{\cdot}5H_2O$ (0.17 g, 0.6 mmol, 0.5 equiv.), sodium ascorbate (0.27 g, 1.3 mmol, 1 equiv.) and 2,6-diethynylpyridine (0.17 g, 1.3 mmol, 1 equiv.) were added and the resulting suspension was stirred at room temperature for 20 h. The suspension was then partitioned between aqueous NH_4OH/EDTA (1 M, 100 mL) and CH_2Cl_2 (100 mL) and the layers separated. The organic phase was washed with H_2O (100 mL) and brine (100 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Chromatography (CH_2Cl_2 then 8:2 acetone/CH_2Cl_2) gave **2b** as an orange/red solid. Yield: 0.63 g, 77%. Mp 165 °C (decomp.); ^1H NMR (300 MHz, $CDCl_3$) δ: 8.08–8.04 (m, 4H, $H_{b,c}$), 7.83 (t, J = 7.5, 1H, H_a), 5.35 (s, 4H, H_d), 4.31 (t, J = 1.8, 4H, H_e), 4.23–4.21 (m, 14H, $H_{f,g}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.1, 148.2, 137.7, 121.5, 119.3, 80.8, 69.1, 69.0, 68.9, 50.3; I.R. (KBr): υ (cm^{-1}) 3105, 3009, 2940, 1603, 1595, 1421, 1345, 1224, 1150, 1072, 1045, 995, 786, 727; HRESI-MS (MeOH): m/z = 610.1037 $[M+H]^+$ (calc. for $C_{31}H_{27}Fe_2N_7$ 610.1100 $[M+H]^+$), 632.0925 $[M+Na]^+$ (calc. for $C_{31}H_{27}Fe_2N_7Na$ 632.0920 $[M+Na]^+$; *Anal.* Calc. for $C_{31}H_{27}Fe_2N_7{\cdot}(H_2O)$: C, 59.31; H, 4.41; N, 15.64. Found: C, 59.35; H, 4.66; N, 15.63%.

*2.2.1.7. 2,6-Bis(1-octyl-1,2,3-triazol-4-yl)pyridine (**2c**).* To a stirred solution of 2,6-diethynylpyridine (0.38 g, 3.0 mmol, 1 equiv.) in DMF/H_2O (15 mL, 4:1) was added NaN_3 (0.41 g, 6.2 mmol, 2.1 equiv.), Na_2CO_3 (0.63 g, 3.0 mmol, 1.0 equiv.), $CuSO_4{\cdot}5H_2O$ (0.15 g, 0.6 mmol, 0.2 equiv.), and ascorbic acid (0.42 g, 3.0 mmol, 1 equiv.). 1-Bromooctane (1.18 g, 6.1 mmol, 2.05 equiv.) was added and the reaction mixture was stirred at 95 °C for 16 h. The suspension was then partitioned between aqueous NH_4OH/EDTA (1 M, 100 mL) and CH_2Cl_2 (100 mL) and the layers separated. The organic phase was washed with H_2O (100 mL) and brine (100 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Chromatography (CH_2Cl_2 then 2% acetone in CH_2Cl_2) gave **2c** as a white solid. Yield: 0.79 g, 88%. Mp 119–121 °C; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.20 (s, 2H, H_c), 8.11 (d, J = 7.8, 2H, H_b), 7.88 (t, J = 7.8, 1H, H_a), 4.44 (t, J = 7.2, 4H, H_d), 1.98 (p, J = 7.4, 4H, H_e), 1.33 (m, 20H, H_{f-j}), 0.89 (t, J = 6.8, 6H, H_k); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.2, 148.4, 137.9, 122.0, 119.3, 50.6, 31.8, 30.4, 29.2, 26.6, 22.7, 14.2; I.R. (KBr): υ (cm^{-1}) 3156, 3039, 2955, 1607, 1576, 1310, 1231, 1216, 1191, 1081, 1045, 992, 975, 797; HRESI-MS (CH_2Cl_2/CH_3CN): m/z = 460.3190 $[M+Na]^+$ (calc. for $C_{25}H_{39}N_7Na$ 460.3159 $[M+Na]^+$); *Anal.* Calc. for $C_{25}H_{39}N_7$: C, 68.61; H, 8.98; N, 22.40. Found: C, 68.74; H, 9.13; N, 22.66%.

*2.2.1.8. 2,6-Bis(1-phenyl-1,2,3-triazol-4-yl)pyridine (**2d**).* To a stirred argon degassed solution of iodobenzene (0.86 g, 4.2 mmol, 2.1 equiv.) in EtOH/H_2O (10 mL, 7:3) was added NaN_3 (0.29 g, 4.4 mmol, 1.2 equiv.), CuI (0.08 g, 0.4 mmol, 0.2 equiv.), N,N′-Dimethylethylenediamine (0.05 g, 0.6 mmol, 0.3 equiv.) and sodium ascorbate (0.20 g, 1.0 mmol, 0.5 equiv.). The reaction was then heated to reflux under an argon atmosphere for 2 h. After this time had elapsed the reaction mixture was cooled to room temperature and 2,6-diethynylpyridine (0.26 g, 2.0 mmol, 1 equiv.), $CuSO_4{\cdot}5H_2O$ (0.10 g, 0.2 mmol, 0.2 equiv.), and sodium ascorbate (0.20 g, 1.0 mmol, 0.5 equiv.) were added to the reaction mixture and the resulting suspension was stirred at room temperature for 20 h. The reaction mixture was then poured into aqueous NH_4OH/EDTA (1 M, 100 mL). The resulting precipitate was isolated by filtration and washed well with H_2O then vacuum dried. Chromatography (CH_2Cl_2 then 9:1 CH_2Cl_2/acetone) gave **2d** as a yellow solid. Yield: 0.64 g, 88%. Mp 201–202 °C; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.67 (s, 2H, H_c), 8.23 (d, J = 7.8, 2H, H_b), 7.96 (t, J = 7.8, 1H, H_a), 7.87 (d, J = 7.7, 4H, H_e), 7.58 (t, J = 7.5, 4H, H_f), 7.49 (t, J = 7.3, 2H, H_g); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.0, 149.1, 138.1, 137.2, 130.1, 129.2, 120.7, 120.5, 120.0; I. R. (KBr): υ (cm^{-1}) 3117, 3061, 2950, 1599, 1592, 1567, 1543, 1411, 1353, 1273, 1237, 1146, 1090, 1073, 1036, 993, 842, 794, 758; HRESI-MS (CH_2Cl_2/MeOH): m/z = 388.1291 $[M+Na]^+$ (calc. for $C_{21}H_{15}N_7Na$ 388.1281 $[M+Na]^+$); *Anal.* Calc. for $C_{21}H_{15}N_7{\cdot}(0.25H_2O)$: C, 68.19; H, 4.22; N, 26.51. Found: C, 68.31; H, 4.40; N, 26.74%.

*2.2.1.9. 2-[(4-Phenyl-1H-1,2,3-triazol-1-yl)methyl]pyridine (**3a**).* To a stirred solution of phenylacetylene (1.12 g, 11 mmol, 1.1 equiv.) in DMF/H_2O (20 mL, 4:1) was added NaN_3 (0.78 g, 12 mmol, 1.2 equiv.), Na_2CO_3 (3.15 g, 30 mmol, 3 equiv.), $CuSO_4{\cdot}5H_2O$ (0.49 g, 2.0 mmol, 0.2 equiv.), and ascorbic acid (1.40 g, 10 mmol, 1.0 equiv.). 2-(Bromomethyl)pyridine hydrobromide (2.52 g, 10 mmol, 1.0 equiv.) was added and the reaction mixture was stirred at room temperature for 16 h. The suspension was then partitioned between aqueous NH_4OH/EDTA (1 M, 100 mL) and CH_2Cl_2 (100 mL) and the layers separated. The organic phase was washed with H_2O (100 mL) and brine (100 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Chromatography (CH_2Cl_2 then CH_2Cl_2/acetone 9:1) gave **3a** as a white solid. Yield: 2.06 g, 88%. Mp 79–80 °C; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.62 (ddd, J = 4.86, J = 1.70, J = 0.90 Hz, 1H, H_a), 7.93 (s, 1H, H_f), 7.86–7.80 (m, 2H, H_g), 7.70 (dt, J = 7.71, J = 7.71, J = 1.81 Hz, 1H, H_c), 7.44–7.22 (m, 5H, $H_{b,d,h,i}$), 5.70 (s, 2H, H_e); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 154.6, 149.9, 148.4, 137.7, 130.7, 129.0, 128.4, 125.9, 123.7, 122.7, 120.4, 55.8; I.R. (KBr): υ (cm^{-1}) 3105, 1603, 1592, 1345, 1217, 1200, 1073, 1044, 996, 976, 910, 850, 818, 801, 760, 727. HRESI-MS (MeOH): m/z = 237.1135 $[M+H]^+$ (calc. for $C_{14}H_{13}N_4$ 237.1140 $[M+H]^+$), 259.0954 $[M+Na]^+$ (calc. for $C_{14}H_{12}N_4Na$ 259.0959 $[M+Na]^+$; *Anal.* Calc. for $C_{14}H_{12}N_4$: C, 71.17; H, 5.12; N, 23.71. Found: C, 71.10; H, 5.15; N, 23.58%.

*2.2.1.10. 2-[(4-Ferrocenyl-1H-1,2,3-triazol-1-yl)methyl]pyridine (**3b**).* To a stirred solution of ethynylferrocene (2.73 g, 13 mmol, 1.2 equiv.) in DMF/H_2O (15 mL, 4:1) was added NaN_3 (0.84 g, 13 mmol, 1.3 equiv.), Na_2CO_3 (3.15 g, 30 mmol, 3 equiv.), $CuSO_4{\cdot}5H_2O$ (0.50 g, 2 mmol, 0.2 equiv.), and ascorbic acid (1.40 g, 8.0 mmol, 0.8 equiv.). 2-(Chloromethyl)pyridine hydrochloride (1.66 g, 10 mmol, 1.0 equiv.) was added and the reaction mixture was stirred at room temperature for 24 h. The suspension was then partitioned between aqueous NH_4OH/EDTA (1 M, 100 mL) and CH_2Cl_2 (100 mL) and the layers separated. The organic phase was washed with H_2O (100 mL) and brine (100 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Chromatography (CH_2Cl_2 then CH_2Cl_2/acetone 9:1) gave **3b** as an orange solid. Yield: 2.80 g, 82%. Mp 162–163 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ: 8.64 (d, J = 4.5, 1H, H_a), 7.71 (td, J = 1.6, 7.7, 1H, H_c), 7.64 (s, 1H, H_f), 7.29 (t, J = 6.2, 1H, H_b), 7.20 (d, J = 7.8, 1H, H_d), 5.69 (s, 2H, H_e), 4.74 (t, J = 1.8, 2H, H_g), 4.31 (t, J = 1.8, 2H, H_h), 4.08 (s, 5H, H_i); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 154.9, 149.9, 147.5, 137.6, 123.6, 122.5, 119.7, 75.6, 69.82, 68.9, 66.9, 55.8; I.R. (KBr): υ (cm^{-1}) 3105, 3011, 2948, 1603, 1589, 1348, 1219, 1190, 1141, 1104, 1086, 1034, 1020, 942, 877, 815, 801, 763, 725; HRESI-MS (MeOH): m/z = 345.0785 $[M+H]^+$ (calc. for $C_{18}H_{17}FeN_4$ 345.0797 $[M+H]^+$), 367.0622 $[M+Na]^+$ (calc. for $C_{18}H_{16}FeN_4Na$ 367.0617 $[M+Na]^+$; *Anal.* Calc. for $C_{18}H_{16}FeN_4$: C, 62.81; H, 4.69; N, 16.28. Found: C, 62.71; H, 4.66; N, 16.19%.

