Cu(I) complexes based on *cis*, *cis*-1,3,5-tris(arylideneamino)cyclohexane ligands: synthesis, structure and CO binding†

Parisa Ebrahimpour, Michael Cushion, Mairi F. Haddow, Andrew J. Hallett and Duncan F. Wass*

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A new series of sterically bulky, facially coordinating N_3-donor tach-based ligands (tach; *cis*,*cis*-1,3,5-triaminocyclohexane) [**2.1**; *cis*,*cis*-1,3,5-tris(2,4-dimethylbenzylideneamino)cyclohexane, **4.1**; *cis*,*cis*-1,3,5-tris(pentamethylbenzylideneamino)cyclohexane, **5.1**; *cis*,*cis*-1,3,5-tris(2,6-dimethoxybenzylideneamino)cyclohexane, **6.1**; *cis*,*cis*-1,3,5-tris(pentafluorobenzylideneamino)-cyclohexane, **7.1**; *cis*,*cis*-1,3,5-tris(3,5-bis(ditrifluoromethyl)benzylideneamino)cyclohexane, **8.1**; *cis*,*cis*-1,3,5-tris(2-trifluoromethylbenzylideneamino)cyclohexane, **9.1**; *cis*,*cis*-1,3,5-tris(2-methoxybenzylideneamino)cyclohexane] have been obtained from the condensation of tach with three equivalents of the appropriate substituted benzaldehyde. Reaction with $[Cu(NCCH_3)_4]PF_6$ gives Cu(I) complexes of tach-based ligands {**2.2–9.2**, *eg*; **2.2**; $[Cu(\mathbf{2.1})(NCCH_3)]PF_6$}. Displacement of the acetonitrile ligand by CO was achieved successfully for all the Cu(I) complexes of tach-based ligands and the resulting complexes have been shown to bind carbon monoxide {**2.3–9.3**, *eg*; **2.3**; $[Cu(\mathbf{2.1})(CO)]PF_6$}. The X-ray single crystal structures of **5.1**, **8.1**, **9.1**, **3.2**, **7.2**, **8.2**, **9.2**, **3.3**, **5.3** and **6.3** have been determined.

Introduction

Ligands based on a *cis*,*cis*-1,3,5-tris(arylamino)cyclohexane framework have attracted attention as they provide a face-capping N_3-coordination environment around a metal centre which is a versatile mimic for metalloenzyme active sites.[1–5] More generally, these ligands form a protected cavity around the metal centre which has been exploited in biomimetic and catalysis research.[6–9] Several synthetic routes for the generation of *cis*,*cis*-1,3,5-triaminocyclohexane (tach) ligands have been reported.[10–12] A general disadvantage of these methods is the undesirable generation of *cis* and *trans* isomers, which are difficult to separate. Planalp and co-workers discovered a synthetic route that almost exclusively produces the *cis*-isomer of tach (**1**) from the commercially available *cis*,*cis*-1,3,5-cyclohexanetricarboxylic acid; this route is key in enabling the use of this ligand framework.[13]

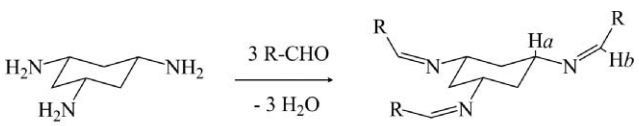
Our interest in such ligands stems from the potential their group 11 complexes to separate simple substrates (such as CO and ethylene) from the mixture of waste gases that are common in petrochemical plants and refining, by weakly binding to such molecules.[14] Moreover such complexes could also be used in concentrating and delivering ^{11}CO, an important development for radiolabelling in positron emission tomography technology.[15]

We have previously communicated the synthesis and preliminary study of one derivative of tach-based ligands, namely *cis*,*cis*-1,3,5-tris(mesitylideneamino)cyclohexane, its copper(I) complex and the substrate binding selectivity of this complex.[16] We report here the syntheses and characterisation of a broader library of novel non-fluorinated and fluorinated N_3-donor tach-based ligands, their Cu(I) complexes and the propensity of such complexes to bind CO.

Results and discussion

Synthesis and structural study of tach-based ligands

Cis,*cis*-1,3,5-tris(arylamino)cyclohexane ligands were prepared by same the method we used to obtain *cis*,*cis*-1,3,5-tris(mesitylideneamino)cyclohexane.[16] Reaction of *cis*,*cis*-1,3,5-triaminocyclohexane (tach) with three equivalents of the appropriate substituted benzaldehyde in toluene and removal of water by azeotropic distillation over an 18–20 h period gave the relevant tach-based ligands in 34 to 81% yield (see Scheme 1). The ^1H NMR spectrum of each ligand exhibited a characteristic broad singlet around 8.50 ppm and a broad triplet of triplets around 3.50 ppm, corresponding to the amine protons (-N=CH_b-) and cyclohexane protons (=N–CH_a-) respectively. All the prepared ligands are stable with respect to ambient conditions.



(1)

2.1: R = 2,4-$(CH_3)_2C_6H_3$
3.1: R = C_6H_5
4.1: R = $C_6(CH_3)_5$
5.1: R = 2,6-$(OCH_3)_2C_6H_3$
6.1: R = C_6F_5
7.1: R = 3,5-$(CF_3)_2C_6H_3$
8.1: R = 2-$(CF_3)C_6H_4$
9.1: R = 2-$(OCH_3)C_6H_4$

Scheme 1 General synthesis of tach-based ligands **2.1–9.1**.

Crystals of **5.1**, **8.1** and **9.1** suitable for single crystal X-ray analysis were obtained by slow evaporation of a CH_2Cl_2 solution under ambient conditions. The structures of **5.1**, **8.1** and **9.1**

School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK BS8 1TS. E-mail: duncan.wass@bristol.ac.uk

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Table 1 Selected bond lengths (Å) and angles (°) for **5.1**·6(H_2O), **8.1** and **9.1**·CH_2Cl_2

5.1·6(H_2O)		**8.1**		**9.1**·CH_2Cl_2	
N1–C3	1.2712(16)	N1–C7	1.268(2)	N1–C7	1.269(2)
N1–C3–C4–C5	−147.88(13)	N2–C15	1.270(2)	N2–C15	1.267(2)
		N3–C23	1.269(2)	N3–C23	1.272(2)
		N1–C7–C8–C13	146.88(14)	N1–C7–C8–C9	−166.70(18)
		N2–C15–C16–C21	−149.84(15)	N2–C15–C16–C17	−173.19(19)
		N3–C23–C24–C29	177.04(14)	N3–C23–C24–C25	176.26(18)

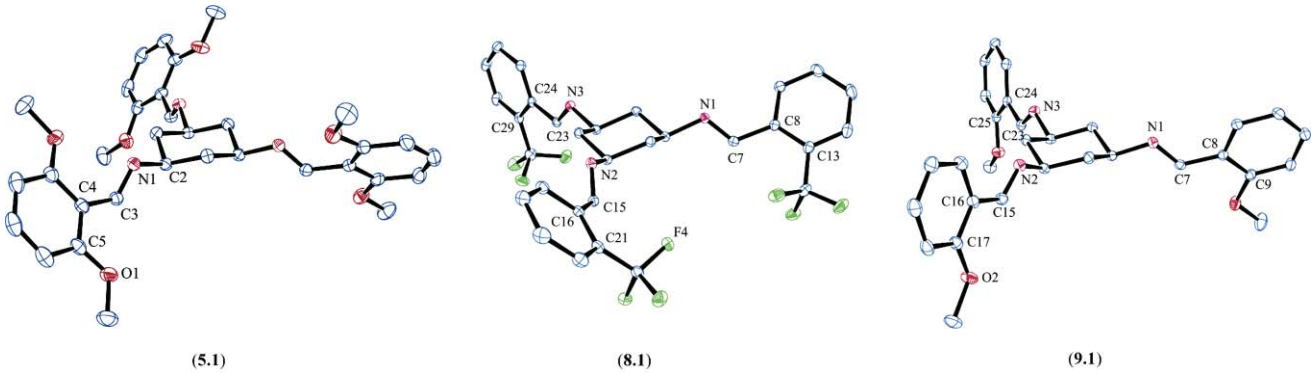


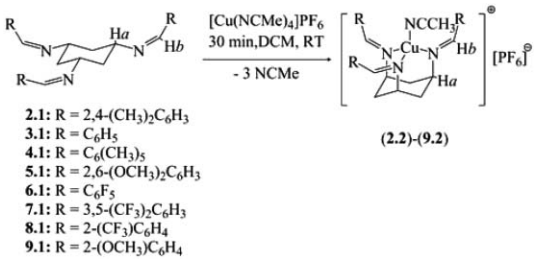
Fig. 1 ORTEP representation of the molecular structures of **5.1**·6(H_2O), **8.1** and **9.1**·CH_2Cl_2. For clarity all hydrogen atoms have been omitted as well as a molecule of CH_2Cl_2 from **9.1** and six molecules of H_2O from **5.1** molecular structures. Thermal ellipsoids are drawn at the 50% probability level.

are shown in Fig. 1 and selected bond and angles given in Table 1.

Molecular structures of **5.1**, **8.1** and **9.1** show the tach-based ligand has three benzyl substituted imino arms that inherit the *cis*,*cis*-stereochemistry. Each imine moiety adopts the sterically favourable equatorial position, whereby the cyclohexane backbone is found in the chair conformation.

Synthesis and molecular structure of complexes [Cu(NCMe)(2.1–9.1)]PF_6 (2.2–9.2)

The Cu(I) complexes of tach-based ligands **2.2–9.2** were synthesised in moderate to excellent yields (25–98%) by reaction with the corresponding ligands **2.1–9.1** with [Cu(I)($NCCH_3$)$_4$]PF_6 in CH_2Cl_2. The reaction between ligand and metal precursor was monitored by ^{1}H NMR spectroscopy. Observation of the H_a protons provided an analytic NMR handle for the quantitative assessment of the reaction progress. These cyclohexyl protons were observed to resonate in the uncoordinated ligands **2.1–9.1** between 3.50–3.90 ppm (see Scheme 2). Upon coordination to Cu(I)-NCMe fragments, these signals typically experience a downfield shift to resonate between 4.10–4.40 ppm. Solid samples of these



Scheme 2 Reaction of tach-based ligands with [Cu(I)($NCCH_3$)$_4$]PF_6.

