ChemPubSoc Europe
DOI: 10.1002/ejic.201600620
EurJIC European Journal of Inorganic Chemistry
Full Paper

Copper(I) Complexes

Homo- and Heteroleptic Copper(I) Complexes with Diazabutadiene Ligands: Synthesis, Solution- and Solid-State Structural Studies

Benjamin Zelenay,[a][‡] Roberto Frutos-Pedreño,[a][‡][‡‡] Jordi Markalain-Barta,[a][‡‡‡] Esmeralda Vega-Isa,[a][‡‡‡‡] Andrew J. P. White,[a] and Silvia Díez-González*[a]

Abstract: The preparation of novel copper(I) complexes of diazabutadiene (DAB) ligands with aliphatic backbones is reported. $[Cu(DAB^R)_2](BF_4)$, $[Cu(DAB^R)(NCMe)_2](BF_4)$ and $[CuCl(DAB^R)]$ are easily synthesised and air-stable. These complexes, which remain scarce in the literature, have been fully characterised, and their behaviour both in the solid state as well as in solution has been studied by means of X-ray crystallography, NMR and UV/Vis spectroscopy.

Introduction

Schiff bases are ubiquitous ligands for transition metals, and they have played a major role not only in the development of their coordination chemistry, but also of their catalytic[1] and biochemical[2] uses. Copper(I) coordination complexes with aromatic diimines gather constant interest due to their important potential chemical and material applications. Indeed, compounds with either 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy) derivatives have shown great promise in the preparation of supramolecular assemblies,[3] as catalysts in organic reactions,[4] or as luminescent materials.[5] In fact, most of the emissive copper(I) complexes reported to date contain N-heterocycles as ligands.

The rigidity of the phen ligands is considered to favour metal coordination by preventing rotation around the C–C bond on the backbone. This feature is particularly relevant as many of these copper(I) complexes exhibit a low configurational stability in solution, and their speciation is hard to control even in non-coordinating solvents.[6] Bis(arylimino)acenaphthene (BIAN, Figure 1) ligands have shown a similar behaviour, while having markedly different properties as the two exocyclic imine groups are not part of an heteroaromatic system.[7] The control and/or understanding of the coordination environment of metal centres is essential for the design and development of catalysts, materials or bioinorganic models.

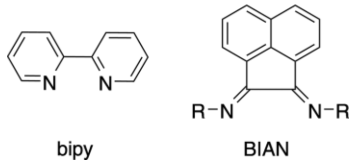


Figure 1. Structures of bidentate N-ligands.

On the other hand, complexes with ligands with less restricted backbones, including bipy, might not be accessible due to the rapid disproportionation of copper(I) to copper(II) and copper(0) species. In these cases, the use of an additional ancillary ligand such as a phosphine is crucial for the preparation of copper(I) complexes.[8] Hence, despite the intensive efforts reported in this area it is not so surprising that well-defined copper complexes with diazadiene ligands remain extremely rare in the literature.[9] Nevertheless, 1,4-diaza-1,3-butadiene (DAB) ligands have been shown to have similar σ-donor properties compared to other common bidentate nitrogen donors such as bipy or BIAN, while being better π-acceptors.[10]

Herein, we describe the synthesis and characterisation of novel cationic and neutral copper(I) complexes bearing diazabutadiene ligands with different substituents on the imino groups. Also, the structures of these complexes both in the solid state and in solution have been carefully examined.

Results and Discussion

Preparation and Characterisation of Copper(I) Complexes

$[Cu(NCMe)_4](BF_4)$ was treated with excess diimine ligands at room temperature to produce the homoleptic cationic complexes **1**–**4** (Scheme 1). These were isolated in good yields after simple recrystallisation. Remarkably, all of these complexes were indefinitely stable towards oxygen and moisture and could be stored/handled without the need of any particular precautions. No mono(diimine)copper(I) complexes could be accessed when a 1:1 Cu/DAB^R stoichiometry was used in differ-

---

[a] *Department of Chemistry, Imperial College London,*
Exhibition Road, South Kensington, London SW7 2AZ, UK
E-mail: s.diez-gonzalez@imperial.ac.uk
http://www.imperial.ac.uk/people/s.diez-gonzalez

[‡] These authors contributed equally to this work.