*2.2.1.11. 2-[(4-Octyl-1H-1,2,3-triazol-1-yl)methyl]pyridine (**3c**).* To a stirred solution of decyne (0.31 g, 2.2 mmol, 1.1 equiv.) in DMF/H_2O (20 mL, 4:1) was added NaN_3 (0.13 g, 2.2 mmol, 1.1 equiv.), Na_2CO_3 (0.90 g, 6.0 mmol, 3 equiv.), $CuSO_4{\cdot}5H_2O$ (0.20 g, 0.8 mmol, 0.4 equiv.), ascorbic acid (0.35 g, 2.0 mmol, 1.0 equiv.) and 2-(bromomethyl)pyridine hydrobromide (0.51 g, 2.0 mmol, 1.0 equiv.) and the reaction mixture was stirred at room temperature for 16 h. The suspension was then partitioned between aqueous NH_4OH/EDTA (1 M, 100 mL) and CH_2Cl_2 (100 mL) and the layers separated. The organic phase was washed with H_2O (100 mL) and brine (100 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Chromatography (CH_2Cl_2 then CH_2Cl_2/acetone 9:1) gave **3c** as a white solid. Yield: 0.50 g, 91%. Mp 48–50 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.59 (d, J = 4.4, 1H, H_a), 7.68 (td, J = 1.8, 7.7, 1H, H_c), 7.42 (s, 1H, H_f), 7.25 (t, J = 7.6, 1H, H_b), 7.15 (d, J = 7.8, 1H, H_d), 5.62 (s, 2H, H_e), 2.71 (t, J = 6.8, 2H, H_g), 1.64 (m, 2H, H_h), 1.28 (m, 10H, $H_{i,j,k,l,m}$), 0.87 (t, J = 6.7, 3H, H_n); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 155.1, 149.8, 149.2, 137.5, 123.5, 122.5, 121.3, 55.7, 32.0, 29.7, 29.6, 29.5, 29.4, 25.9, 22.8, 14.3; I.R. (KBr): υ (cm^{-1}) 3583, 3120, 3065, 1595, 1585, 1571, 1555, 1302, 1218, 1157, 1121, 1053, 1028, 966, 861, 834, 801, 761, 750; HRESI-MS (MeOH): m/z = 273.2078 $[M+H]^+$ (calc. for $C_{15}H_{25}N_4$ 273.2074 $[M+H]^+$), 295.1939 $[M+Na]^+$ (calc. for $C_{16}H_{24}N_4Na$ 295.1893 $[M+Na]^+$; *Anal.* Calc. for $C_{16}H_{24}N_4{\cdot}(0.33H_2O)$: C, 69.04; H, 8.89; N, 20.13. Found: C, 68.93; H, 9.04; N, 20.24%.

*2.2.1.12. 2,6-Bis[(4-phenyl-1H-1,2,3-triazol-1-yl)methyl]pyridine (**4a**).* To a stirred solution of phenylacetylene (1.12 g, 11 mmol, 1.1 equiv.) in DMF/H_2O (20 mL, 4:1) was added NaN_3 (0.72 g, 11 mmol, 2.1 equiv.), Na_2CO_3 (0.53 g, 5 mmol, 1 equiv.), $CuSO_4{\cdot}5H_2O$ (0.49 g, 2.0 mmol, 0.2 equiv.) and ascorbic acid (0.88 g, 5.0 mmol, 1.0 equiv.). 2,6-(Bromomethyl)pyridine (1.32 g, 5.0 mmol, 1.0 equiv.) was added and the reaction mixture was stirred at room temperature for 16 h. The suspension was then partitioned between aqueous NH_4OH/EDTA (1 M, 100 mL) and CH_2Cl_2 (100 mL) and the layers separated. The organic phase was washed with H_2O (100 mL) and brine (100 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Chromatography (CH_2Cl_2 then CH_2Cl_2/acetone 9:1) gave **4a** as a white solid. Yield: 1.88 g, 90%. Mp 159–161 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.89 (s, 2H, H_d), 7.86–7.77 (m, 2H, H_a), 7.72 (t, J = 7.8, 1H, H_b), 7.36 (m, 8H, $H_{e,f}$), 7.21 (d, J = 7.8, 2H, H_g), 5.70 (s, 4H, H_c); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 154.9, 149.9, 147.5, 137.5, 123.7, 123.6, 122.5, 119.7, 119.6, 55.8; I.R. (KBr): υ (cm^{-1}) 3105, 3067, 2976, 1603, 1592, 1345, 1217, 1200, 1073, 1044, 996, 976, 910, 850, 818, 801, 760, 727. HRESI-MS (MeOH): m/z = 394.4505 $[M+H]^+$ (calc. for $C_{23}H_{20}N_7$ 394.4518 $[M+H]^+$), 416.1613 $[M+Na]^+$ (calc. for $C_{23}H_{19}N_7Na$ 416.1600 $[M+Na]^+$. *Anal.* Calc. for $C_{23}H_{19}N_7$: C, 70.21; H, 4.87; N, 24.92. Found: C, 69.93; H, 4.95; N, 25.13%.

*2.2.1.13. 2,6-Bis[(4-ferrocenyl-1H-1,2,3-triazol-1-yl)methyl]pyridine (**4b**).* To a stirred solution of ethynylferrocene (1.38 g, 6.6 mmol, 2.2 equiv.) in DMF/H_2O (20 mL, 4:1) was added NaN_3 (0.45 g, 6.9 mmol, 2.3 equiv.), Na_2CO_3 (0.94 g, 8.9 mmol, 3 equiv.), $CuSO_4{\cdot}5H_2O$ (0.40 g, 1.5 mmol, 0.5 equiv.) and ascorbic acid (0.53 g, 3.0 mmol, 1.0 equiv.). 2-(Bromomethyl)pyridine hydrobromide (1.34 g, 3.0 mmol, 1.0 equiv.) was added and the reaction mixture was stirred at room temperature for 24 h. The suspension was then partitioned between aqueous NH_4OH/EDTA (1 M, 100 mL) and CH_2Cl_2 (100 mL) and the layers separated. The organic phase was washed with H_2O (100 mL) and brine (100 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Chromatography (CH_2Cl_2 then gradient to CH_2Cl_2/acetone 8:2) gave **4b** as an orange/red solid. Yield: 1.20 g, 65%. Mp 192–194 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.71 (t, J = 7.8, 1H, H_a), 7.58 (s, 2H, H_d), 7.13 (d, J = 7.8, 2H, H_b), 5.67 (s, 4H, H_c), 4.73 (t, J = 1.8, 4H, H_e), 4.31 (t, J = 1.8, 4H, H_f), 4.08 (s, 10H, H_g); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 155.1, 147.7, 138.9, 121.9, 119.8, 76.1, 70.8, 69.4, 67.2, 55.4; I.R. (KBr): υ (cm^{-1}) 3115, 3102, 3083, 2929, 1654, 1593, 1574, 1338, 1231, 1220, 1201, 1191, 1151, 1106, 1097, 1050, 1030, 999, 893, 878, 821, 807, 773, 761, 722; HRESI-MS (MeOH): m/z = 610.1146 $[M+H]^+$ (calc. for $C_{31}H_{28}Fe_2N_7$ 610.1100 $[M+H]^+$), 632.0975 $[M+Na]^+$ (calc. for $C_{23}H_{19}N_7Na$ 632.0920 $[M+Na]^+$; *Anal.* Calc. for $C_{31}H_{27}Fe_2N_7$: C, 61.11; H, 4.47; N, 16.09. Found: C, 61.37; H, 4.49; N, 16.39%.

*2.2.1.14. 2,6-Bis[(4-octyl-1H-1,2,3-triazol-1-yl)methyl]pyridine (**4c**).* To a stirred solution of decyne (0.58 g, 4.2 mmol, 2.1 equiv.) in DMF/H_2O (20 mL, 4:1) was added NaN_3 (0.27 g, 4.2 mmol, 2.1 equiv.), Na_2CO_3 (0.22 g, 2.0 mmol, 1 equiv.), $CuSO_4{\cdot}5H_2O$ (0.20 g, 0.8 mmol, 0.4 equiv.), ascorbic acid (0.35 g, 2.0 mmol, 1.0 equiv.) and 2,6-(bromomethyl)pyridine (0.53 g, 2 mmol, 1.0 equiv.) and the reaction mixture was stirred at room temperature for 16 h. The suspension was then partitioned between aqueous NH_4OH/EDTA (1 M, 100 mL) and CH_2Cl_2 (100 mL) and the layers separated. The organic phase was washed with H_2O (100 mL) and brine (100 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure to give **10c** as a white solid. Yield: 0.86 g, 92%. Mp 114–115 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.67 (t, J = 7.8, 1H, H_a), 7.38 (s, 2H, H_d), 7.08 (d, J = 7.8, 2H, H_b), 5.62 (s, 4H, H_c), 2.74 (t, J = 6.8, 4H, H_e), 1.71–1.67 (m, 4H, H_f), 1.31 (m, 20H, H_{g-j}), 0.89 (t, J = 6.7, 6H, H_l); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 155.2, 149.3, 138.7, 121.7, 121.4, 55.3, 32.0, 29.7, 29.6, 29.5, 29.4, 25.9, 22.8, 14.3; I.R. (KBr): υ (cm^{-1}) 3112, 3063, 2926, 1593, 1575, 1557, 1325, 1215, 1178, 1119, 1051, 1030, 997, 928, 863, 839, 824, 805, 770; HRESI-MS (MeOH): m/z = 488.3465 $[M+Na]^+$ (calc. for $C_{27}H_{43}N_7Na$ 488.3472 $[M+Na]^+$; *Anal.* Calc. for $C_{27}H_{43}N_7$: C, 69.64; H, 9.31; N, 21.05. Found: C, 69.23; H, 9.36; N, 21.31%.