Cu(I) complexes can be handled under ambient conditions for approximately two weeks without any apparent decomposition; polyfluorination of these ligands has been shown to increase the thermal stability and the solubility in fluorocarbon solvents of these metal complexes.[17,18] Corresponding properties were observed for the complexes **6.2** and **8.2**, where an increased degree of fluorination is present. Crystals containing **3.2**, **7.2**, **8.2** and **9.2** were grown from saturated dichloromethane–hexane solutions. X-Ray crystallography data of **3.2**·CH_2Cl_2, **7.2**, **8.2** and **9.2**·CH_2Cl_2 are given in Table 5. Molecular structures of **7.2**, **8.2** and **9.2**·CH_2Cl_2 (Fig. 2, with selected bond lengths and angles in Table 2) show that the phenyl rings are arranged facially around the copper centre, producing a cavity, in which one molecule of acetonitrile can be accommodated (Scheme 1). The coordination geometry around the Cu(I) centre is pseudo-tetrahedral, whereby the N_{tach}–Cu–N_{tach} bond angles range between 86°–102° and the N_{MeCN}–Cu–N_{tach} bond angles range between 114°–129°. A slight shortening of the C_{MeCN} –N_{MeCN} bond length (1.132 to 1.143 Å) in comparison with free acetonitrile (1.155 Å) is observed and it is expected upon coordination to a copper centre.[19]

The Cu-complex of ligand **3.1** (compound **3.2**) was obtained from its reaction with [Cu($NCMe$)$_4$]PF_6 in CH_2Cl_2, following exactly the same method as other complexes. Surprisingly the ^{1}H NMR and elemental analysis obtained was not consistent with the expected compound, analogous to other examples. This mystery was illuminated by the X-ray crystal structure of **3.2** (Fig. 3), showing co-crystallisation of the expected **3.2(A)** with **3.2(B)**. The molecular structure of **3.2(B)** contains two **3.1** ligands in which the phenyl arms of the two ligands are in equatorial position. Three copper centres are coordinated to the nitrogen of each ligand and adopt a linear geometry with an angle of 173.03°. The Cu–N distance is 1.909 Å on average and N═C are approximately

Table 2 Selected bond lengths (Å) and angles (°) for **7.2**, **8.2** and **9.2**·CH_2Cl_2

7.2		**8.2**		**9.2**·CH_2Cl_2	
N4–C1	1.137(4)	N2–C1	1.138(5)	N1–C1	1.143(4)
N4–Cu1	1.922(2)	N2–Cu1	1.899(3)	N1–Cu1	1.943(3)
N1–C9	1.275(4)	N1–C5	1.269(3)	N2–C9	1.283(4)
N2–C27	1.274(4)	Cu1–N2–C1	180.00(16)	N3–C17	1.276(4)
N3–C18	1.283(4)	N1–C5–C6–C7	−118.4(3)	N4–C25	1.273(4)
Cu1–N4–C1	175.5(3)			Cu1–N1–C1	178.0(3)
N1–C9–C10–C15	−40.2(4)			N2–C9–C10–C15	162.0(3)
N2–C27–C28–C33	−45.6(4)			N3–C17–C18–C23	153.2(3)
N3–C18–C19–C20	157.4(3)			N4–C25–C26–C31	37.5(4)

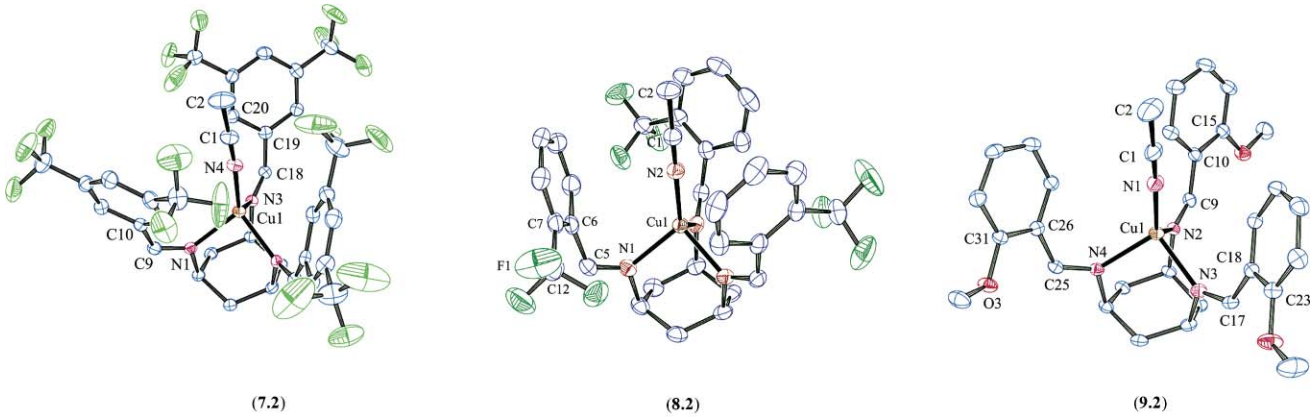


Fig. 2 ORTEP representation of the molecular structures of **7.2**, **8.2** and **9.2**·CH_2Cl_2. For clarity all hydrogen atoms and the $[PF_6]^-$ counter ions have been omitted as well as a molecule of CH_2Cl_2 from the molecular structure of **9.2**. Thermal ellipsoids are drawn at the 50% probability level.

Table 3 Selected bond lengths (Å) and angles (°) for **3.2**·CH_2Cl_2

3.2(A)		**3.2(B)**	
Cu1–N1	2.105(7)	Cu2–N9	1.902(6)
Cu1–N2	2.068(7)	Cu2–N5	1.922(6)
Cu1–N3	2.063(7)	Cu3–N6	1.913(6)
Cu1–N4	1.933(7)	Cu3–N10	1.906(6)
N1–C9	1.283(10)	Cu4–N7	1.909(6)
N2–C16	1.270(13)	Cu4–N8	1.907(6)
N4–C7	1.132(10)	N10–C77	1.282(9)
Cu1–N4–C7	176.8(7)	N6–C43	1.269(9)
		N7–C50	1.292(9)
		N8–C63	1.291(9)
		N9–C70	1.288(9)
		N5–C36	1.265(9)
		N6–Cu3–N10	172.8(3)
		N6–Cu3–N10	172.4(3)
		N6–Cu3–N10	173.9(3)

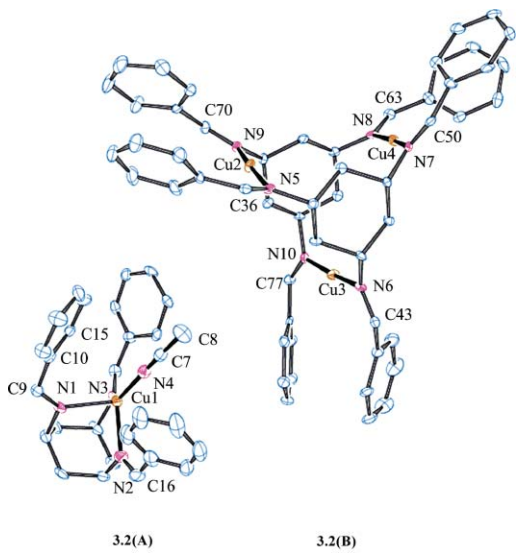


Fig. 3 ORTEP representation of the molecular structure of **3.2**·CH_2Cl_2. For clarity all hydrogen atoms have been omitted as well as a molecule of CH_2Cl_2 and the $[PF_6]^-$ counter ions. Thermal ellipsoids are drawn at the 50% probability level.

1.281 Å (see Table 3) whereby the other complex shows that the Cu centre is four-coordinate and adopts a pseudo tetrahedral geometry. The phenyl rings are arranged facially around the coordinated acetonitrile. The coordinated acetonitrile is linear and the bond length of N_{MeCN}–C7 is 1.132(10) Å which is slightly shorter than free acetonitrile (1.155 Å). Other characterising data (NMR spectra, elemental analysis) is consistent with this co-crystalline product. Whilst the formation of **3.2(B)** is certainly unexpected, it is noteworthy that ligand **3.1** is the least sterically bulky of those investigated, and therefore potentially the best able to accommodate this structure.

Reactivity of tach-based Cu(I) complexes with CO

Treatment of Cu(I) complexes (**2.2–9.2**) with CO in CH_2Cl_2 leads to a marked colour change from intense yellow to much paler yellow or colourless, and the complete replacement of acetonitrile as monitored by ^{1}H NMR. The IR spectra of these complexes show the expected ν(CO) between 2099–2073 cm^{-1} indicating minimal

backbonding to the coordinated CO ligand.[16,18] The trends in ν(CO) are very much as expected with complex **5.3**, containing a ligand with an electron-releasing 2,6-dimethoxy aryl substitution pattern, appearing at 2073 cm^{-1}, and complex **7.3**, containing an electron-withdrawing 3,5-ditrifluoromethyl aryl substitution pattern, appearing at 2099 cm^{-1}. As previously reported, copper causes fast relaxation of proximal nuclei, and it was not possible to observe the ^{13}C NMR resonance for the coordinated CO.[16]

Suitable crystals of **3.3**, **5.3** and **6.3** for X-ray structure determination were grown by slow diffusion of *n*-hexane into CH_2Cl_2 solutions of these complexes. The molecular structures are illustrated in Fig. 4, with selected bond lengths and angles in Table 4. Crystals of **3.3**, **5.3**·CH_2Cl_2 and **6.3** form in the space groups $C2/c$, $P2_13$ and $P\bar{3}c1$ respectively. Compound **6.3** has crystallographically-imposed threefold symmetry (as do compounds **5.1** and **8.2**). The copper complexes adopt a very similar conformation to **3.2**, **8.2** and **9.2**, *i.e.* a pseudo tetrahedral

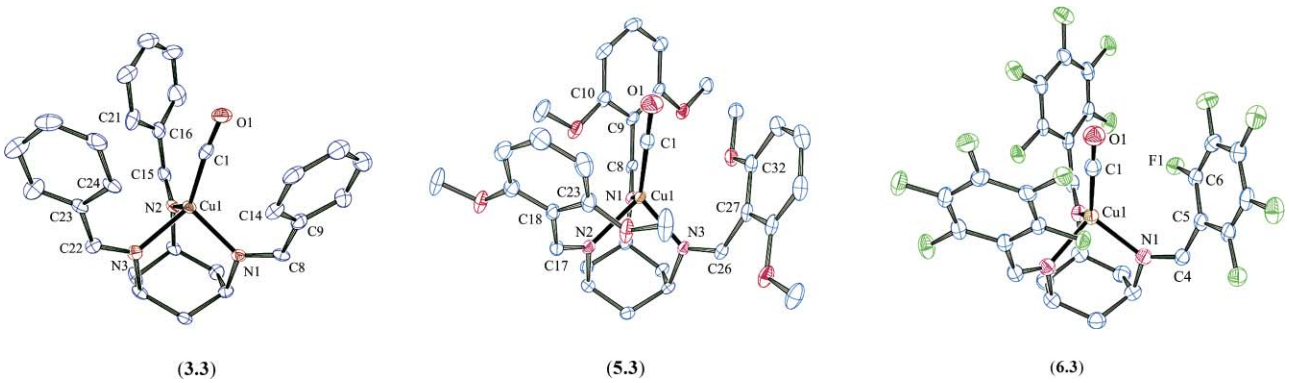


Fig. 4 ORTEP representation of the molecular structures of **3.3**, **5.3**·$CH_2Cl_2$and **6.3**. For clarity all hydrogen atoms and the $[PF_6]^-$ counter ions have been omitted as well as a molecule of CH_2Cl_2 from the molecular structure of **5.3**. Thermal ellipsoids are drawn at the 50% probability level.