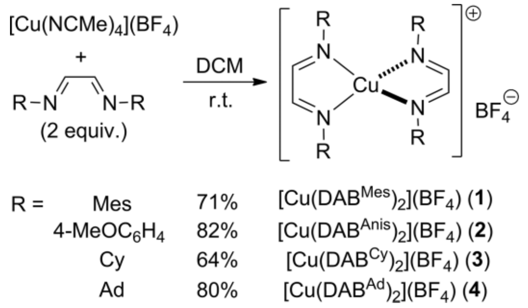
[‡‡] Visiting PhD student from Universidad de Murcia (Spain)

[‡‡‡] Erasmus student from Universidad de Barcelona (Spain)

[‡‡‡‡] Visiting PhD student from Universidad de Oviedo (Spain)

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/ejic.201600620.

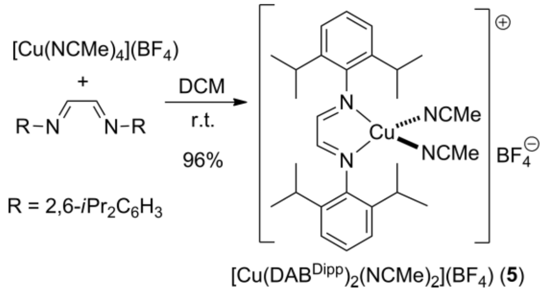
ent solvents (DCM, acetone or MeCN), and only the reported homoleptic complexes were isolated in all cases.



Scheme 1. Preparation of cationic homoleptic complexes.

Even though the structure of **1** has been reported in the literature,[11] no spectroscopic data or yield was provided. Hence, we treated this complex as all the others in the series.

In stark contrast, when a diimine with 2,6-diisopropylphenyl substituents on the nitrogen atoms was used in the preparation of cationic complexes, only heteroleptic complex **5** was obtained in an excellent yield (Scheme 2). The outcome of the reaction remained unchanged even when different stoichiometries and/or more forcing reaction conditions were employed.



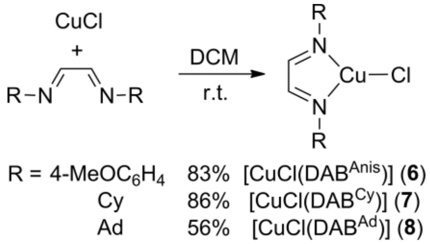
Scheme 2. Cationic heteroleptic complex **5**.

Compound **5** is a dark red complex that can be handled in air, but it slowly decomposes over time (i.e. 3 months) if not stored under an inert atmosphere. A similar reactivity has been disclosed in the literature for DAB ligands with triphenylmethyl groups on the nitrogen atoms.[12]

On the other hand, the reaction between an equimolar mixture of a diimine and CuCl afforded the corresponding copper(I) complexes **6**–**8** bearing one N-ligand per copper centre (Scheme 3). These complexes were isolated in fair to excellent yields after recrystallisation. However, when DAB ligands bearing bulkier aromatic groups (Mes or Dipp) were used, only the starting materials were recovered, even when the reaction temperature was increased.

These deep red/nearly black complexes did not decompose over months when stored in the solid state. However, after 3 days, solutions in dichloromethane started showing significant broadening of the signals in the ^{1}H NMR spectra, indicative of oxidation to paramagnetic copper(II) species.

All isolated complexes were fully characterised by spectroscopic methods as well as elemental analysis and single-crystal X-ray diffraction. In the ^{1}H NMR spectra, the resonances of the imino protons on the backbone of the ligands appear considerably shifted to lower field after metal coordination, consistent with the expected electron donation from the diimine ligands to the copper centre. This effect is particularly strong in complexes bearing DAB ligands with alkyl substituents (i.e. δ = 8.52 ppm for complex **8**, compared to δ = 7.90 ppm in the free ligand) or with a *para*-anisyl group (i.e. δ = 8.95 ppm for complex **2**, compared to δ = 8.42 ppm in the free ligand). Interestingly, the expected downfield shift for the CH=N signal in the ^{13}C{^{1}H} NMR spectra was only evidenced for complexes **2** and **6** bearing one or two DAB^{Anis} ligands. This observation implies that DAB^{Anis} is the best π-acceptor ligand of the series, and in consequence, there is a larger paramagnetic contribution in those two complexes from π-back-bonding. Even so, only a very small deshielding was observed (1.7 and 0.9 ppm for **2** and **6**, respectively). For all the other complexes, a small shift upfield of 2–3 ppm was observed instead.



Scheme 3. Preparation of neutral heteroleptic complexes.