2.2.2. Synthesis of $CuCl_2$ complexes

*2.2.2.1. [(**1a**)$_2$CuCl](Cl).* A solution (5 mL, MeOH) of anhydrous $CuCl_2$ (0.067 g, 0.5 mmol, 0.5 equiv.) was added dropwise slowly to a $CHCl_3$ (5 mL) solution of the ligand **1a** (0.236 g, 1.0 mmol, 1 equiv.). The resulting blue-green solution was stirred at room temperature for 1 h. The volume of solvent was reduced by half under reduced pressure and a blue/green solid precipitated. The solid

was filtered off and was washed Et_2O and petrol. Yield: 0.295 g, 95%. X-ray quality blue-green crystals were obtained by slow evpouration of a methanol solution of [(**1a**)$_2$CuCl](Cl). Mp 204 °C (decomp.); I.R. (KBr): υ (cm^{-1}) 3500–3200 (br), 3081, 2925, 1616, 1580, 196, 1348, 1294, 1272, 1248, 1216, 1153, 1119, 1095, 1063, 1027, 995, 918, 867, 827, 798, 782, 735; HRESI-MS (MeOH): m/z = 535.1436 [Cu(**1a**)$_2$]$^+$ (calc. for $C_{28}H_{24}CuN_8$ 535.1420 [Cu(**1a**)$_2$]); Λ_M (MeOH) = 145 Ω^{-1} cm^2 mol^{-1}; *Anal.* Calc. for $C_{28}H_{24}CuCl_2N_8\bullet(3H_2O)$: C, 50.87; H, 4.57; N, 16.95. Found: C, 51.19; H, 3.92; N, 17.16%.

*2.2.2.2. [(**2a**)CuCl$_2$].* A solution (5 mL, MeOH) of anhydrous $CuCl_2$ (0.078 g, 0.57 mmol, 1 equiv.) was added dropwise slowly to a CH_2Cl_2 (5 mL) solution of the ligand **2a** (0.226 g, 0.57 mmol, 1 equiv.). A green solid precipitated immediately and the resulting suspension was stirred at room temperature for 1 h. The volume of solvent was reduced by half under reduced pressure and the green solid isolated by filtration and was purified by recrystallization (hot CH_3OH) to give copper complex [(**2a**)$CuCl_2$] as a blue-green solid (0.280 g, 91%). Mp 236 °C (decomp.); I.R. (KBr): υ (cm^{-1}) 3300–3200 b, 3130, 3075, 2936, 1617, 1585, 1268, 1210, 1157, 1119, 1063, 1051, 1025, 974, 813, 765, 719. HRESI-MS (MeOH): m/z = 456.1012 [Cu(**2a**)]$^+$ (calc. for $C_{23}H_{19}CuN_7$ 456.0998 [Cu(**2a**)]$^+$), 424.6353 [Cu(**2a**)$_2$]$^{2+}$ (calc. for $C_{46}H_{38}CuN_{14}$ 424.6350 [Cu(**2a**)]$^+$), 416.1572 (calc. for $C_{23}H_{19}N_7Na$ 416.1600 [Na(**2a**)]$^+$); Λ_M (MeOH) = 94 Ω^{-1} cm^2 mol^{-1}; *Anal.* Calc. for $C_{23}H_{19}Cl_2CuN_7\cdot H_2O$: C, 50.60; H, 3.88; N, 17.96. Found: C, 50.89; H, 3.84; N, 18.08%.

*2.2.2.3. [(**3a**)$_2$CuCl$_2$].* A solution (5 mL, MeOH) of anhydrous $CuCl_2$ (0.067 g, 0.5 mmol, 0.5 equiv.) was added dropwise slowly to a $CHCl_3$ (5 mL) solution of the ligand **3a** (0.236 g, 1.0 mmol, 1 equiv.). The resulting blue-green solution was stirred at room temperature for 1 h. The volume of solvent was reduced by half under reduced pressure and a blue/green solid precipitated. The solid was filtered off and was washed with Et_2O and petrol. Yield: 0.243 g, 80%. X-ray quality blue-green crystals were obtained by slow evaporation of a methanol solution of [(**3a**)$_2$CuCl$_2$]. Mp 158–159 °C; I.R. (KBr): υ (cm^{-1}) 3118, 3080, 3023, 2940, 1607, 1572, 1313, 1226, 1195, 1150, 1077, 1064, 1025, 973, 828, 758, 721. HRESI-MS (MeOH): m/z = 535.1405 [Cu(**3a**)$_2$]$^+$ (calc. for $C_{28}H_{24}CuN_8$ 535.1420 [Cu(**3a**)$_2$]); Λ_M (MeOH) = 77 Ω^{-1} cm^2 mol^{-1}; *Anal.* Calc. for $C_{28}H_{24}CuCl_2N_8$: C, 55.40; H, 3.99; N, 18.46. Found: C, 55.42; H, 3.97; N, 18.21%.

*2.2.2.4. [(**4a**)CuCl$_2$].* A solution (5 mL, MeOH) of anhydrous $CuCl_2$ (0.068 g, 0.50 mmol, 1 equiv.) was added dropwise slowly to a CH_2Cl_2 (5 mL) solution of the ligand **4a** (0.200 g, 0.50 mmol, 1 equiv.). A green solid precipitated immediately and the resulting suspension was stirred at room temperature for 1 h. The volume of solvent was reduced by half under reduced pressure and the green solid isolated by filtration and was purified by recrystallization (hot CH_3OH) to give [(**4a**)$CuCl_2$] as blue-green crystals (0.190 g, 71%). Mp 159–160 °C; I.R. (KBr): υ (cm^{-1}) 3130, 3079, 2930, 1609, 1578, 1316, 1277, 1250, 1192, 1165, 1085, 1019, 974, 833, 766, 722. HRESI-MS (MeOH): m/z = 456.0980 [Cu(**4a**)]$^+$ (calc. for $C_{23}H_{19}CuN_8$ 456.0998 [Cu(**4a**)]$^+$), 416.1579 (calc. for $C_{23}H_{19}N_7Na$ 416.1600 [Na(**4a**)]$^+$); Λ_M (MeOH) = 62 $\Omega^{-1}cm^2$ mol^{-1}; *Anal.* Calc. for $C_{23}H_{19}Cl_2CuN_7$: C, 52.33; H, 3.63; N, 18.57. Found: C, 52.60; H, 3.72; N, 18.68%.

2.2.3. Synthesis of silver(I) complexes

*2.2.3.1. [(**1a**)$_2$Ag](SbF$_6$).* A solution (acetone, 5 mL) of $AgSbF_6$ (0.067 g, 0.2 mmol, 1 equiv.) was added dropwise slowly to a solution (CH_2Cl_2, 5 mL) of the ligand **1a** (0.094 g, 0.4 mmol, 2 equiv.). The resulting colourless solution was stirred at room temperature in the absence of light for 1 h, during which time a white solid slowly precipitated. The volume of solvent was halved under reduced pressure and the solid was filtered off and was washed with Et_2O and petrol. X-ray quality colourless crystals were obtained by vapour diffusion of acetone solution of [(**1a**)$_2$Ag](SbF_6) with methanol. Yield: 0.132 g, 82%. Mp 220–221 °C; ^{1}H NMR (300 MHz, d_6-acetone) δ: 9.02 (s, 2H, H_e), 8.71 (d, J = 5.0, 2H, H_a), 8.16–8.06 (m, 4H, $H_{c,d}$), 7.58 (ddd, J = 2.5, 5.1, 6.2, 2H, H_b), 7.53–7.39 (m, 10H, $H_{g,h,i}$), 5.85 (s, 4H, H_f); ^{13}C NMR (75 MHz, d_6-acetone) δ 150.9, 147.4, 145.6, 139.4, 135.1, 129.2, 129.0, 128.6, 125.1, 124.4, 122.3, 54.8; I.R. (KBr): υ (cm^{-1}) 3136, 3077, 2936, 1601, 1570, 1559, 1348, 1239, 1199, 1158, 1107, 1088, 1062, 1048, 1008, 992, 891, 833, 795, 783, 734; HRESI-MS (CH_3CN): m/z = 343.0076 [**1a**Ag]$^+$ (calc. for $C_{14}H_{12}N_4Ag$ 343.0112 [**1a**Ag]$^+$), 579.1137 [**1a**$_2$Ag]$^+$ (calc. for $C_{28}H_{24}N_8Ag$ 579.1174 [**1a**$_2$Ag]$^+$); Λ_M (CH_3CN) = 162 Ω^{-1} cm^2 mol^{-1}; *Anal.* Calc. for $C_{28}H_{24}AgF_6N_8Sb$: C, 41.20; H, 2.96; N, 13.73. Found: C, 41.47; H, 2.96; N, 13.74%.

*2.2.3.2. [(**3a**)$_2$Ag](SbF$_6$).* A solution (acetone, 5 mL) of $AgSbF_6$ (0.067 g, 0.2 mmol, 1 equiv.) was added dropwise slowly to a (CH_2Cl_2, 5 mL) solution of the ligand **3a** (0.94 g, 0.4 mmol, 2 equiv.). The resulting colourless solution was stirred at room temperature in the absence of light for 1 h. The volume of solvent was halved under reduced pressure and the white solid isolated by filtration and washed well with Et_2O and petrol. The product was recrystallized from acetone/Et_2O. Yield: 0.090 g, 82%. Mp 148–149 °C; ^{1}H NMR (300 MHz, d_6-acetone) δ 8.87 (ddd, J = 0.7, J = 1.6, J = 5.1, 2H, H_a), 8.81 (s, 2H, H_f), 8.21 (td, J = 1.7, J = 7.7, 2H, H_c), 8.03 (dd, J = 0.9, J = 6.9, 2H, H_d), 7.87–7.79 (m, 4H, H_g), 7.70 (ddd, J = 1.3, 5.1, 7.7, 2H, H_b), 7.47–7.37 (m, 4H, H_h), 7.37–7.28 (m, 2H, H_i), 6.15 (s, 4H, H_e); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 153.5, 149.7, 141.6, 130.5, 130.1, 129.6, 127.4, 127.2, 126.6, 124.8, 56.8; I.R. (KBr): υ (cm^{-1}) 3500–3200 (br), 3143, 3088, 3030, 2951, 1600, 1574, 1557, 1309, 1231, 1195, 1149, 1090, 1056, 972, 825, 764, 723; HRESI-MS (CH_3CN): m/z = 579.1150 [**3a**$_2$Ag]$^+$ (calc. for $C_{28}H_{24}N_8Ag$ 579.1174 [**3a**$_2$Ag]$^+$); Λ_M (CH_3CN) = 122 Ω^{-1} cm^2 mol^{-1}; *Anal.* Calc. for $C_{28}H_{24}AgF_6N_8Sb$: C, 41.20; H, 2.96; N, 13.73. Found: C, 41.36; H, 2.90; N, 13.54. X-ray quality colourless crystals were obtained by vapour diffusion of acetone solution of the product with methanol.