Table 4 Selected bond lengths (Å) and angles (°) for **3.3**, **5.3**·CH_2Cl_2 and **6.3**

3.3		**5.3**·CH_2Cl_2		**6.3**	
C1–O1	1.150(6)	C1–O1	1.202(3)	C1–O1	1.117(9)
Cu1–C1	1.808(6)	Cu1–C1	1.938(2)	Cu1–C1	1.824(7)
N1–C8	1.294(6)	N1–C8	1.274(3)	N1–C4	1.273(5)
N2–C15	1.270(6)	N2–C17	1.227(3)	Cu1–C1–O1	180.0
N3–C22	1.294(6)	N3–C26	1.228(3)	N1–C4–C5–C6	–46.5(5)
Cu1–C1–O1	171.9(5)	Cu1–C1–O1	179.4(2)		
N1–C8–C9–C14	44.9(8)	N1–C8–C9–C10	–50.4(3)		
N2–C15–C16–C21	–45.2(7)	N2–C17–C18–C23	–55.7(3)		
N3–C22–C23–C24	–31.2(8)	N3–C26–C27–C32	–48.0(3)		

Table 5 X-Ray crystallography data of **5.1**.6H_2O, **7.1** and **9.1**·CH_2Cl_2

Compound	**5.1**.6H_2O	**7.1**	**9.1**·CH_2Cl_2
Colour, habit	Yellow needle	Colourless plate	Yellow block
Empirical formula	$C_{33}H_{39}N_3O_6.6(H_2O)$	$C_{30}H_{24}F_9N_3$	$C_{30}H_{33}N_3O_3{\cdot}CH_2Cl_2$
M	681.77	597.52	568.52
Crystal system	Trigonal	Monoclinic	Monoclinic
Space group	$R\bar{3}$	$P2_1/n$	$P2_1/c$
a/Å	21.4700(7)	14.9989(7)	20.8117(17)
b/Å	21.4700(7)	8.0442(4)	13.7364(10)
c/Å	13.9509(10)	23.7247(11)	10.7141(7)
α (°)	90.00	90.00	90.00
β (°)	90.00	102.2680(10)	103.852(4)
γ (°)	120.00	90.00	90.00
V/Å^3	5569.3(5)	2797.1(2)	2973.8(4)
Z	6	4	4
μ/mm^{-1}	0.093	0.126	0.254
T/K	100(2)	100(2)	100(2)
Reflections: (measured/unique/observed)	33104/4488/3081	24293/6481/4585	6951/6901/4459
R_{int}	0.0578	0.0370	—
R_1(observed reflection)[$I \geq 2\ \sigma$ (I)]	0.0565	0.0396	0.0505
wR_2(all reflection)	0.1769	0.1015	0.1162

coordination for the Cu(I) centre. Notable is the significant increase in the bond length of CO (1.20 Å) in **5.3** compared with free CO (1.128 Å).[20] This is in contrast to the CO bond length of 1.171 Å in **6.3**, and is consistent with the increased donor ability of this methoxy-substituted derivative compared to the fluorinated analogue.

One of the notable features of the complexes reported in our preliminary communication is the preference for CO binding over ethylene.[16] Again with this wider set of derivatives, the facile substitution of acetonitrile with CO is in contrast to the lack of substitution reactivity of the same acetonitrile complexes with olefins. Bubbling ethylene through dichloromethane solutions of (**2.2–9.2**) gives no reaction. Only in the case of complex **8.2** when pressurised with 1–5 bar of ethylene in a high pressure NMR tube, was the signal corresponding to coordinated ethylene observed. Upon coordination of ethylene to the copper centre, resonance for the olefinic protons was upfield shifted from 5.40 ppm for free ethylene to 5.23 ppm (–20 °C) for coordinated ethylene in [(**8.1**)Cu(η^2-C_2H_4)]PF_6.[21] The moderate upfield shifting demonstrates a weak π-back donation from the copper centre to ethylene.[18,21,22] Compound [(**8.1**)Cu(η^2-C_2H_4)]PF_6 was observed to be stable under positive pressure of ethylene. However, it was not possible to isolate the compound under ambient pressure, suggesting a reversible complexation of ethylene to the copper centre.

Conclusions

A set of novel non-fluorinated and fluorinated N_3-donor tach-based ligands (**2.1–9.1**) were synthesised and structurally characterised. Cu-complexes of these ligands were obtained from their reaction with [Cu(NCMe)$_4$]PF_6. The X-ray structures reveal a sterically constrained cavity around the fourth coordination site of the copper centre in which one molecule of acetonitrile can be easily accommodated. In order to assess the ability of the prepared Cu(I)–NCMe complexes of tach-based ligands (**2.2–9.2**) to accommodate σ-donating and π-accepting small molecules, exchange reactions with CO were carried out. The reactions were monitored by solution IR spectrometry and successful displacement of the acetonitrile ligand by CO was observed for all the Cu(I) complexes of tach-based ligands. By contrast, and in line with our previous observations even for this broader library of derivatives, ethylene is a poor ligand for such complexes.

Experimental

General

All operations were carried out under an inert atmosphere of argon or dinitrogen using standard Schlenk line techniques or an MBraun glove box. Dry N_2-saturated solvents were purified using an anhydrous engineering Grubbs-type system.[23] All other chemicals were used as received unless otherwise stated. NMR spectra were recorded using Varian VNMR S500, Jeol GX400, Joel ECP (Eclipse) 400, Jeol ECP300 and Jeol Lambda 300 spectrometers. Compounds **1** and **3.1** were prepared as described in the literature.[13,24]

IR solution spectra were recorded on a Perkin–Elmer 1600 series FTIR Spectrometer in dichloromethane. Mass spectra were recorded on VG Analytical Quattro (ESI). Microanalyses were carried out by the Microanalytical Laboratory of the School of Chemistry at the University of Bristol.

Synthesis of ligands and complexes

Synthesis of tach-based ligands 2.1–9.1

The synthesis of tach-based ligands **2.1–9.1** will be described in detail for *cis*,*cis*-1,3,5-tris(2,4-dimethylbenzylideneamino)-cyclohexane (**2.1**) and is representative for the synthesis of ligands **3.1–9.1**.

Synthesis of *cis*,*cis*-1,3,5-tris(2,4-dimethylbenzylideneamino)-cyclohexane (2.1). Compound *cis*,*cis*-1,3,5-triaminocyclohexane **1** (0.50 g, 1.4 mmol) was dissolved in a solution of three equivalents of sodium hydroxide (0.17 g, 4.2 mmol) in water (10 mL), followed by addition of toluene (30 mL) and three equivalents of 2,4-dimethylbenzaldehyde (0.56 g, 0.57 mL, 4.2 mmol). The reaction was heated to 150 °C for 18–22 h, during which time water was removed *via* azeotropic distillation with a Dean–Stark trap. The solution was allowed to cool to ambient temperature, passed through a short celite plug and the solvent was removed under reduced pressure to leave a pale yellow solid. The crude product was recrystallised from a minimal amount of hot diethylether and dried *in vacuo* to give **2.1** as a white powder (0.31 g, 47% yield) after purification. ^{1}H NMR (400.18 MHz, CD_2Cl_2): δ 8.68 (s, 3H, *H*C═N), 7.78 (d, 3H, $^3J_{HH}$ 7.77 Hz, H_5Ar), 7.07 (d, 3H, $^3J_{HH}$ 7.82 Hz, H_6Ar), 7.04 (s, 3H, H_3Ar), 3.58 (tt, 3H, $^3J_{HH}$11.47 Hz, $^3J_{HH}$ 3.79 Hz, -C*H*-N═), 2.50 (s, 9H, *ortho*-ArCH_3), 2.35 (s, 9H, *para*-ArCH_3), 2.01 (q, br, 3H, $^3J_{HH}$ 11.93 Hz, *trans*-C*H*H-), 1.86 (dt, br, 3H, $^3J_{HH}$11.73 Hz, $^3J_{HH}$ 3.79 Hz, *cis*-CH*H*-). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 157.7 (s, *C*═N), 140.3 (s, Ar-C_2), 137.6 (s, Ar-C_4), 131.5 (s, Ar-C_3), 127.4 (s, Ar-C_6), 126.9 (s, Ar-C_5), 123.5 (s, Ar-C_1), 67.1 (s, cy-*C*H), 41.6 (s, cy-*C*H$_2$), 21.1 (s, *ortho*-Ar*C*H$_3$) and 19.1 (s, *para*-Ar*C*H$_3$). ESI mass spectrum: m/z = 500.30 [M + Na]$^+$, 478.322 [M+H]$^+$. CI HR mass spectrum: m/z = 500.3042 [M +Na]$^+$ (calcd 500.3036), 478.3223 [M +H]$^+$ (calcd 478.3216). Anal. calc. for $C_{33}H_{39}N_3$: C, 82.97. H, 8.23. N, 8.80. Found: C, 83.00. H, 8.43. N, 8.71%.