The IR spectra of these complexes display medium absorption bands around 1599–1624 cm^{-1}, the typical absorption region for C=N symmetric stretching vibrations. These values are shifted to lower wavenumbers with respect to those of the free diimine ligands, which agrees with the coordination of both nitrogen atoms of the DAB ligands to the copper centre. Additionally, cationic complexes **1**–**5** display a single stretching band at ca. 1050 cm^{-1} for the B–F bonds, as expected for complexes without significant interaction with the metal centre. Mass spectra of all cationic complexes showed peaks for the expected metal cation, [Cu(DAB^R)$_2$]$^+$ for **1**–**4**, or [Cu(DAB^{Dipp})]$^+$ for complex **5**. No molecular peaks were obtained for neutral complexes **6**–**8**, and values of *m/z* consistent with [Cu(DAB^R)(NCMe)]$^+$ species were systematically observed instead.

Structural Studies

Suitable crystals for single-crystal X-ray diffraction were obtained for complexes **1**–**7** by slow diffusion of hexane into DCM solutions, except for complex **4**, where an acetone/pentane combination was used instead. A summary of the crystallographic data for these compounds is provided in the Supporting Information (Table S1). Ball-and-stick representations of the obtained structures are given in Figures 2, 3, 4, 5, 6, 7 and 8, and selected bond lengths are provided in the captions of these figures. Complexes **3** and **6** contain four independent units (**A**–**D**) in their crystals, and their respective bond lengths and angles for the structures not shown (**B**–**D**) are provided in the Supporting Information (Table S2 and S4).

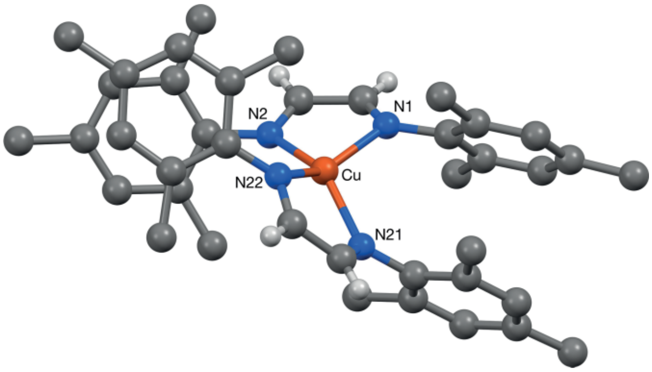


Figure 2. Structure of the cation present in the crystal of [Cu(DAB^{Mes})$_2$](BF$_4$) (**1**). Most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu–N(1) 2.0239(16), Cu–N(2) 2.0256(17), Cu–N(21) 2.0268(15), Cu–N(22) 2.0334(17); N(1)–Cu–N(2) 82.24(7), N(1)–Cu–N(21) 108.44(7), N(1)–Cu–N(22) 145.46(7), N(2)–Cu–N(21) 145.49(7), N(2)–Cu–N(22) 107.64(7), N(21)–Cu–N(22) 82.41(6).

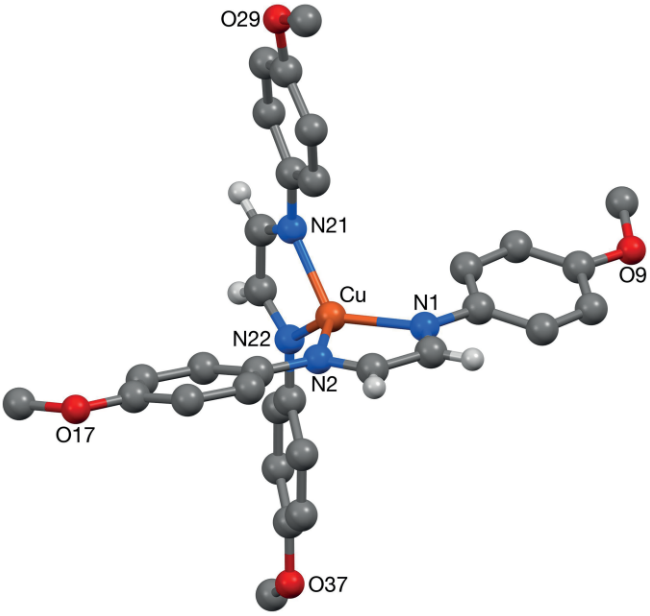


Figure 3. Structure of the cation present in the crystal of [Cu(DAB^{Anis})$_2$](BF$_4$) (**2**). Most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu–N(1) 2.0099(17), Cu–N(2) 2.0095(17), Cu–N(21) 2.0292(18), Cu–N(22) 2.0027(17), N(1)–Cu–N(2) 82.35(7), N(1)–Cu–N(21) 121.46(7), N(1)–Cu–N(22) 126.91(7); N(2)–Cu–N(21) 120.85(7), N(2)–Cu–N(22) 128.18(7), N(21)–Cu–N(22) 82.41(6), 145.46(7), N(2)–Cu–N(21) 145.49(7), N(2)–Cu–N(22) 107.64(7), N(21)–Cu–N(22) 82.41(6).