*2.2.3.3. [(**2a**)Ag](SbF$_6$).* A solution (acetone, 5 mL) of $AgSbF_6$ (0.034 g, 0.1 mmol, 1 equiv.) was added dropwise slowly to a CH_2Cl_2 (2 mL) solution of the ligand **2a** (0.039 g, 0.1 mmol, 1 equiv.). The resulting colourless solution was stirred at room temperature in the absence of light for 1 h. The volume of solvent was halved under reduced pressure and the white solid isolated by filtration and was washed with Et_2O (10 mL) and petrol (10 mL) then vacuum dried (0.046 g, 62%). Mp 228 °C (decomp.); ^{1}H NMR (300 MHz, d_6-acetone) δ 8.92 (sb, 2H, H_c), 7.59 (t, J = 7.8, 1H, H_a), 7.50 (sb, 2H, H_b), 7.20 (s, 10H, $H_{e,f,g}$), 5.76 (s, 4H, H_d); ^{13}C NMR (75 MHz, d_6-acetone) δ 145.9, 145.1, 140.1, 134.1, 128.9, 128.8, 128.0, 125.5, 121.9, 55.1; I.R. (KBr): υ (cm^{-1}) 3146, 3034, 2926, 1606, 1582, 1564, 1497, 1453, 1438, 1405, 1381, 1346, 1268, 1245, 1194, 1159, 1115, 1098, 1074, 1057, 1022, 926, 848, 812, 782, 761, 705. HRESI-MS (MeOH/CH_3CN): m/z = 500.0714 [(**2a**)Ag]$^+$ (calc. for $C_{23}H_{19}AgN_7$ 500.0747), 416.1563 [(**2a**)+Na]$^+$ (calc. for $C_{23}H_{19}N_7Na$ 416.1600); Λ_M (CH_3CN) = 135 Ω^{-1} cm^2 mol^{-1}; *Anal.* Calc. for $C_{23}H_{19}AgF_6N_7Sb$: C, 37.48; H, 2.60; N, 13.30. Found: C, 37.40; H, 2.69; N, 13.06%.

*2.2.3.4. [(**4a**)Ag](SbF$_6$).* A solution (acetone, 5 mL) of anhydrous $AgSbF_6$ (0.034 g, 0.10 mmol, 1 equiv.) was added dropwise slowly to a CH_2Cl_2 (2 mL) solution of the ligand **4a** (0.039 g, 0.10 mmol, 1 equiv.). The resulting colourless solution was stirred at room temperature in the absence of light for 1 h. The volume of solvent

was halved under reduced pressure and the white solid isolated by filtration and was washed with Et_2O (10 mL) and petrol (10 mL) then vacuum dried (0.064 g, 86%). Mp >250 °C; ^{1}H NMR (300 MHz, d_6-acetone) δ 8.91 (s, 2H, H_d), 8.31 (t, J = 7.8, 1H, H_a), 8.05 (d, J = 7.7, 2H, H_b), 7.72 (d, J = 7.5, 4H, H_e), 7.39 (t, J = 7.3, 3H, H_g), 7.24 (t, J = 7.4, 4H, H_f), 6.05 (s, 4H, H_c); ^{13}C NMR (75 MHz, d_6-acetone) δ: 154.3, 150.3, 142.7, 130.9, 130.3, 128.9, 127.3, 127.2, 125.7, 57.4; I.R. (KBr): υ (cm^{-1}) 3127, 3085, 3028, 2945, 1711, 1607, 1593, 1575, 1485, 1462, 1437, 1359, 1330, 1266, 1219, 1200, 1159, 1092, 1082, 1074, 1044, 1009, 985, 976, 850, 838, 818, 764, 725; HRESI-MS (MeOH/CH_3CN): m/z = 500.0718 [(**2a**)Ag]$^+$ (calc. for $C_{23}H_{19}AgN_7$ 500.0747), 416.1571 [(**2a**)+Na]$^+$ (calc. for $C_{23}H_{19}N_7Na$ 416.1600), 394.1753 [(**2a**)+H]$^+$; Λ_M (CH_3CN) = 141 Ω^{-1} cm^2 mol^{-1}; *Anal.* Calc. for $C_{23}H_{19}AgF_6N_7Sb\cdot(C_2H_6O)$: C, 38.34; H, 3.22; N, 12.52. Found: C, 38.72; H, 3.19; N, 12.24%.

2.3. X-ray data collection and refinement

X-ray data for **1c**, **2c**, **3b**, **4b**, [**2a**$CuCl_2$], [**3a**$_2CuCl_2$], [**1a**$_2$Ag](SbF_6), [**2a**Ag](SbF_6), [**3a**$_2$Ag](SbF_6) and [**4a**Ag](SbF_6) were recorded using a Bruker APEX II CCD diffractometer at 90(2) K. The structures were solved by direct methods using SIR97 [68] with the resulting Fourier map revealing the location of all non-hydrogen atoms. Weighted full matrix refinement on F^2 was carried out using SHELXL-97 [69] with all non-hydrogen atoms being refined anisotropically. The hydrogen atoms were included in calculated positions and were refined as riding atoms with individual (or group, if appropriate) isotropic displacement parameters. The [**3a**$_2CuCl_2$] crystal studied has an inversion twin with a 0.47(2):0.52(2) domain ratio. The space group for this structure was examined carefully and the structure was found to solve and refine in $P2_1$ satisfactorily. However in the space group $P2_1/c$ no solution was found. In [**2a**$CuCl_2$], one of the benzyl substituents was disordered over two sites and was modeled satisfactorily with 60:40 contributions for the two orientations. Crystals of [**3a**$_2$Ag](SbF_6) were of modest quality, and while the [**3a**$_4Ag_3]^{3+}$ cation and the acetone and methanol solvate molecules were well resolved, two of the SbF_6 anions and the [**3a**$_2$Ag]$^+$ cation were disordered. The silver (I) ion of the [**3a**$_2$Ag]$^+$ cation is disordered over two sites about a crystallographic center of inversion. This disorder could not be satisfactorily resolved and as such some of the thermal parameters associated with this cationic fragment are large. All ORTEP [70] diagrams have been drawn with 50% probability ellipsoids. Crystal data and collection parameters are given in Table 1.

Table 1
Crystal data and structure refinement for ligands **1c**, **2c**, **3b**, **4b,** copper(II) and silver(I) complexes.

	1c	**2c**	**3b**	**4b**	[(**3a**)$_2CuCl_2$]
Identification code	CCDC 728064	CCDC 728065	CCDC 728062	CCDC 728063	CCDC 728300
Empirical formula	$C_{18}H_{16}FeN_4$	$C_{31}H_{27}N_7Fe_2$	$C_{18}H_{16}N_4Fe$	$C_{31}H_{27}N_7Fe_2$	$C_{28}H_{24}N_8Cl_2Cu$
Formula weight	344.20	609.30	344.20	609.30	606.99
T (K)	90(2)	90(2)	90(2)	90(2)	90(2)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1$
a (Å)	5.7798(6)	15.551(2)	9.063(1)	8.372(7)	12.122(5)
b (Å)	28.458(3)	9.480(1)	14.830(1)	8.763(7)	8.282(3)
c (Å)	9.3468(9)	17.927(3)	11.598(1)	18.257(14)	13.269(5)
α (°)	90.00	90.00	90.00	94.633(4)	90.00
β (°)	98.859(5)	100.198(8)	104.229(3)	98.838(4)	92.000(2)
γ (°)	90.00	90.00	90.00	101.370(4)	90.00
V (Å^3)	1519.0(3)	2601.1(8)	1511.0(12)	1289.0(17)	1331.3(9)
Z	4	4	4	2	2
ρ_{calc} (mg mm^3)	1.505	1.556	1.513	1.570	1.514
μ (mm^{-1})	0.997	1.152	1.002	1.162	1.056
Crystal size, color, habit	0.44 × 0.25 × 0.13, orange, plate	0.52 × 0.47 × 0.33, red, rod	0.74 × 0.43 × 0.31, orange, rhomb.	0.64 × 0.22 × 0.12 mm, red, block	0.55 × 0.32 × 0.06, blue, irregular
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0398 wR_2 = 0.1528	R_1 = 0.0345 wR_2 = 0.0884	R_1 = 0.0243 wR_2 = 0.0638	R_1 = 0.0232 wR_2 = 0.0569	R_1 = 0.0388 wR_2 = 0.1109
Final R indexes [all data]	R_1 = 0.0472 wR_2 = 0.1581	R_1 = 0.0376 wR_2 = 0.0908	R_1 = 0.0248 wR_2 = 0.0643	R_1 = 0.0246 wR_2 = 0.0584	R_1 = 0.0399 wR_2 = 0.1119
Identification code	[(**2a**)$CuCl_2$] CCDC 728301	[(**1a**)$_2$Ag](SbF_6) CCDC 728302	[(**3a**)$_4Ag_3$](SbF_6)$_3$ + 0.5[(**3a**)$_2$Ag](SbF_6) CCDC 728303	{[(**4a**)Ag](SbF_6)}$_\infty$ CCDC 728304	{[(**2a**)Ag](SbF_6)}$_4$ CCDC 728432
Empirical formula	$C_{79}H_{64}O_5Cl_6Cu_3N_{21}$	$C_{28}H_{24}N_8SbAgF_6$	$C_{74}H_{66}O_4F_{32}Ag_4Sb_5N_{20}$	$C_{26}H_{25}AgF_6N_7OSb$	$C_{94}H_{76}Ag_4F_{24}N_{28}O_6Sb_4$
Formula weight	3399.47	816.17	2492.64	795.15	3068.35
T (K)	90(2)	90(2)	90(2)	90(2)	90(2)
Crystal system	triclinic	monoclinic	triclinic	monoclinic	tetragonal
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$I4_1cd$
a (Å)	14.147(1)	10.294(5)	17.0758(7)	13.050(3)	21.737(11)
b (Å)	15.295(1)	23.221(1)	17.654(7)	15.467(3)	21.737(11)
c (Å)	20.095(2)	12.259(6)	18.227(7)	14.283(4)	
α (°)	98.474(4)	90.00	114.50(2)	90.00	90.00
β (°)	95.836(4)	93.143(2)	95.97(2)	96.451(12)	90.00
γ (°)	111.901(4)	90.00	110.52(2)	90.00	90.00
V (Å^3)	3932.0(9)	2926(2)	4477(4)	2864.7(12)	22519(30)
Z	6	4	2	4	8
ρ_{calc} (mg mm^3)	1.436	1.853	1.842	1.844	1.810
μ (mm^{-1})	1.071	1.665	1.883	1.700	1.728
Crystal size, color, habit	0.44 × 0.30 × 0.16, green, rhomb.	0.50 × 0.25 × 0.15, colourless, irregular	0.52 × 0.23 × 0.22, colourless, rhomb.	0.40 × 0.14 × 0.03, colourless, needle	0.39 × 0.19 × 0.06, colourless, irregular
Final R indexes [$I>2\sigma(I)$]	R_1 = 0.0651 wR_2 = 0.1759	R_1 = 0.0253 wR_2 = 0.0589	R_1 = 0.0749 wR_2 = 0.2090	R_1 = 0.0307 wR_2 = 0.0603	R_1 = 0.1288 wR_2 = 0.3105
Final R indexes [all data]	R_1 = 0.0756 wR_2 = 0.1855	R_1 = 0.0302, wR_2 = 0.0619	R_1 = 0.0985 wR_2 = 0.2369	R_1 = 0.0385, wR_2 = 0.0637	R_1 = 0.1720 wR_2 = 0.3245