Synthesis of *cis*,*cis*-1,3,5-tris(benzylideneamino)cyclohexane (3.1). Sodium hydroxide (0.16 g, 4.2 mmol) in water (10 mL) was added to compound **1** (0.5 g, 1.4 mmol), followed by toluene (30 mL) and benzaldehyde (0.43 mL, 4.2 mmol). Yielded **3.1** as a cream solid (0.4 g, 73%) after purification. ^{1}H NMR (499.9 MHz, CD_2Cl_2): δ 8.30 (s, br, 3H, *H*C═N), 7.66 (m, br, 6H, *H*Ar), 7.33 (m, br, 9H, *H*Ar), 3.50 (tt, 3H, $^3J_{HH}$ 11.44 Hz, $^3J_{HH}$ 3.81 Hz, -C*H*-N═), 1.89 (dd, 3H, $^3J_{HH}$ 11.60 Hz, *trans*-C*H*H-), 1.77 (m, 3H, $^3J_{HH}$ 11.90 Hz, $^3J_{HH}$ 3.97 Hz, *cis*-CH*H*-). ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ 158.5 (s, *C*═N), 135.9 (s, Ar-C_{ipso}), 129.7 (s, Ar-C_{para}), 127.7 (s, Ar-C_{ortho}), 127.3 (s, Ar-C_{meta}), 65.6 (s, cy-*C*H), 40.3 (s, cy-*C*H$_2$).

Synthesis of *cis*,*cis*-1,3,5-tris(pentamethylbenzylideneamino)-cyclohexane (4.1). Compound **1** (4.00 g, 10.75 mmol) was treated by a solution of sodium hydroxide (1.29 g, 32.26 mmol) in water (10 mL) followed by toluene (100 mL) and pentamethylbenzaldehyde (5.68 g, 32.26 mmol). The reaction was carried out under the general reaction conditions for making tach-based-ligands. The ligand **4.1** was obtained as a white/cream microcrystalline

solid (2.23 g, 34% yield). ^{1}H NMR (300.5 MHz, $CDCl_3$): δ 8.75 (s, br, 3H, *H*C═N), 3.70 (tt, 3H, $^3J_{HH}$ 11.30 Hz, $^3J_{HH}$ 3.80 Hz, -C*H*-N═), 2.25 (s, 18H, *ortho*-CH_3), 2.24 (s, 9H, *para*-CH_3), 2.20 (s, 18H, *meta*-CH_3), 2.02 (d, 3H, $^3J_{HH}$ 12.11 Hz, *trans*-C*H*H), *trans*-CH*H*- obscured by ArCH_3 signals. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 161.9 (s, *C*═N), 140.1 (s, Ar-C_{ortho}), 133.7 (Ar-C_{meta}), 132.6 (Ar-C_{para}), 131.4 (Ar-C_{ipso}), 67.5 (cy-*C*H), 41.3 (cy-*C*H_2), 17.4 (Ar–C_{para}), 16.8 (Ar–C_{meta}) and 15.9 (Ar-C_{ortho}). ESI mass spectrum: m/z = 626.44 [M + Na]$^+$, 604.46 [M+H]$^+$ (calcd 603.46). CI HR mass spectrum: m/z = 626.4444 [M +Na]$^+$ (calcd 626.4443), 604.4625 [M +H]$^+$ (calcd 604.4625).

Synthesis of *cis*,*cis*-1,3,5-tris(2,6-dimethoxybenzylideneamino)-cyclohexane (5.1). Treatment of compound **1** (0.74 g, 1.9 mmol) in a solution of sodium hydroxide (0.15 g, 3.8 mmol) in water (10 mL) and toluene (30 mL) with 2,6-dimethoxybenzaldehyde (0.63 g, 3.8 mmol). Yielded **5.1** as a white solid (0.54 g, 47%). ^{1}H NMR (400.18 MHz, CD_2Cl_2): δ 8.62 (s, 3H, *H*C═N), 7.32 (t, 3H, $^3J_{HH}$ 8.42 Hz, H_{para}Ar), 6.63 (d, 6H, $^3J_{HH}$ 8.43 Hz, H_{meta}Ar), 3.85 (s,18H, -OCH_3), 3.54 (tt, 3H, $^3J_{HH}$ 11.27 Hz, $^3J_{HH}$ 3.85 Hz, -C*H*-N═), 2.02 (q, br, 3H, $^3J_{HH}$ 11.61 Hz, *trans*-C*H*H-), 1.89 (m, 3H, *cis*-CH*H*-). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 159.5 (s, Ar-C_{ortho}), 154.3 (s, *C*═N), 130.8(s, Ar-C_{para}), 104.3 (s, Ar-C_{meta}), 103.7(s, Ar-C_{ipso}), 68.3 (s, cy-*C*H), 56.1 (s, -O*C*H_3), 41.5 (s, cy-*C*H_2). ESI mass spectrum: m/z = 574.29 [M+H]$^+$. CI HR mass spectrum: m/z = 574.2930 [M +H]$^+$ (calcd 574.2911).

Synthesis of *cis*,*cis*-1,3,5-tris(pentafluorobenzylideneamino)-cyclohexane (6.1). Ligand **6.1** was obtained by addition of sodium hydroxide (0.22 g, 3.6 mmol) in water (10 mL) to compound **1** (0.70 g, 1.8 mmol) followed by toluene (30 mL) and pentafluorobenzaldehyde (0.67 mL, 3.6 mmol), under general reaction conditions. Yielded **6.1** (0.54 g, 44%) as a cream solid. ^{1}H NMR (299.9 MHz, CD_2Cl_2): δ 8.47 (s, 3H, *H*C═N), 3.60 (tt, 3H, $^3J_{HH}$ 11.38 Hz, $^3J_{HH}$ 4.13 Hz, -C*H*-N═), 2.03 (q, br, 3H, *trans*-C*H*H-), 1.88 (m, br, 3H, *cis*-CH*H*-). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 147.5 (s, *C*═N), 145.2 (dm, $^1J_{CF}$ 256.27 Hz, Ar-C_{ortho}), 141.3 (dm, $^1J_{CF}$ 256.27 Hz, Ar-C_{para}), 136.9 (dm, $^1J_{CF}$ 253.36 Hz, Ar-C_{meta}), 110.6 (m br, Ar-C_{ipso}), 66.8 (s, cy-*C*H), 39.3 (s, cy-*C*H_2). ^{19}F{^{1}H} NMR (282 MHz, CD_2Cl_2): δ –143.25 (m, 6F, F_{ortho}-Ar), –152.13 (t, 3F, $^3J_{FF}$ 20.56 Hz, *Fpara*-Ar), –166.80 (m, 6F, F_{meta}-Ar). ESI mass spectrum: m/z = 664.09 [M+H]$^+$, 686.07 [M+Na]$^+$ (calcd 663.08).), CI HR mass spectrum: m/z = 686.0684 [M +Na]$^+$ (calcd 686.0699), 664.0864 [M +H]$^+$ (calcd 664.0864).

Synthesis of *cis*,*cis*-1,3,5-tris(3,5-bis(ditrifluoromethyl)-benzylideneamino)cyclohexane (7.1). Treatment of **1** (1.0 g, 2.0 mmol) in a solution of sodium hydroxide (0.25 g, 6.00 mmol) in water (10 mL) and toluene (30 mL) with 3,5-bis(trifluoromethyl)benzaldehyde (1.00 mL, 1.45 g, 6.00 mmol). Yielded **7.1** as a white solid (0.85 g, 53%). ^{1}H NMR (299.9 MHz, CD_2Cl_2): δ 8.46 (s, 3H, *H*C═N), 8.23 (br s, 6H, H_{ortho}-Ar), 7.93 (ms, 3H, H_{para}-Ar), 3.69 (tt, 3H, $^3J_{HH}$ 11.3 Hz, $^3J_{HH}$ 4.0 Hz, -C*H*-N═), 2.05 (q, 3H, $^3J_{HH}$ 11.6 Hz, *trans*-C*H*H-), 1.89 (dt, 3H, $^3J_{HH}$ 11.93 Hz, $^3J_{HH}$ 3.7 Hz, *cis*-CH*H*-). ^{13}C NMR (75.57 MHz, CD_2Cl_2): δ 156.6 (s, *C*═N), 138.5 (s, Ar-C_{ipso}), 131.9 (q, $^2J_{CF}$ 34.04 Hz, Ar-C_{meta}), 128.1 (s, Ar-C_{para}), 123.9 (s, Ar-C_{ortho}), 123.3 (q, $^1J_{CF}$ 272.87 Hz, -CF_3), 66.0 (s, cy-*C*H), 40.4 (s, cy-*C*H_2). ^{19}F{^{1}H} NMR (282.78 MHz, CD_2Cl_2): δ –63.23 (m, -CF_3). ESI mass spectrum: m/z = 802.16 [M+H]$^+$, 824.14 [M+Na]$^+$ (calcd 801.14), CI HR mass spectrum: m/z = 824.1340 [M +Na]$^+$ (calcd 824.1349), 802.1521 [M +H]$^+$ (calcd 802.1509). Anal. calc. for $C_{33}H_{21}F_{18}N_3$: C, 49.45. H, 2.64. N, 5.24. Found: C, 49.32, H, 2.83, N, 5.18%.

Synthesis of *cis*,*cis*-1,3,5-tris(2-trifluoromethylbenzylidene-amino)cyclohexane (8.1). Sodium hydroxide (0.46 g, 12.09 mmol) in water (10 mL) was added to **1** (1.50 g, 4.03 mmol), followed by toluene (30 mL) and 2-(trifluoromethyl)benzaldehyde (1.59 mL, 2.11 g, 12.09 mmol). Yielded **8.1** as a white solid (1.94 g, 81%) after purification. ^{1}H NMR (299.9 MHz, CD_2Cl_2): δ 8.73 (m, 3H, *H*C═N), 8.22 (d, 3H, $^3J_{HH}$ 7.71 Hz, H_{ortho}-Ar), 7.67 (m, 3H, $H_{meta(3)}$-Ar), 7.60 (m, 3H, $H_{meta(5)}$-Ar), 7.51 (m, 3H, H_{para}-Ar), 3.66 (tt, 3H, $^3J_{HH}$ 11.40 Hz, $^3J_{HH}$ 4.0 Hz, -C*H*-N═), 2.03 (q, 3H, $^3J_{HH}$ 11.74 Hz, *trans*-C*H*H-), 1.85 (dt, 3H, $^3J_{HH}$ 11.74 Hz, $^3J_{HH}$ 4.12 Hz, *cis*-CH*H*-). ^{13}C NMR (75.57 MHz, CD_2Cl_2): δ 155.9 (s, *C*═N), 134.6 (s, Ar-C_5), 132.1 (s, Ar-C_6), 130.1 (s, Ar-C_4), 128.4 (q, $^2J_{CF}$ 32.31 Hz, Ar-C_2), 128.4 (s, Ar-C_1), 125.5 (s, Ar-C_{meta3}), 124.4 (q, $^1J_{CF}$ 274.60 Hz -CF_3), 66.5 (s, cy-*C*H), 40.6 (s, cy-*C*H_2). ^{19}F{^{1}H} NMR (282.78 MHz, CD_2Cl_2): δ –57.42 (s, -CF_3). ESI mass spectrum: m/z = 620.17 [M+Na]$^+$, 598.19 [M+H]$^+$. CI HR mass spectrum: m/z = 620.1732 [M +Na]$^+$ (calcd 620.1718), 598.1917 [M +H]$^+$ (calcd 598.1899).