3. Results and discussion

3.1. Ligand synthesis

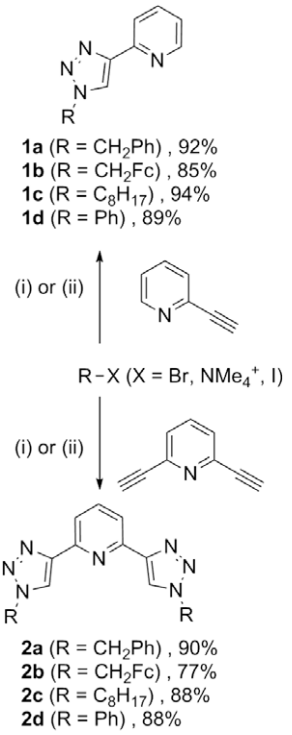
An examination of the literature showed that there are a number of one pot CuAAC methodologies in which the organic azides are generated *in situ* from alkyl, benzyl and aryl halides [71–77]. Using the synthesis of the known ligands **1a** [37,40,78,79] and **2a** [80] we screened these methods and found the conditions of Fokin [71] to be the most convenient. Simply mixing either 2-ethynylpyridine or 2,6-diethynylpyridine, benzyl bromide, NaN_3, $CuSO_4{\cdot}5H_2O$, Na_2CO_3 and ascorbic acid in DMF/H_2O (4:1) then stirring at room temperature for 20 h (Scheme 1) provided, after work up, the desired ligands in excellent yields (**1a,** 92% and **2a,** 90%) without the need for isolating the potentially hazardous benzyl azide. Indeed the yields of the ligands **1a** and **2a** obtained from the one pot method are comparable if not better than those reported using preformed isolated benzyl azide [37,40,78–80]. Following on from this initial success we then attempted the synthesis of the ferrocenylmethyl[2] [81] (**1b** and **2b**) and octyl (**1c** and **2c**) substituted ligands. Under the standard Fokin conditions only modest yields of the desired products were obtained presumably because the substitution of the halide (or pseudo halide) leaving groups by azide was slow at room temperature. However, simply increasing the temperature of the reaction to 95 °C enabled the desired ligands to be generated in excellent isolated yields (Scheme 1).

By modifying [82–84] the one pot CuAAC method developed by Liang [74,77] we were also able to synthesise the aryl (phenyl) substituted ligands (**1d** and **2d**)[3]. Iodobenzene, NaN_3, CuI, DMEDA and sodium ascorbate were refluxed in a degassed EtOH/H_2O (7:3) solution for 2 h, to generate azidobenzene *in situ*, then the reaction mixture was cooled to room temperature. $CuSO_4{\cdot}5H_2O$, sodium ascorbate and either 2-ethynylpyridine or 2,6-diethynylpyridine were added as solids to the reaction mixture and the resulting solution was stirred at room temperature for 20 h, yielding the desired aryl functionalized ligands (Scheme 1).

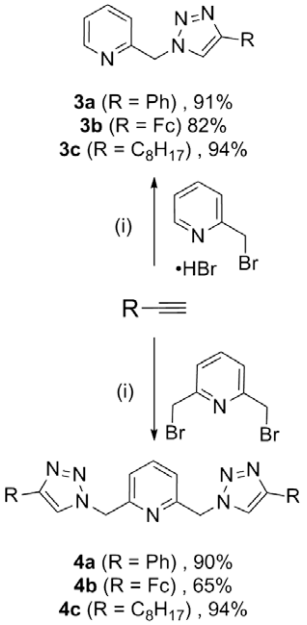
Additionally, we were also able to exploit the one pot CuAAC methodology to generate methylene bridged, aryl and alkyl substituted pyridyl-1,2,3-triazole ligands (**3a-c** and **4a-c**) in excellent yields (Scheme 2).

The ligands **1a–d**, **2a–d, 3a–c** and **4a–c** have been fully characterized by elemental analysis, HR-ESMS, IR, ^1H and ^{13}C NMR. These pyridyl-1,2,3-triazole derivatives were characterized by the lack of an azide (~2095 cm^{-1}) or alkyne (~2150 cm^{-1}) band in their IR spectra and by the diagnostic singlet of the triazole unit (found between 8.6 and 7.5 ppm) in their ^1H NMR spectra (see Supporting information). In the case of the ferrocene substituted ligands (**1c**, **2c**, **3b** and **4b**) the structures were confirmed by X-ray crystallography (Fig. 1 and Fig. 2, Table 1).

The compounds **1c** and **2c** both crystallise in the monoclinic space group $P2_1/n$ and the structures of **1c** and **2c** are consistent with the other collected experimental data (Fig. 1). The cp rings of the ferrocene units are eclipsed, the triazoles rings are planar 1,4 substituted isomers. The pyridine and triazole units are essentially coplanar (the N–C–C–N dihedral angles vary from 3° to 14°), and the bond lengths and angles are similar to those observed in related structures [40,43,85]. Additionally, the nitrogen donor atoms of the chelating units adopt the *anti* (**1c**) or *anti–anti* (**2c**) conformations as is commonly observed in related heterocyclic ligands [40,46,86].



Scheme 1. (i) NaN_3, $CuSO_4{\cdot}5H_2O$, ascorbic acid, Na_2CO_3, DMF/H_2O (4:1), RT or 95 °C, 20 h; (ii) a) NaN_3, CuI, DMEDA, EtOH/H_2O (7:3), 100 °C, 2 h, (b) $CuSO_4{\cdot}5H_2O$, ascorbic acid, Na_2CO_3, RT, 20 h. Isolated yield after chromatography.



Scheme 2. (i) NaN_3, $CuSO_4{\cdot}5H_2O$, ascorbic acid, Na_2CO_3, DMF/H_2O (4:1), RT, 20 h.

The structures of **3b** and **4b** along with the bond length and angles are shown in Fig. 2. Compound **3b** crystallises in the monoclinic space group $P2_1/n$ whereas **4b** crystallises in the triclinic space group $P\bar{1}$. Like **1c** and **2c** the cp rings of the ferrocene units are once again found in the expected eclipsed conformation and the triazoles rings are planar 1,4 substituted isomers. The triazole units are twisted away from the pyridine rings presumably to

[2] Ferrocene containing compounds have found applications as sensors, catalysts and as drugs, see Ref. [81]. As such the attempted incorporation of the ferrocene functional group seemed a logical choice.

[3] The synthesis of these ligands has been recently reported by Fletcher et al., see Ref. [52].

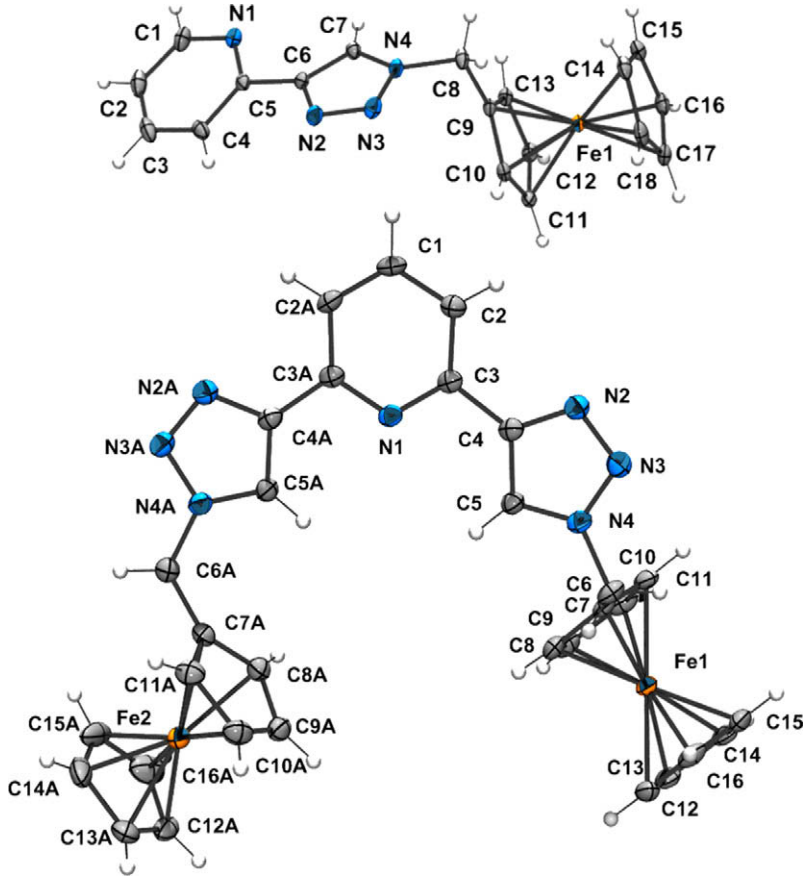


Fig. 1. Labelled ORTEP diagrams of (a) **1c** and (b) **2c**. The thermal ellipsoids are shown at the 50% probability. Selected bond lengths (Å) and angles (°) for **1c**: N2–N3 1.3144(14), N3–N4 1.3474(13), N4–C7 1.3525(14), N2–C6 1.3656(14), N2–C6–C7 108.51(9), N3–N3–C6 108.69(9), N2–N3–N4 107.51(9), N4–C6–C7 104.24(9), N3–N4–C7 111.06(9). Selected bond lengths (Å) and angles (°) for **2c**; C4–N2 1.355(3), C4–C5 1.340(3), N2–N3 1.316(3), N3–N4 1.352(3); N3–N2 C4 108.6(2), N2–N4 107.2(2), C5–N4–N3 110.7(2), C5–N4–C6 128.8(2), N3–N4–C6 120.4(2).

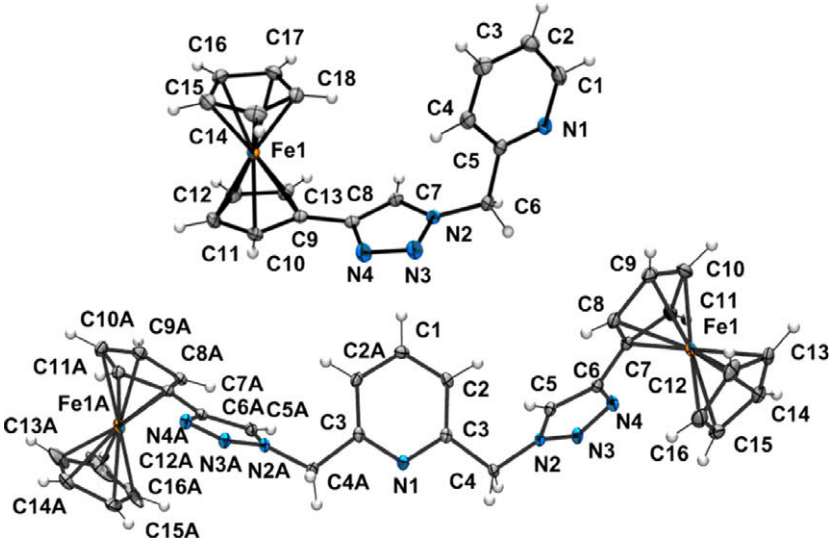


Fig. 2. Labelled ORTEP diagrams of (a) **3b** and (b) **4b**. The thermal ellipsoids are shown at the 50% probability. Selected bond lengths (Å) and angles (°) for **3b**: C8–N4 1.362(2), C8–C7 1.373(2), C7–N2 1.347(2), N4–N3 1.3172(19), N3–N2 1.3453(18); N4–C8–C7 108.22(13), N3–N2–C6 120.32(12), N4–C8–C9 121.79(13), C7–N2–C6 128.54(13), C7–C8–C9 129.98(13), N2–C7–C8 104.73(12), N2–C6–C5 113.00(12), N3–N4–C8 108.94(13), N4–N3–N2 107.09(12), N3–N2–C7 111.02(12). Selected bond lengths (Å) and angles (°) for **4b**: C5–N2 1.352(2), C5–C6 1.377(2), C6–N4 1.370(2), N2–N3 1.3523(19), N3–N4 1.3168(19); C5–N2–N3 111.21(12), C5–N2–C4 129.54(13), N3–N2–C4 119.05(13), N4–N3–N2 107.06(13), N3–N4–C6 108.92(13) .