Synthesis of *cis*,*cis*-1,3,5-tris(2-methoxybenzylideneamino)-cyclohexane (9.1). Treatment of **1** (5.00 g, 13.44 mmol) in a solution of sodium hydroxide (1.62 g, 40.35 mmol) in water (10 mL) and toluene (100 mL) with three equivalents of 2-methoxybenzaldehyde (4.87 mL, 5.49 g, 40.35 mmol). Yielded **9.1** as a cream solid (0.54.33 g, 67%). ^{1}H NMR (400.18 MHz; CD_2Cl_2): δ 8.84 (s, br, 3H, *H*C═N), 7.98 (dd, 3H, $^3J_{HH}$ 7.7 Hz, $^4J_{HH}$ 1.8 Hz, H_6-Ar), 7.42 (ddd, 3H, $^3J_{HH}$ 8.3 Hz, $^3J_{HH}$ 7.2 Hz, H_5-Ar), 7.01 (t, 3H, $^3J_{HH}$ 7.50 Hz, H_4-Ar), 6.98 (d, 3H, $^3J_{HH}$ 8.30 Hz, H_3-Ar), 3.90 (s, 9H, –O–CH_3), 3.61 (tt, 3H, $^3J_{HH}$ 11.30 Hz, $^3J_{HH}$ 3.90 Hz, -C*H*-N═), 2.00 (q, 3H, $^3J_{HH}$ 11.80 Hz, *trans*-C*H*H-), 1.87 (dt, 3H, $^3J_{HH}$ 11.80 Hz, $^3J_{HH}$ 3.90 Hz, *cis*-CH*H*-). ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ 158.9 (s,Ar-C_2), 155.2 (s, *C*═N),131.8 (s, Ar-C_5), 127.3 (s, Ar-C_6), 125.0 (s, Ar-C_1), 120.7 (s, Ar-C_4), 111.2 (s, Ar-C_3), 66.9 (cy-*C*H), 55.6 (s, –O–CH_3), 41.5 (cy-*C*H_2). ESI mass spectrum: m/z = 484.25 [M+H]$^+$. CI HR mass spectrum: m/z = 484.2575 [M +H]$^+$ (calcd 484.2594).

Synthesis of tach-based Cu(I)-NCMe complexes 2.2–9.2

The synthesis of tach-based Cu(I)-NCMe complexes **2.2–9.2** will be described in detail for [Cu(I)(**2.1**)(NCMe)][PF_6] (**2.2**) and is representative for the synthesis of complexes **3.2–9.2**.

Synthesis of [Cu(I)(2.1)(NCMe)][PF_6] (2.2). Compound **2.1** (0.1 g, 0.2 mmol) was dissolved in CH_2Cl_2 (5 mL) and treated with the dropwise addition of a solution of an equivalent amount of [$Cu(CH_3CN)_4$]PF_6 (0.07 g, 0.2 mmol) in CH_2Cl_2 (5 mL). The mixture of the reaction was stirred for $\frac{1}{2}$ h at ambient condition. Product was precipitated by addition of *n*-hexane, collected by filtration and dried *in vacuo* to obtain bright white powder of **2.2** (0.09 g, 64%).^{1}H NMR (400.18 MHz; CD_2Cl_2): δ 9.07 (s, 3H, *H*C═N), 7.43 (d, 3H, $^3J_{HH}$ 7.82 Hz, H_5Ar), 7.07 (s, 3H, H_3Ar), 6.28 (d, 3H, $^3J_{HH}$ 7.82 Hz, H_6Ar), 4.39 (tt, br, 3H, $^3J_{HH}$ 11.24 Hz, $^3J_{HH}$ 4.40 Hz, -C*H*-N═), 2.92 (tt, br 3H, $^3J_{HH}$ 12.46 Hz, *trans*-C*H*H-), 2.77 (q, br, 3H, $^3J_{HH}$ 12.46 Hz, *cis*-CH*H*-). 2.49 (s, 9H, *ortho*-ArCH_3), 2.19 (t, br, 9H, *para*-ArCH_3), 1.95 (m, 3H,

$^3J_{HH}$ 12.46 Hz, *cis*-CH*H*-) and 1.46 (s, 3H, –NCC*H*3). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 171.2 (s, *C*═N), 144.6 (s, Ar-C_2), 139.8 (s, Ar-C_4), 131.7 (s, Ar-C_3), 129.5 (s, Ar-C_6), 127.2 (s, Ar-C_5), 125.6 (s, Ar-C_1), 65.5 (s, cy-*C*H), 42.9 (s, cy-*C*H_2), 21.3 (s, *ortho*-Ar*C*H_3), 18.7 (s, *para*-Ar*C*H_3) and 2.2 (s, -NC*C*H_3).

Synthesis of [Cu(I)(3.1)(NCMe)][PF_6] (3.2). Compound **3.2** was obtained by reaction of **3.1** (0.10 g, 0.25 mmol) in CH_2Cl_2 (5 mL) and a solution of [Cu(CH_3CN)$_4$]PF_6 (0.09 g, 0.25 mmol) in CH_2Cl_2 (5 mL). The bright yellow powder of **3.2** was obtained. Yield (0.04 g, 25%). ^{1}H NMR (400.18 MHz, CD_2Cl_2): δ 8.49 (s, 3H, *H*C═N), 7.80 (m, br, 6H, *H*Ar), 7.46 (m, br, 9H, *H*Ar), 4.22 (s, 3H, -C*H*-N═), 2.47 (tt, 3H, $^3J_{HH}$ 11.90 Hz, $^3J_{HH}$ 4.15 Hz, *trans*-C*H*H-) and 2.16 (d, 3H, $^3J_{HH}$ 11.90 Hz, *cis*-CH*H*-). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 162.5 (s, *C*═N), 132.9 (s, Ar-C_{ipso}), 131.8 (s, Ar-C_{para}), 128.9 (s, Ar-C_{ortho}), 128.3 (s, Ar-C_{meta}), 66.3 (s, cy-*C*H), 37.5 (s, cy-*C*H_2). Anal. calc. for $C_{29}H_{30}CuN_3$. $C_{54}H_{54}Cu_3N_6$. 4PF_6: C, 48.52. H, 4.07. N, 6.82. Found: C, 48.26, H, 4.07, N, 6.43%. ESI mass spectrum: *m*/*z*; 456.15 [M-(-NCCH_3, PF_6)]$^+$. CI HR mass spectrum: *m*/*z* = 456.1495 [M-(-NCCH_3, PF_6)]$^+$ (calcd 456.1502).

Synthesis of [Cu(I)(4.1)(NCMe)][PF_6] (4.2). Compound **4.1** (0.26 g, 0.33 mmol) was dissolved in CH_2Cl_2 (5 mL) and a solution of [Cu(CH_3CN)$_4$]PF_6 (0.12 g, 0.33 mmol) in CH_2Cl_2 (5 mL) was added. The green cream precipitate of **4.2** was obtained. Yield (0.10 g, 28%). ^{1}H NMR (399.8 MHz, $CDCl_3$): δ 8.49 (s, 3H, *H*C═N), 4.12 (s, 3H, -C*H*-N═), 2.02 (dt, 3H, $^3J_{HH}$ 14.70 Hz, $^3J_{HH}$ 3.90 Hz, *trans*-C*H*H), 2.08 (s, 9H, *para*-CH_3), 1.99 (d, 3H, $^3J_{HH}$ 14.70 Hz, *cis*-CH*H*-), 1.92 (s, 18H, *meta*-CH_3), 1.83 (s, 18H, *ortho*-CH_3) and 0.78 (s, 3H, –NCC*H*3). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 164.9 (s, *C*═N), 135.3 (s, Ar-C_{ortho}), 132.4 (s, Ar-C_{meta}), 132.0 (s, Ar-C_{para}), 131.3 (s, Ar-C_{ipso}), 65.8 (s, cy-*C*H), 37.6 (s, cy-*C*H_2), 17.1 (Ar–C_{meta}), 16.6 (s, Ar–C_{ortho}), 15.5 (Ar-C_{ortho}) and 2.19 (s, -NCCH_3).

Synthesis of [Cu(I)(5.1)(NCMe)][PF_6] (5.2). Treatment of a CH_2Cl_2 (5 mL) solution of **5.1** (0.10 g, 0.17 mmol) with a solution of [Cu(CH_3CN)$_4$]PF_6 (0.07 g, 0.17 mmol) in CH_2Cl_2 (5 mL) led to a bright green yellow powder which was collected by slow diffusion of *n*-hexane into the CH_2Cl_2 solution of **5.2** at –18 °C. ^{1}H NMR (499.9 MHz, CD_2Cl_2): δ 8.94 (s, 3H, *H*C═N), 7.38 (t, 3H, $^3J_{HH}$ 8.54 Hz, H_{para}Ar), 6.52 (d, $^3J_{HH}$ 8.55 Hz, 6H, H_{meta}Ar), 4.11 (m, br, 3H, -C*H*-N═), 3.54 (s, br, 18H, -OCH_3), 2.74 (m, br, 3H, *trans*-C*H*H-), 2.43 (m, br, 3H, *cis*-CH*H*-), 1.18 (s, 3H, NCCH_3). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 164.2 and 161.3 (Ar-C_{ortho}), 158.5 (*C*═N), 134.9 and 134.5 (Ar-C_{para}), 109.1 (Ar-C_{meta}), 103.9 and 103.15 (Ar-C_{ipso}), 66.3 (cy-*C*H), 55.2 (-O*C*H_3), 41.0 (cy-*C*H_2) and 10.9 (-NC*C*H_3).

Synthesis of [Cu(I)(6.1)(NCMe)][PF_6] (6.2). Compound **6.1** (0.06 g, 0.09 mmol) in CH_2Cl_2 (5 mL) was treated by a solution of [Cu(CH_3CN)$_4$]PF_6 (0.033 g, 0.09 mmol) in CH_2Cl_2 (5 mL) to give a deep yellow precipitate of **6.2** (0.052 g, 63%). ^{1} H NMR (299.9 MHz, CD_2Cl_2): δ 8.37 (s, 3H, *H*C═N), 4.29 (s, 3H, -C*H*-N═), 2.52 (tt, $^3J_{HH}$ 15.20 Hz, $^3J_{HH}$ 4.03 Hz 3H, *trans*-C*H*H-), 1.88 (d, $^3J_{HH}$ 15.20 Hz, 3H, *cis*-CH*H*-), 1.92 (s, br, -NCCH_3). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 150.8 (s, *C*═N), 144.0 (dm, $^1J_{CF}$ 259.21 Hz, Ar-C_{ortho}), 143.9 (dm, $^1J_{CF}$ 257.25 Hz, Ar-C_{para}), 136.7 (dm, $^1J_{CF}$ 258.23 Hz, Ar-C_{meta}), 109.5 (m br, Ar-C_{ipso}), 65.6 (s, cy-*C*H), 36.2 s, cy-*C*H_2), 14.3 (s, -NC*C*H_3). ^{19}F{^{1}H} NMR (282 MHz, CD_2Cl_2): δ –72.06 (s, 3F, BF_6), –74.57 (s, 3F, BF_6), –139.19 (d, 6F, $^3J_{FF}$ 16.24 Hz, F_{ortho}-Ar), –150.43 (t, 3F, $^3J_{FF}$ 20.56 Hz, *Fpara*-Ar), –162.06 (m, 6F, F_{meta}-Ar). ESI mass spectrum: *m*/*z*; 726.01 [M-(-NCCH_3, PF_6)]$^+$ (calcd 726.01). CI HR mass spectrum: *m*/*z* = 726.0082 [M-(-NCCH_3, PF_6)]$^+$ (calcd 726.0111).

Synthesis of [Cu(I)(7.1)(NCMe)][PF_6] (7.2). Compound **7.1** (0.20 g, 0.24 mmol) was dissolved in CH_2Cl_2 (5 mL) and a solution of [Cu(CH_3CN)$_4$]PF_6 (0.09 g, 0.24 mmol) in CH_2Cl_2 (5 mL) was added. A bright yellow precipitate of **7.2** (0.23 g, 92%) was obtained after purification. ^{1}H NMR (299.9 MHz, CD_2Cl_2): δ 8.63 (s, 3H, *H*C═N), 8.07 (br s, 6H, H_{ortho}-Ar), 7.98 (s, 3H, H_{para}-Ar), 4.28 (s, 3H, -C*H*-N═), 2.51 (dt, 3H, $^3J_{HH}$ 15.4 Hz, J_{HH} 3.9 Hz, *trans*-C*H*H-), 2.24 (d, 3H, $^3J_{HH}$ 15.23 Hz, *cis*-CH*H*-) and 1.22 (br s, 3H,-NCCH_3). ^{13}C NMR (75.57 MHz, CD_2Cl_2): δ161.8 (s, *C*═N), 136.0 (s, Ar-C_{ipso}), 131.8 (q, $^2J_{CF}$ 34.04 Hz, Ar-C_{meta}), 128.9 (s, Ar-C_{para}), 124.8 (s, Ar-C_{ortho}), 122.9 (q, $^1J_{CF}$ 272.87 Hz, -CF_3), 66.5 (s, cy-*C*H), 36.8 (s, cy-*C*H_2). ^{19}F{^{1}H} NMR (282.78 MHz, CD_2Cl_2): δ –63.35 (m, 18F, -CF_3), –71.32 (s, 3F, PF_6), –73.84 (s, 3F, PF_6). Anal. calc. for $C_{35}H_{24}CuF_{18}N_4$.PF_6: C, 39.99, H, 2.30, N, 5.33. Found: C, 40.26, H, 2.54, N, 5.76%.

Synthesis of [Cu(I)(8.1)(NCMe)][PF_6] (8.2). Compound **8.1** (0.51 g, 0.84 mmol) was dissolved in CH_2Cl_2 (5 mL) and a solution of [Cu(CH_3CN)$_4$]PF_6 (0.32 g, 0.84 mmol) in CH_2Cl_2 (5 mL) was added. A deep yellow precipitate of **8.2** (0.62 g, 92%) was obtained after purification. ^{1}H NMR (400.2 MHz, CD_2Cl_2): δ 8.74 (q, 3H, *J* 2.69 Hz, *H*C═N), 7.71 (d, 3H, $^3J_{HH}$ 7.71 Hz, H_{ortho}-Ar), 7.59 (m, 3H, H_{para}-Ar), 7.46 (m, 6H, H_{meta}-Ar), 4.24 (br s, 3H, -C*H*-N═), 2.49 (dt, 3H, $^3J_{HH}$ 15.03 Hz, $^3J_{HH}$ 4.09 Hz, *trans*-C*H*H-), 2.15 (d, 3H, $^3J_{HH}$ 14.9 Hz, *cis*-CH*H*-), 1.19 (br s, 3H, -NCCH_3). ^{13}C NMR (100.62 MHz, CD_2Cl_2): δ 161.1 (s, *C*═N), 133.2 (s, Ar-C_5), 131.6 (s, Ar-C_6), 130.7 (s, Ar-C_4), 129.9 (s, Ar-C_1), 128.3 (q, $^2J_{CF}$ 32.31 Hz, Ar-C_2), 125.8 (s, Ar-C_2), 123.9 (q, $^1J_{CF}$ 273.66 Hz, Ar-*C*F_3), 65.6 (s, cy-*C*H), 37.0 (s, cy-*C*H_2). ESI mass spectrum: *m*/*z*; 660.11 [M-(-NCCH_3, PF_6)]$^+$, CI HR mass spectrum: *m*/*z* = 660.1117 [M-(-NCCH_3, PF_6)]$^+$ (calcd 660.1121).

Synthesis of [Cu(I)(9.1)(NCMe)][PF_6] (9.2). Treatment of a CH_2Cl_2 (5 mL) solution of **9.1** (0.50 g, 1.03 mmol) with a solution of [Cu(CH_3CN)$_4$]PF_6 (0.39 g, 1.03 mmol) in CH_2Cl_2 (5 mL) led to a bright yellow solution which was precipitated by addition of *n*-hexane to give **9.2** (0.74 g, 98%) as yellow powder. ^{1}H NMR (400.18 MHz; CD_2Cl_2): δ 8.68 (s, br, 3H, *H*C═N), 7.77 (d, 3H, $^3J_{HH}$ 7.3 Hz, H_6-Ar), 7.48 (t, 3H, $^3J_{HH}$ 7.8 Hz, H_5-Ar), 6.99 (d, 3H, $^3J_{HH}$ 8.3 Hz, H_4-Ar), 6.87 (d, 3H, $^3J_{HH}$ 7.5 Hz, H_3-Ar), 4.17 (s, 3H, -C*H*-N═), 3.88 (s, 9H, –O–CH_3), 2.43 (br d, 3H, $^3J_{HH}$ 14.7 Hz, *trans*-C*H*H-), 2.12 (d, 3H, $^3J_{HH}$ 14.7 Hz, *cis*-CH*H*-), 1.54(s, 3H, -NC–CH_3). ^{13} C NMR (125.7 MHz, CD_2Cl_2): δ 159.4 (s, *C*═N), 159.0 (s,Ar-C_2), 133.0 (s, Ar-C_5), 129.5 (s, Ar-C_6), 123.2 (s, Ar-C_1), 119.5 (s, Ar-C_3), 111.2 (s, Ar-C_4), 66.3 (cy-*C*H), 55.8 (s, –O–CH_3), 37.8 (cy-*C*H_2), 1.89 (s, -NC*C*H_3). ESI mass spectrum: *m*/*z* 546.18 [M-(-NCCH_3, PF_6)]$^+$, CI HR mass spectrum: *m*/*z* = 546.1812 [M-(-NCCH_3, PF_6)]$^+$ (calcd 546.1829).

Synthesis of tach-based Cu(I)–CO complexes 2.3–9.3

Synthesis of [Cu(I)(2.1)(CO)][PF_6] (2.3). Carbon monoxide was bubbled through a CH_2Cl_2 solution (10 mL) **2.2** (0.05 g, 0.10 mmol) for $\frac{1}{2}$ h to give a pale yellow solution. The product was precipitated by addition of *n*-hexane (20 mL) and dried *in vacuo*.

The (0.08 g, 76%) cream solid of **2.3** was obtained. ^{1}H NMR (499.9 MHz, CD_2Cl_2): δ 8.66 (s, 3H, *H*C═N), 7.09 (d, 3H, $^3J_{HH}$ 7.08 Hz, H_6Ar), 6.96 (s, 3H, H_3Ar), 6.81 (d, 3H, $^3J_{HH}$ 7.63 Hz, H_5Ar), 4.16 (s, br, 3H, -C*H*-N═), 2.40 (dt, 3H, $^3J_{HH}$ 15.00 Hz, $^3J_{HH}$ 3.80 *trans*-C*H*H-), 2.21 (s, 9H, *ortho*-ArCH_3), 2.19 (s, 9H, *para*-ArCH_3), 2.02 (d, 3H, $^3J_{HH}$ 14.65 Hz, *cis*-CH*H*-). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 163.8 (s, *C*═N), 140.1 (s, Ar-C_2), 135.0 (s, Ar-C_4), 129.0 (s, Ar-C_3), 125.8 (s, Ar-C_6), 125.4 (s, Ar-C_5), 124.4 (s, Ar-C_1), 63.7 (s, cy-*C*H), 35.8 (s, cy-*C*H_2), 19.32 (s, *ortho*-Ar*C*H_3) and 16.8 (s, *para*-Ar*C*H_3). IR/cm^{-1} (CH_2Cl_2): ν(CO) 2091.8 s.