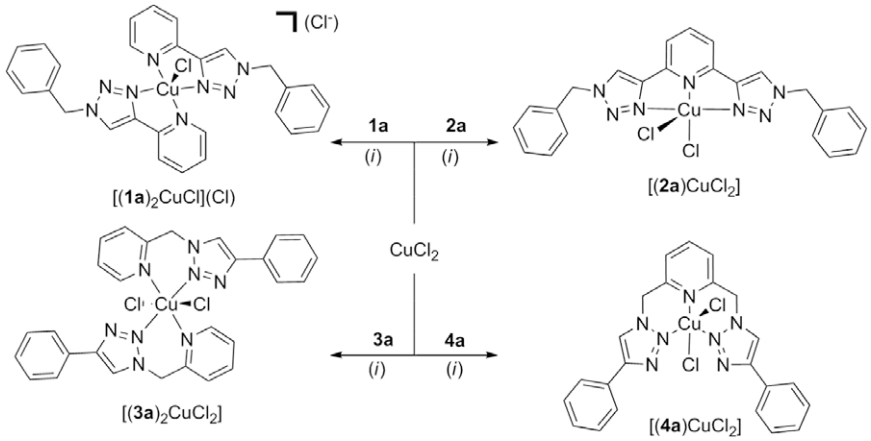
remove any repulsive interactions between the nitrogen atoms lone pairs of electrons.

Having successfully developed a facile one pot method for the generation of pyridyl-1,2,3-triazole ligands we then examined

their metal complexation properties. Because the complexation chemistry of related pyridyl-1,2,3-triazoles with metal ions that exhibit a rigid octahedral geometry (Fe(II), Ru(II), Re(I), Tc(I)) has already been well studied [33,37–53], we investigated the coordination chemistry of these ligands with the more geometrically flexible copper(II) and silver(I) metal ions.

3.2. Synthesis of Cu(II) complexes

The rich and varied coordination chemistry of copper(II) with nitrogen heterocycles has been extensively studied [87–90], and as such it was of interest to explore how copper(II) would interact with the pyridyl-1,2,3-triazole ligands. The complexes were prepared by adding an ethanol solution of $CuCl_2$ (1 equiv.) to a chloroform solution of one of the ligands (**1a**, **2a**, **3a**, or **4a,** 1 or 2 equiv.). The suspension which formed was then heated at 60 °C for 1 h and the resulting blue-green microcrystalline powders were isolated by filtration (Scheme 3). Recrystallization from hot methanol furnished green or blue crystals suitable for X-ray crystallography. Elemental analysis indicated that the bidentate ligands (**1a** and **3a**) formed copper(II) chloride complexes of a 1:2 metal:ligand stoichiometry whereas the tridentate ligands (**2a** and **4a**) formed 1:1 metal:ligand complexes. These formulations were further supported by the electrospray mass spectrometry (ESMS). The ESMS spectra of the copper(II) chloride complexes of the ligands **1a** and **3a** in acetonitrile solution both showed a signal at $m/z = 535$ corresponding to a $[\mathbf{L}_2Cu]^+$ ion, whereas spectra of the $CuCl_2$ complexes of the tridentate ligands, **2a** and **4a,** contained signals $m/z = 456$ and 416 due to the $[\mathbf{L}Cu]^+$ and $[\mathbf{L}Na]^+$ ions, respectively. Additionally, a weak signal was observed at $m/z = 424$ in the spectra of the Cu(II) complex of **2a** which corresponds to the $[(\mathbf{2a})_2Cu]^{2+}$ ion. Conductivity measurements in methanol indicate that the copper(II) complexes formed with **2a**, **3a**, and **4a** are non-electrolytes, suggesting that the anionic chloride ligands are



Scheme 3. (i) $CuCl_2$, EtOH, $CHCl_3$, 60 °C, 1 h.

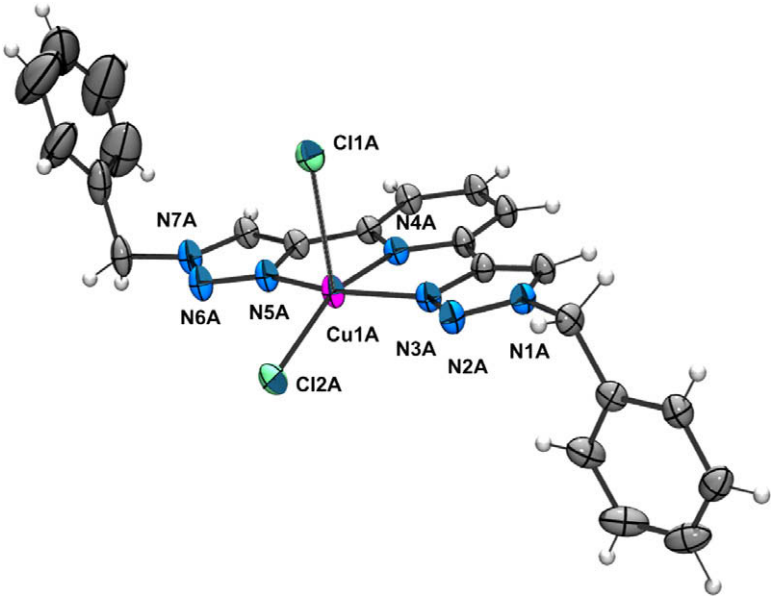


Fig. 3. A representative labelled ORTEP diagram of one of the independent molecules of [(**2a**)$CuCl_2$] in the unit cell. The thermal ellipsoids are shown at the 50% probability. Selected bond lengths (Å) and angles (°) for [(**2a**)$CuCl_2$]: N3A–Cu1A 2.021(4), N4A–Cu1A 2.017(4), N5A–Cu1A 2.035(4), Cl1A–Cu1A 2.4483(13), Cl2A–Cu1A 2.2395(14); N4A–Cu1A–N3A 78.19(15), N4A–Cu1A–N5A 77.86(15), N3A–Cu1A–N5A 155.13(15), N4A–Cu1A–Cl2A 152.15(11), N3A–Cu1A–Cl2A 98.10(12), N5A–Cu1A–Cl2A 99.93(11), N4A–Cu1A–Cl1A 100.39(11), N3A–Cu1A–Cl1A 97.50(11), N5A–Cu1A–Cl1A 93.29(11), Cl2A–Cu1A–Cl1A 107.46(5).

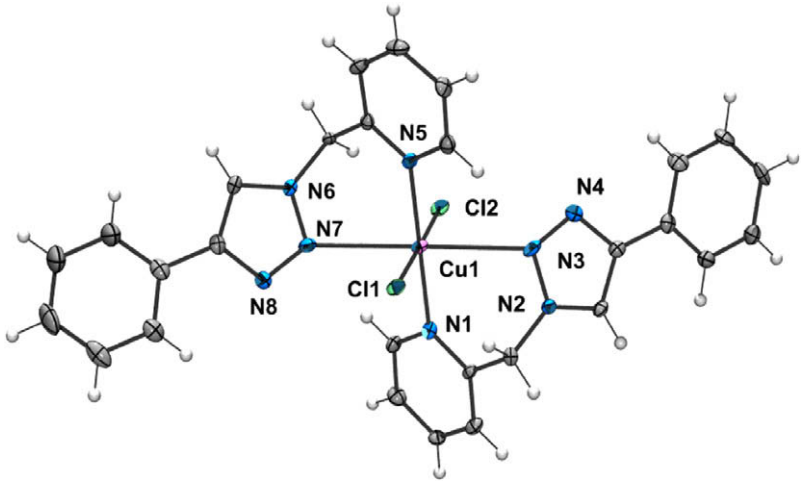
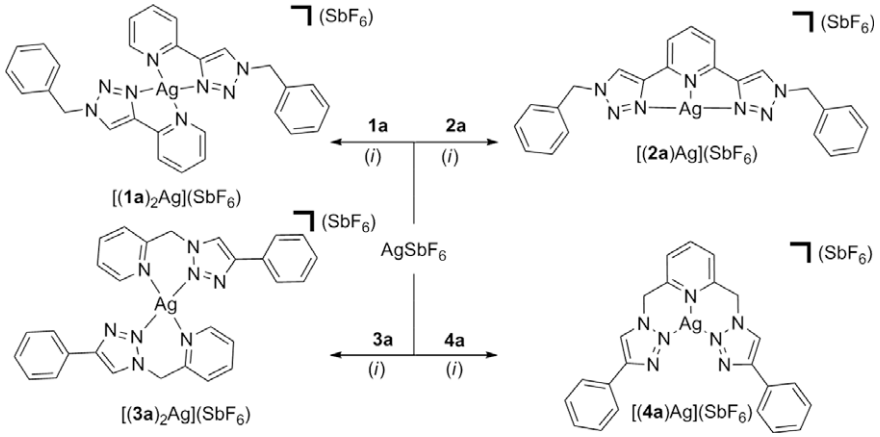


Fig. 4. A labelled ORTEP diagram of $[(\mathbf{3a})_2CuCl_2]$. The thermal ellipsoids are shown at the 50% probability. Selected bond lengths (Å) and angles (°) for $[(\mathbf{3a})_2CuCl_2]$: N1A–Cu1 2.043(4), N1–Cu1 2.040(3), Cl1–Cu1 2.287(2), Cl2–Cu1 2.295(2), N3A–Cu1 2.693(2), N3–Cu1 2.672(2); N1–Cu1–N1A 179.4(3), N1–Cu1–Cl1 88.98(15), N1A–Cu1–Cl1 91.52(14), N1–Cu1–Cl2 91.07(15), N1A–Cu1–Cl2 88.43(14), Cl1–Cu1–Cl2 178.63(7).



Scheme 4. (i) Acetone, CH_2Cl_2, RT, 1 h.

coordinated to the Cu(II) ions, while the conductivity of the Cu(II) complex of **1a** is in the range usually observed for a 1:1 electrolyte [91], presumably because one of the chloride ions is acting as a non-coordinating counterion (Scheme 3).