Synthesis of [Cu(I)(3.1)(CO)][PF$_6$] (3.3). Carbon monoxide was bubbled through a CD_2Cl_2 solution of **3.2** (0.02 g), which had been loaded in the NMR tube, for $\frac{1}{2}$ h to give a pale yellow solution. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.74 (s, 3H, *H*C═N), 7.54 (t, 9H, *H*Ar), 7.42 (t, 6H, *H*Ar), 4.28 (s, 3H, -C*H*-N═), 2.50 (d, 3H, $^3J_{HH}$ 14.90 Hz, *trans*-C*H*H-), 2.21 (m, 3H, *cis*-CH*H*-). ^{13}C NMR (100 MHz, CD_2Cl_2): δ CO signal not observed, 166.4 (s, *C*═N), 134.9 (s, Ar-C_{ipso}), 131.9 (s, Ar-C_{para}), 128.7 (s, Ar-C_{ortho}), 128.3 (s, Ar-C_{meta}), 66.2 (s, cy-*C*H), 37.2 (s, cy-*C*H_2). ESI mass spectrum: *m*/*z*; 456.15 [M-(-CO, PF_6)]$^+$. CI HR mass spectrum: *m*/*z* = 456.1495 [M-(-CO, PF_6)]$^+$ (calcd 456.1504). IR/cm^{-1} (CD_2Cl_2): ν(CO) 2092 s.

Synthesis of [Cu(I)(4.1)(CO)][PF$_6$] (4.3). Carbon monoxide was bubbled through a CD_2Cl_2 solution of **4.2** (0.04 g, 0.005 mmol) which had been loaded in the NMR tube, for $\frac{1}{2}$ h to give a pale yellow solution. ^{1}H NMR (399.8 MHz, $CDCl_3$): δ 8.75 (s, 3H, *H*C═N), 4.32 (s, 3H, -C*H*-N═), 2.52 (dt, 3H, $^3J_{HH}$ 15.00 Hz, $^3J_{HH}$ 3.70 Hz, *trans*-C*H*H), 2.15 (s, 9H, *para*-CH_3), 1.99 (d, 3H, $^3J_{HH}$ 14.43 Hz, *cis*-CH*H*-), 1.99 (s, 18H, *meta*-CH_3) and 1.90 (s, 18H, *ortho*-CH_3). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 166.3 (s, *C*═N), 134.9 (s, Ar-C_{ortho}), 130.9 (s, Ar-C_{meta}), 130.6 (s, Ar-C_{para}), 128.4 (s, Ar-C_{ipso}), 63.4 (s, cy-*C*H), 35.2 (s, cy-*C*H_2), 15.1 (Ar–C_{meta}), 14.4 (s, Ar–C_{ortho}), and 13.3 (Ar-C_{ortho}). IR/cm^{-1} (CD_2Cl_2); ν(CO) 2091 s.

Synthesis of [Cu(I)(5.1)(CO)][PF$_6$] (5.3). Carbon monoxide was bubbled through a CD_2Cl_2 solution of **5.2** (0.02 g), which had been loaded in the NMR tube, for 1 h to give a pale yellow solution. ^{1}H NMR (499.9 MHz, CD_2Cl_2): δ 8.33 (s, 3H, *H*C═N), 7.22 (t, 3H, $^3J_{HH}$ 8.39 Hz, H_{para}Ar), 6.37 (d, 6H, $^3J_{HH}$ 8.24 Hz, H_{meta}Ar), 4.00 (s, br, 3H, -C*H*-N═), 3.43 (s,18H, -OCH_3), 2.27 (d, br, 3H, $^3J_{HH}$ 14.95 Hz *trans*-C*H*H-), 2.09(d, br, $^3J_{HH}$ 14.95 Hz, 3H, *cis*-CH*H*-). ^{13}C NMR (125 MHz, CD_2Cl_2): δ CO signal not observed, 158.5 (s, *C*═N), 157.8 (s, Ar-C_{ortho}), 131.8 (s, Ar-C_{para}), 111.6 (s, Ar-C_{meta}), 102.8 (s, Ar-C_{ipso}), 65.8 (s, cy-*C*H), 54.2 (s, -O*C*H_3), 36.8 (s, cy-*C*H_2). IR/cm^{-1} (CD_2Cl_2): ν(CO) 2073 s.

Synthesis of [Cu(I)(6.1)(CO)][PF$_6$] (6.3). Carbon monoxide was bubbled through a CD_2Cl_2 solution of **6.2** (0.04 g), which had been loaded in the NMR tube, for 1 h to give a very pale yellow solution. ^{1}H NMR (400.18 MHz, CD_2Cl_2): δ 8.36 (s, 3H, *H*C═N), 4.28 (s, 3H, -C*H*-N═), 2.50 (dt, 3H, $^2J_{HH}$ 15.23 Hz, $^3J_{HH}$ 4.04 Hz, *trans*-C*H*H-), 2.10 (d, br, 3H, $^2J_{HH}$ 14.86 Hz, *cis*-CH*H*-). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 151.6 (*C*═N), 146.5 (dm, $^1J_{CF}$ 259.21 Hz, Ar-C_{ortho}), 143.2 (dm, $^1J_{CF}$ 257.25 Hz, Ar-C_{para}), 139.2 (dm, $^1J_{CF}$ 258.23 Hz, Ar-C_{meta}), 110.2 (m br, Ar-C_{ipso}), 66.3 (cy-*C*H), 37.0 (cy-*C*H2). ^{19}F{^{1}H} NMR (282 MHz, CD_2Cl_2): δ –72.05 (s, 3F, PF_6), –74.56 (s, 3F, PF_6), –139.18 (d, 6F, $^3J_{FF}$ 16.24 Hz, Ar-F_{ortho}), –150.41 (t, 3F, $^3J_{FF}$ 20.56 Hz, Ar-F_{para}), –162.05 (m, 6F, Ar-F_{meta}). IR/cm-1 (CD_2Cl_2): ν(CO) 2091.3 s.

Synthesis of [Cu(I)(7.1)(CO)][PF$_6$] (7.3). Carbon monoxide was bubbled through a CH_2Cl_2 solution (5 mL) of **7.2** (0.1 g, 0.09 mmol) for $\frac{1}{2}$ h to give a pale yellow solution. The product was precipitated by addition of *n*-hexane (10 mL) and dried *in vacuo* to give **7.3** (0.08 g, 86%). ^{1}H NMR (299.9 MHz, CD_2Cl_2): δ 8.84 (s, $3H_b$, *H*C═N), 7.97 (t, 3H, $^4J_{HH}$ 1.47 Hz, H_{para}-Ar), 7.86 (d, 6H, $^4J_{HH}$ 1.3 Hz, H_{ortho}-Ar), 4.37 (s, $3H_a$, -C*H*-N =), 2.51 (dt, 3H, $^2J_{HH}$ 15.41 Hz, $^3J_{HH}$ 3.80 Hz, *trans*-C*H*H-), 2.34 (d, 3H, $^2J_{HH}$ 15.05 Hz, *cis*-CH*H*-). ^{13}C NMR (75.57 MHz, CD_2Cl_2): δ 165.1 (s, *C*═N), 136.3 (s, Ar-C_{ipso}), 132.2 (q, $^2J_{CF}$ 34.04 Hz, Ar-C_{meta}), 128.3 (s, Ar-C_{para}), 125.3 (s, Ar-C_{ortho}), 122.4 (q, $^1J_{CF}$ 272.87 Hz, -*C*F_3), 66.1 (s, C_{tach}-N), 36.3 (s, -$C_{tach}H_2$). ^{19}F{^{1}H} NMR (282.78 MHz, CD_2Cl_2): δ –63.88 (m, 18F, -CF_3), –70.72 (s, 3H, PF_6), –73.24 (s, 3H, PF_6). IR/cm^{-1} (CH_2Cl_2): ν(CO) 2099 s.

Synthesis of [Cu(I)(8.1)(CO)][PF$_6$] (8.3). Carbon monoxide was bubbled through a CH_2Cl_2 solution (5 mL) of **8.2** (0.5 g, 0.59 mmol) for $\frac{1}{2}$ h to give a pale yellow solution. The product was precipitated by addition of *n*-hexane and dried *in vacuo*. The cream solid of **8.3** (0.45 g, 92%) was obtained. ^{1}H NMR (400.2 MHz, CD_2Cl_2): δ 8.91 (br s, 3H, *H*C═N), 7.71 (d, 3H, $^3J_{HH}$ 7.8 Hz, H_{ortho}-Ar), 7.58 (t, 3H, $^3J_{HH}$ 7.9 Hz, H_{para}-Ar), 7.51 (t, 3H, $^3J_{HH}$ 7.3 Hz H_{meta5}-Ar), 7.36 (d, 3H, $^3J_{HH}$ 7.3 Hz, H_{meta3}-Ar), 4.36 (br s, 3H, -C*H*-N═), 2.55 (dt, 3H, $^3J_{HH}$ 15.1 Hz, $^3J_{HH}$ 3.7 Hz, *trans*-C*H*H-), 2.21 (d, 3H, $^3J_{HH}$ 15.8 Hz, *cis*-CH*H*-). ^{13}C NMR (100.62 MHz, CD_2Cl_2): δ 164.6 (s, *C*═N), 133.9 (s, Ar-C_5), 132.1 (s, Ar-C_6), 131.3 (s, Ar-C_4), 128.9 (s, Ar-C_1), 128.0 (q, $^2J_{CF}$ 32.29 Hz, Ar-C_2), 126.3 (s, Ar-C_2), 123.8 (q, $^1J_{CF}$ 273.66 Hz, Ar-*C*F_3), 65.5 (s, cy-*C*H), 36.4 (s, cy-*C*H_2). ESI mass spectrum: *m*/*z*; 660.11 [M-(-CO, PF_6)]$^+$. CI HR mass spectrum: *m*/*z* = 660.1117 [M-(-CO, PF_6)]$^+$ (calcd 660.1132). IR/cm^{-1} (CH_2Cl_2): ν(CO) 2093.6 s.