X-ray crystallography was used to determine the molecular structures of the complexes formed with the ligands **2a** and **3a**. Fig. 3 shows a perspective view of the structure of the copper complex formed with the tridentate **2a.** The compound crystallises in the triclinic space group $P\bar{1}$ and there are three independent molecules within the unit cell. Compound $[(\mathbf{2a})CuCl_2]$ adopts a distorted square pyramidal coordination geometry (Fig. 3) with a τ_5 parameter [92] of 0.05 (the other independent molecules of $[(\mathbf{2a})CuCl_2]$ have τ_5 parameters of 0.065 and 0.097, respectively).[4] Although there is some disorder associated with the peripheral benzyl rings, the metal coordination core in each of the independent molecules is well defined and almost identical. The coordination core of tridentate ligand, **2a**, is essentially planar and the Cu–N bond lengths range from 2.01 to 2.04 Å. The chloride ligand that makes up the square plane is slightly bent out of the planarity (N4A–Cu1A–Cl2A 152.15(11)°) at a distance Cl2A–Cu1A 2.2395(14), whereas the axial Cu1A–Cl1A bond is slightly longer at 2.4483(13). It is of interest to note that overall the structure is very similar to that reported for a related $[Cu(terpy)Cl_2]$ complex [93].

The copper(II) complex formed with **3a** crystallises in the monoclinic space group $P2_1$ with one complete molecule of $[(\mathbf{3a})_2CuCl_2]$ in the asymmetric unit. The copper(II) ion lies in a Jahn–Teller distorted octahedral coordination environment (Fig. 4). The pyridyl and chloride donor units adopt a square planar array around the Cu(II) ion and the Cu–N (ca. 2.04 Å) and Cu–Cl (ca. 2.28) bond lengths of these ligands are in the expected ranges. The Cu–N bond lengths between the Cu(II) ion and the axial triazole donors are much longer (ca. 2.68 Å) on the edge of what would normally be considered to constitute a bonding interaction[5][94,95]. However, we note that the triazole rings are oriented such that the N-donor atom is directed toward Cu(II) ion, as such the coordination geometry is best described as a distorted octahedron.

[4] The τ_5 parameter was introduced ($\tau_5 = \beta - \alpha/60$) for penta-coordinated complexes. This parameter serves as a semiquantitative criterion to distinguish between trigonal bipyramidal (TB) ($\tau_5 = 1$ for regular TB stereochemistry) and square based pyramidal (SBP) ($\tau_5 = 0$ for regular SBP stereochemistry) geometries. The τ_5 parameter calculated for $[\mathbf{2a}CuCl_2]$ of 0.05 indicates that the coordination geometry of is best described as a distorted square based pyramid.

[5] A search of the Cambridge Structural Database (CSD) Version 5.3, showed that the Cu–N bond distances for six-coordinate Cu(II)–triazine complexes range from 1.81 to 2.82 Å with a mean distance of 2.07 Å.

Disappointingly, despite collecting X-ray diffraction data sets from the crystals of [(**1a**)$_2$CuCl](Cl) and [(**4a**)CuCl$_2$] we have been unable to satisfactorily solve the structures of these molecules. However, the inspection of the electron density maps indicated that [(**1a**)$_2$CuCl](Cl) adopts a distorted square pyramidal coordination geometry while [(**4a**)CuCl$_2$] has a trigonal bipyramidal structure similar to those found in related pyridine containing CuCl$_2$ complexes [96,97].

3.3. Synthesis of silver(I) complexes

The coordination chemistry of silver(I) with nitrogen heterocycles has undergone a renaissance in recent times [7,98–101], due to this motif's usefulness in constructing metallosupramolecular architectures. With this in mind we attempted to synthesize and structurally characterise silver(I) complexes of the pyridyl-1,2,3-triazole ligands. The complexes were prepared by adding an acetone solution of AgSbF$_6$ (1 equiv.) to a dichloromethane solution of one of the ligands (**1a**, **2a**, **3a**, or **4a,** 1 or 2 equiv.) and stirring the resulting solutions at room temperature for 1 h (Scheme 4). Addition of diethyl ether to the reaction mixtures led to the precipitation of white microcrystalline powders which were isolated by filtration.

Elemental analysis indicated that both the bidentate ligands (**1a** and **3a**) formed silver(I) complexes of a 1:2 metal:ligand ratio while the tridentate ligands (**2a** and **4a**) formed complexes of a 1:1 metal:ligand stoichiometry with AgSbF$_6$. Consistently, the ESMS spectrum of [(**1a**)$_2$Ag](SbF$_6$) in acetonitrile showed two signals at m/z = 343 and 579 corresponding to the species [(**1a**)Ag]$^+$ and [(**1a**)$_2$Ag]$^+$ whereas the mass spectrum of the isomeric [(**3a**)$_2$Ag](SbF$_6$) contained a single signal at m/z = 579 corresponding to [(**3a**)$_2$Ag]$^+$. The ESMS spectra of silver(I) complexes of the tridentate ligands, **2a** and **4a**, contained two signals at m/z = 500 and 416 corresponding to the species [**L**Ag]$^+$ and [**L**Na]$^+$. Conductivity measurements in acetonitrile indicated that the silver(I) complexes formed with **1a**, **2a**, **3a**, and **4a** are 1:1 electrolytes [91] with the SbF$_6^-$ anion acting, as expected, as a non-coordinating counterion. ^{1}H NMR spectra of the silver(I) complexes were recorded at room temperature in d_6-acetone (see Supporting information) and in general, the spectra show a simple pattern containing one set of proton signals, suggesting the formation of single symmetric species. Compared with the spectra of the ligands **1a, 3a** and **4a**, the proton signals of the corresponding silver complexes are sharp and shifted downfield indicative of metal complexation in solution. However, the silver complex of **2a** exhibits a broad ^{1}H NMR spectrum. The singlet due to the triazole ring is shifted downfield compared to the ligand **2a,** whereas all the other proton signals of the silver complex are upfield shifted compared to the free ligand (see Supporting information). We postulate that this is due to the formation of a dimeric (or higher oligomeric) species such as **5**, similar to those observed in related Ag-Terpy structures [102–104], but note that we do not see any evidence for this or larger aggre-

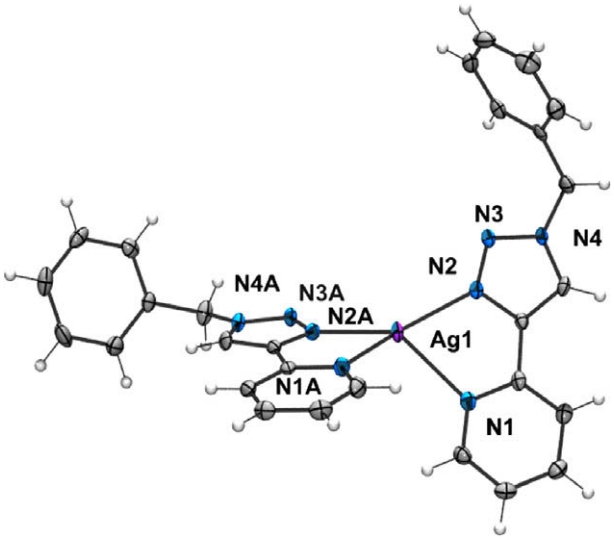


Fig. 5. A labelled ORTEP diagram of [(**1a**)$_2$Ag](SbF$_6$). The thermal ellipsoids are shown at the 50% probability. Selected bond lengths (Å) and angles (°) for [(**1a**)$_2$Ag](SbF$_6$): Ag1–N2 2.230(2), Ag1–N2A 2.234(2), Ag–N1A 2.439(2), Ag–N1 2.442(2); N2–Ag1–N2A 144.41(8), N2–Ag1–N1A 136.52(8), N2A–Ag1–N1A 72.41(8), N2–Ag1–N1 71.29(9), N2A–Ag1–N1 138.55(8), N1A–Ag1–N1 91.54(8).

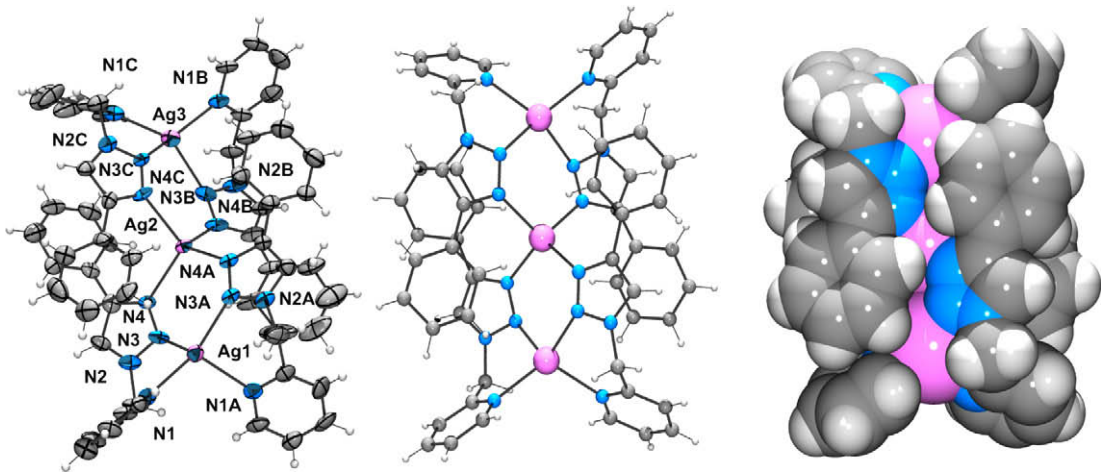


Fig. 6. Three views of the molecular structure of the[(**3a**)$_4$Ag$_3$]$^{3+}$ cation, (a) a labelled ORTEP diagram, (b) a ball and stick diagram, and (c) a space filling diagram. The thermal ellipsoids are shown at the 50% probability. Selected bond lengths (Å) and angles (°) for [(**3a**)$_4$Ag$_3$]$^{3+}$: Ag1–N1A 2.258(7), Ag1–N3 2.279(7), Ag1–N1 2.365(7), Ag1–N3A 2.443(7), Ag2–N4C 2.312(7), Ag2–N4A 2.316(7), Ag2–N4B 2.356(6), Ag2–N4 2.378(7), Ag3–N1C 2.301(7), Ag3–N1B 2.319(9), Ag3–N3B 2.369(7), Ag3–N3C 2.391(7); N1A–Ag1–N3 150.6(3), N1A–Ag1–N1 106.3(2), N3–Ag1–N1 87.5(3), N1A–Ag1–N3A 85.5(3), N3–Ag1–N3A 105.1(2), N1–Ag1–N3A 131.0(3), N4C–Ag2–N4A 114.7(2), N4C–Ag2–N4B 109.5(2), N4A–Ag2–N4B 107.0(2), N4C–Ag2–N4 106.7(3), N4A–Ag2–N4 109.5(2), N4B–Ag2–N4 109.4(2), N3–Ag1–N3A 105.1(2), N1–Ag1–N3A 131.0(3), N1C–Ag3–N1B 113.7(3), N1C–Ag3–N3B 140.4(3), N1B–Ag3–N3B 87.0(3), N1C–Ag3–N3C 86.8(2), N1B–Ag3–N3C 134.8(3), N3B–Ag3–N3C 102.3(2) .