Synthesis of [Cu(I)(9.1)(CO)][PF$_6$] (9.3). Carbon monoxide was bubbled through a CH_2Cl_2 solution (10 mL) of **9.2** (0.13 g, 17.73 mmol) for $\frac{1}{2}$ h to give a pale yellow solution. The product was precipitated by addition of *n*-hexane to give **9.3** (0.116 g, 92%). ^{1}H NMR (400.18 MHz; CD_2Cl_2): δ 8.78 (s, br, 3H, *H*C═N), 7.49 (ddd, 3H, $^3J_{HH}$ 7.33 Hz, $^4J_{HH}$ 1.71 Hz, H_5-Ar), 7.41 (br d, 3H, $^3J_{HH}$ 7.3 Hz, H_5-Ar), 7.00 (d, 3H, $^3J_{HH}$ 8.3 Hz, H_3-Ar), 6.87 (t, 3H, $^3J_{HH}$ 7.3 Hz, H_4-Ar), 4.25 (br s, 3H, -C*H*-N═), 3.87 (s, 9H, –O–CH_3), 2.47 (dt, 3H, $^2J_{HH}$ 14.7 Hz, $^3J_{HH}$ 4.0 Hz, *trans*-C*H*H-), 2.17 (d, 3H, $^3J_{HH}$ 14.9 Hz, *cis*-CH*H*-). ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ 163.6 (s, *C*═N), 158.7 (s,Ar-C_2), 133.5 (s, Ar-C_5), 128.7 (s, Ar-C_6), 124.0 (s, Ar-C_1), 120.0 (s, Ar-C_3), 111.2 (s, Ar-C_4), 65.9 (cy-*C*H), 55.7 (s, –O–CH_3), 37.5 (cy-*C*H_2). IR/cm^{-1} (CH_2Cl_2): ν (CO) 2089.4 s.

X-Ray experimental

An X-ray diffraction experiment on **9.2** was carried out at 100 K on a Bruker Microstar diffractometer using Cu-K_α radiation (λ = 1.54178 Å) and the rest were carried out at 100 K on a Bruker Apex II Kappa CCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Intensities were integrated from several series of exposures measuring 0.5° in ω or φ using the Apex II or proteum program.[25] Absorption corrections were based on equivalent reflections using SADABS,[26] and structures were refined against all F_o^2 data with hydrogen atoms (on carbon atoms) riding in calculated positions using SHELXL.[27]

Structure **9.1**·CH_2Cl_2 and **3.2**·CH_2Cl_2 were non-merohedral twins with two and three domains respectively, which were

Table 6 X-Ray crystallography data of **3.2**·CH_2Cl_2, **7.2**, **8.2** and **9.2**·CH_2Cl_2

Compound	**3.2**·CH_2Cl_2	**7.2**	**8.2**	**9.2**·CH_2Cl_2
Colour, habit	Yellow plate	Yellow needle	Yellow plate	Yellow plate
Empirical formula	$C_{54}H_{54}Cu_3N_6$,$C_{29}H_{30}CuN_4$,$(PF_6)_4$,CH_2Cl_2	$C_{35}H_{24}CuF_{18}N_4$.PF_6	$C_{32}H_{27}CuF_9N_4$.PF_6	$C_{32}H_{36}CuN_4O_3$.PF_6. CH_2Cl_2
M	2140.61	1051.10	847.09	818.09
Crystal system	Monoclinic	Monoclinic	Cubic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_13$	$P\bar{1}$
a/Å	16.3400(7)	11.1581(3)	15.2741(8)	11.5586(18)
b/Å	13.4089(6)	18.9132(6)	15.2741(8)	12.640(2)
c/Å	40.1113(13)	38.9605(13)	15.2741(8)	14.529(2)
α (°)	90.00	90.00	90.00	67.007(4)
β (°)	90.042(2)	96.126(2)	90.00	72.472(4)
γ (°)	90.00	90.00	90.00	70.142(4)
V/Å^3	8788.4(6)	8175.1(4)	3563.4(3)	1802.7(5)
Z	4	8	4	2
μ/mm^{-1}	1.191	0.717	0.766	3.263
T/K	100(2)	100(2)	100(2)	100(2)
Reflections: (measured/unique/observed)	20271/20271/22357	134390/18814/12880	10671/1517/2511	21258/6187/5722
R_{int}	—	0.0651	0.0432	0.0418
R_1(observed reflection)[$I \geq 2\ \sigma$(I)]	0.0945	0.0501	0.0314	0.0510
wR_2(all reflection)	0.2434	0.1278	0.0819	0.1421
Flack parameter	—	—	0.012(14)	—

Table 7 X-Ray crystallography data of **3.3**·CH_2Cl_2, **5.3**·CH_2Cl_2 and **6.3**

Compound	**3.3**·CH_2Cl_2	**5.3**·CH_2Cl_2	**6.3**
Colour, habit	Colourless plate	Pale yellow prisms	Colourless
Empirical formula	$C_{28}H_{27}CuN_3O.PF_6{\cdot}CH_2Cl_2$	$C_{34}H_{39}CuN_3O_7.PF_6{\cdot}CH_2Cl_2$	$C_{28}H_{12}CuF_{15}N_3O.PF_6$
M	714.97	895.13	899.93
Crystal system	Orthorhombic	Monoclinic	Trigonal
Space group	$Pbca$	$C2/c$	$P\bar{3}1$
a/Å	15.1755(8)	27.2710(13)	10.2405(5)
b/Å	17.9772(8)	16.6962(7)	10.2405(5)
c/Å	18.5659(9)	21.3580(17)	38.022(4)
α (°)	90.00	90.00	90.00
β (°)	90.00	125.248(2)	90.00
γ (°)	90.00	90.00	120.00
V/Å^3	3488.36(4)	7941.8(8)	3453.1(4)
Z	8	8	4
μ/mm^{-1}	1.015	0.803	0.822
T/K	100(2)	100(2)	100(2)
Reflections: (measured/unique/observed)	26243/9399/3385	44613/16548/9047	34014/2661/2400
R_{int}	0.1148	0.0447	0.0248
R_1(observed reflection)[$I \geq 2\ \sigma$ (I)]	0.0657	0.0510	0.0578
wR_2(all reflection)	0.1346	0.1593	0.2056

separated using CELLNOW or the APEX II program. The structures were solved using ShelXS refined for all domains simultaneously which resulted in ratios (0.07 : 0.93) and (0.04 : 0.10 : 0.86) for the structures.

Structural and refinement data for **5.1**·$6H_2O$, **7.1** and **9.1**·CH_2Cl_2 are in Table 5, Crystal and refinement data for **3.2**·CH_2Cl_2, **7.2**, **8.2** and **9.2**·CH_2Cl_2 are given in Table 6 and the structural data for **3.3**·CH_2Cl_2, **5.3**·CH_2Cl_2 and **6.3** are in Table 7.

References

1 B. Greener, M. H. Moore and P. H. Walton, *Chem. Commun.*, 1996, 27.
2 L. Cronin and P. H. Walton, *Chem. Commun.*, 2003, 1572.
3 C. J. Boxwell and P. H. Walton, *Chem. Commun.*, 1999, 1647.
4 L. Cronin, B. Greener, S. P. Foxon, S. L. Heath and P. H. Walton, *Inorg. Chem.*, 1997, **36**, 2594.
5 B. Greener, S. P. Foxon and P. H. Walton, *New J. Chem.*, 2000, **24**, 269.
6 G. Park, E. Dadachova, A. Przyborowska, S. Lai, D. Ma, G. Broker, R. D. Rogers, R. P. Planalp and M. W. Brechdiel, *Polyhedron*, 2001, **20**, 3155–3163.
7 L. Turculet and T. D. Tilley, *Organometallics*, 2002, **21**, 3961–3972.
8 A. K. Nairn, S. J. Archibald, R. Bhalla, C. J. Boxwell, A. C. Whitwood and P. H. Walton, *Dalton Trans.*, 2006, 1790.
9 B. Greener, L. Cronin, G. D. Wilson and H. Walton, *J. Chem. Soc., Dalton Trans.*, 1996, 401.
10 R. A. D. Wentworth, *Inorg. Chem.*, 1968, **7**, 1030.
11 R. A. D. Wentworth and J. J. Felten, *J. Am. Chem. Soc.*, 1968, **90**, 621.
12 H. Stetter, D. Theisen and G. Steffens, *Chem. Ber.*, 1970, **103**, 200.
13 T. Bowen, R. P. Planalp and M. W. Brechbiel, *Bioorg. Med. Chem. Lett.*, 1996, **6**, 807.
14 M. Komiyama, *Chem. Eng. Technol.*, 1989, **12**, 356; W. S. W. Ho, G. Doyle, D. Savage and R. L. Pruett, *Ind. Eng. Chem. Res.*, 1988, **27**, 334; T. Suzuki, R. D. Noble and C. A. Koval, *Inorg. Chem.*, 1997, **36**, 136.
15 P. W. Miller, N. J. Long, A. J. deMello, R. Vilar, H. Audrain,D. Bender, J. Passchier and A. Gee, *Angew. Chem., Int. Ed.*, 2007, **46**, 2875.
16 M. Cushion, P. Ebrahimpour, M. F. Haddow, A. J. Hallett, S. M. Mansell, A. G. Orpen and D. F. Wass, *Dalton Trans.*, 2009, 1632–1635.
17 R. H. V. Dias, H. Lu, H. J. Kim, S. A. Polach, T. Goh, G. Browning and C. J. Lovely, *Organometallics*, 2002, **21**, 1466–1473.

18 H. V. Rasika Dias, S. Singh and J. A. Flores, *Inorganic Chemistry*, 2006, **45**, 8859-8-861.
19 B. Swanson, D. F. Shriver and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 2182.
20 K. Mogi, Y. Sakai, T. Sonoda, Q. Xu and Y. Souma, *THEOCHEM*, 2001, **537**, 125–138.
21 Y. Suenaga, L. Ping Wu, T. Kuroda-sowa, M. Munakata and M. Maekawa, *Polyhedron*, 1997, **16**, 67–70.
22 H. Masuda, N. Yamamoto, T. Taga and K. Machida, *J. Organomet. Chem.*, 1987, **322**, 121–129.
23 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.
24 B. Greener, M. H. Moore and P. H. Walton, *Chem. Commun.*, 1996, 27–28.
25 *Apex2*, Bruker-AXS Inc., 2008, Madison, Wisconsin.
26 G. M. Sheldrick (2008), *SADABS V2008/1*, Bruker-AXS Inc., Madison, Wisconsin, USA.
27 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.