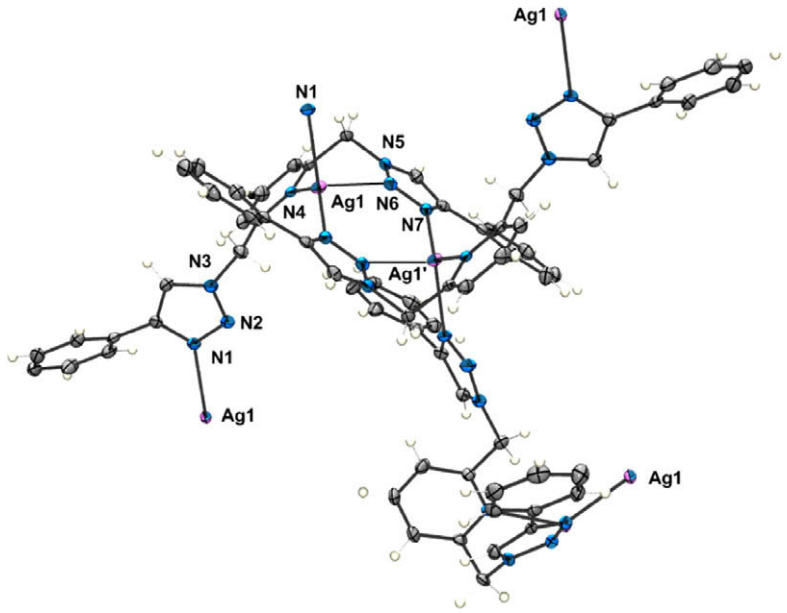
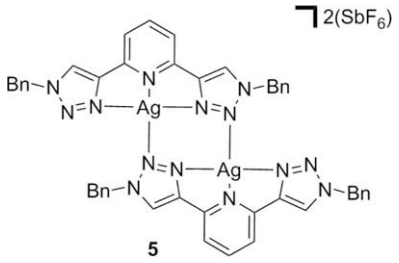


Fig. 7. (a) A labelled ORTEP diagram showing a representative coordination environment for the polymeric $\{[(\mathbf{4a})Ag](SbF_6)\}_\infty$ and the presence of symmetry related Ag1 ions. The SbF_6 counter ion has been omitted for clarity, the thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°) for $\{[(\mathbf{4a})Ag](SbF_6)\}_\infty$: Ag1–N1 2.321(3), Ag1–N4 2.317(2), Ag–N6 2.493(3), Ag1–N7 2.233(3); N7–Ag1–N4 135.42(9), N7′–Ag1–N1 111.79(9), N4–Ag1–N1 106.70(9), N7′–Ag1–N6 108.84(9), N4–Ag1–N6 82.48(9), N1–Ag1–N6 103.40(9). (symmetry codes: $1-x, -y, 1-z$).

gates in the ESMS spectrum of the complex. However, we have confirmed crystallographically that the 1,2,3-triazole unit can act as a bridging ligand in related examples, see Figs. 6 and 7.



Single crystals of the silver complexes of **1a, 2a, 3a** and **4a**, suitable for X-ray crystallography, were obtained by vapour diffusion of methanol into acetone solutions of the complexes. Fig. 5 shows a perspective view of the structure of the silver(I) complex formed with the bidentate ligand **1a.** The molecule crystallises in the monoclinic space group $P2_1/c$ and has a molecular formula $[(\mathbf{1a})_2Ag](SbF_6)$ which is consistent with the other collected experiment data. The silver(I) ion adopts a distorted tetrahedral coordination geometry ($\tau_4 = 0.56$, indicative of a distorted tetrahedral or seesaw structure)[6] [100] with the ligands coordinated through both the pyridyl and triazole donors in the expected bidentate fashion (Fig. 5). Interestingly, the Ag–N bond length to the triazole units (ca. 2.23 Å) are much shorter than the corresponding bond length between the pyridyl units and the silver ion (ca. 2.44 Å).

The X-ray crystallography of the silver(I) complex formed with the bidentate **3a** was surprising**.** The complex crystallises in the triclinic space group $P\bar{1}$ and interestingly, shows the presence of not only the expected $[(\mathbf{3a})_2Ag]^+$ cation (Supporting information) but also the trisilver complex $[(\mathbf{3a})_4Ag_3]^{3+}$ (Fig. 6). The trisilver cation $[(\mathbf{3a})_4Ag_3]^{3+}$ is well resolved, but there is some disorder in the $[(\mathbf{3a})_2Ag]^+$ cation and two of the hexafluoroantimonate counterions. The $[(\mathbf{3a})_2Ag]^+$ complex adopts a rare square planar [99] coordination geometry ($\tau_4 = 0.25$), but because the silver ion is disordered over two sites the Ag–N bond length and angles are unreliable (Fig. 5, Supporting information). Conversely, the silver ions of the trisilver unit $[(\mathbf{3a})_4Ag_3]^{3+}$ are found to be tetrahedrally coordinated to the **3a** ligands with all the Ag–N bond lengths in the range 2.25–2.39 Å. The trisilver complex is composed of two $[(\mathbf{3a})_2Ag]^+$ units sandwiching the third Ag (I) ion and the phenyl substituents of the two $[(\mathbf{3a})_2Ag]^+$ cations are interdigitated. The central silver ion (Ag2) is tetrahedrally ($\tau_4 = 0.97$) coordinated to each of the "spare" triazole nitrogen atoms of the **3a** ligands, while the silver ions at the ends of the trimer adopt distorted tetrahedral or seesaw coordination environments (for Ag1, $\tau_4 = 0.56$, for Ag3, $\tau_4 = 0.60$). As far as we are aware this is only the second crystallographically characterized example of a 1,2,3-triazole acting as a bridging ligand [56], however, 1,2,4-triazoles have been extensively exploited as metal bridging ligands [106–108]. The trisilver complex is further stabilized by a π–π interaction between the phenyl group on one ligand with the 1,2,3 triazole unit of another ligand. Although the three silver ions adopt a linear arrangement (Ag1–Ag2–Ag3 176.85°), the silver–silver distances (Ag1–Ag2 4.073 Å, Ag2–Ag3 4.137 Å) preclude any additional stabilization from Ag(I)–Ag(I) interactions. It appears that the formation of the trisilver complex is driven by crystal packing forces. The crystal used for the X-ray crystallography was dissolved in acetonitrile and the ESMS spectrum acquired. Disappointingly, only the $[\mathbf{3a}_2Ag]^+$ fragment at $m/z = 579$ was observed, suggesting that the trisilver unit is either not stable under the conditions of the ESMS experiment or is unstable in solution, potentially because the electrostatic repulsion generated between the three cationic silver ions is enough to overcome the relatively weak Ag–N coordination bonds.

Despite the solution data indicating that $[(\mathbf{4a})Ag](SbF_6)$ forms a discrete complex the molecule crystallises as a coordination poly-

[6] Inspired by the τ_5 parameter, Houser et al. (Ref. [105]) have developed a similar semiquantitative method for determining the coordination geometry of a four coordinated complexes, τ_4. The τ_4 parameter ($\tau_4 = 360° - (\beta + \alpha)/141°$) is used to distinguish between tetrahedral ($\tau_4 = 1$) and square planar ($\tau_4 = 0$) geometries.

mer, where the ligand **4a** does not interact in the expected tridentate manner. The asymmetric unit contained one silver(I) ion, one ligand, one molecule of acetone and one SbF_6^- counterion. The silver ion is tetrahedrally (τ_4 = 0.80) coordinated to four nitrogen donor atoms. The pyridyl (N4) and one of the triazole (N6) units of **4a** from a bidentate chelate with the silver ion and the other two coordination sites are taken by triazole units from different molecules of **4a**. The triazole unit that forms the bidentate chelate is additionally coordinated, in a bridging fashion, to an adjacent silver ion through N7 and the final coordination site is occupied by the triazole unit (N1) in the other arm of the ligand **4a.** This arrangement gives rise to a 4,4 net (Supporting information).

The X-ray crystallography of the silver(I) complex formed with the tridentate ligand **2a** was also surprising. The complex crystallises in the tetragonal space group $I4_1cd$ and shows the presence of the tetrameric $[(\mathbf{2a})Ag]_4^{4+}$ cation (supporting information). While the connectivity of this tetrasilver cation $[(\mathbf{2a})Ag]_4^{4+}$ is well defined we have been unable to satisfactorily refine the data, despite collecting multiple diffraction data sets from several different crystals of reasonable quality. As such we present only a qualitative summary of the data. Similar to the silver complex with the tridentate ligand **4a**, **3a** does not interact in the expected tridentate manner. There are two crystallographically distinct silver atoms, both of which adopt a distorted tetrahedral coordination geometry (τ_4 = 0.62 and 0.65) involving the coordination of one pyridyl and three triazole donors. The pyridyl and one of the triazole units of ligand **3a** forms a planar bidentate chelate with one silver ion and the second triazole unit of the ligand is coordinated, in a bridging fashion, to two adjacent silver ions. This generates a complex intertwined tetrameric architecture that is further stabilized by multiple π–π interactions between the pyridyl, triazole and benzyl groups of the ligand and additionally, a Ag-Ag interaction (supporting information). Despite the difficulties with the structure refinement we note that the architecture of $[(\mathbf{2a})Ag]_4(SbF_6)_4$ is completely consistent with the solution ^{1}H NMR data (i.e the extensive π–π interactions within the molecular architecture of $[(\mathbf{2a})Ag]_4(SbF_6)_4$ are responsible for the observed upfield shifts in ^{1}H NMR).

4. Conclusion

We have developed a facile, high yielding, one pot, multi-component CuAAC method for the synthesis of alkyl, benzyl or aryl substituted pyridyl-1,2,3-triazole ligands from their corresponding halides, sodium azide and alkynes. The disclosed method is safer and more efficient than the previously reported synthetic approaches to these types of ligand scaffolds. This modular method should find application in a range of different areas that require readily functionalized ligand architectures, including drug discovery and catalysis [1–17]. We are currently investigating the use of this methodology for the synthesis of more complex polydentate and macrocyclic ligands. Additionally, we have demonstrated that these ligands readily form a variety of interesting coordination complexes with Cu(II) and Ag(I) ions. In most of the examined cases these simple pyridyl-1,2,3-triazole ligands act as readily functionalised bipy and terpy analogues. However, the presence of the addition nitrogen donor in the 1,2,3-triazole unit can lead to formation of quite complex molecular architectures, including unexpected interdigitated tri and tetrasilver complexes.

Acknowledgements

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Appendix A. Supplementary material

CCDC 728064, 728065, 728062, 728063, 728301, 728300, 728302, 728303, 728304 and 728432 contain the supplementary crystallographic data for **1c**, **2c**, **3b**, **4b**, $[(\mathbf{2a})CuCl_2]$, $(\mathbf{3a})_2CuCl_2]$, $[(\mathbf{1a})_2Ag](SbF_6)]$, $[(\mathbf{3a})_4Ag_3](SbF_6)_3 + 0.5[(\mathbf{3a})_2Ag](SbF_6)$, $[(\mathbf{4a})Ag](SbF_6)]_\infty$ and $[(\mathbf{2a})_4Ag_4](SbF_6)_4]$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.06.010.

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