All structures **1**–**7** (Figures 2–8) show tetracoordinated copper centres. These might be described as tetrahedral, but in order to quantify the distortion with respect to an ideal tetrahedral geometry, we calculated the τ_4 geometry index introduced by Houser in 2007.[13] This is based on the formula $\tau_4 = \{360° - (\alpha + \beta)\}/141°$, where α and β are the two largest θ angles in the four-coordinate species. The values of τ_4 range from 1.00 for a tetrahedral to 0.00 for an ideal square-planar geometry. The calculated τ_4 values for complexes **2**–**7** are between 0.88 (for **4** and **5**) and 0.74 (for **2**), in accordance to distorted tetrahedral arrangements.

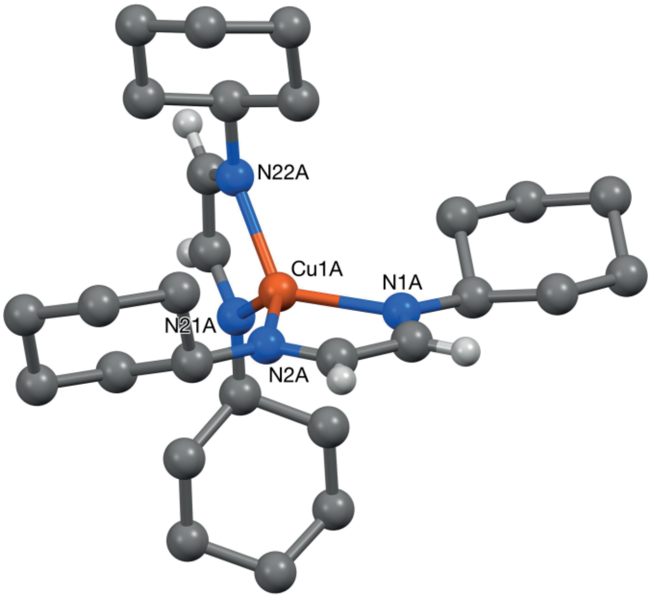


Figure 4. Structure of one (**3-A**) of the four independent cations present in the crystal of [Cu(DAB^{Cy})$_2$](BF$_4$) (**3**). Most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu(1)–N(1) 2.041(3), Cu(1)–N(2) 2.011(3), Cu(1)–N(21) 2.020(3), Cu(1)–N(22) 2.031(3); N(1)–Cu(1)–N(2) 82.31(12), N(1)–Cu(1)–N(21) 117.44(12), N(1)–Cu(1)–N(22) 121.20(11), N(2)–Cu(1)–N(21) 135.45(12), N(2)–Cu(1)–N(22) 124.09(12), N(21)–Cu(1)–N(22) 81.47(11).

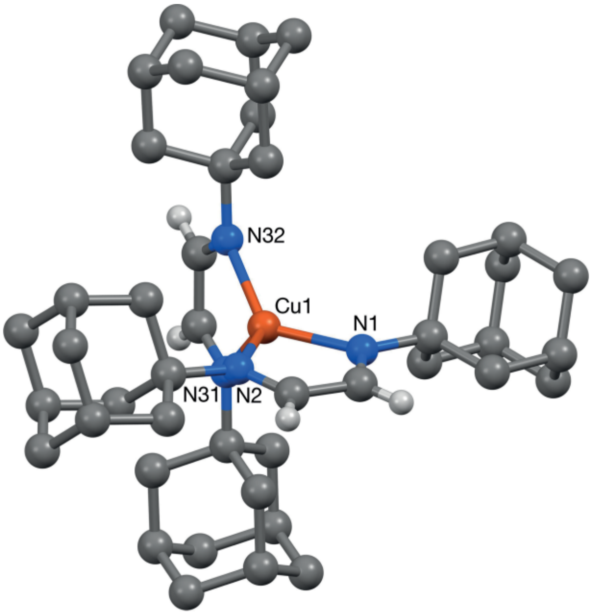


Figure 5. Structure of the cation present in the crystal of [Cu(DAB^{Ad})$_2$](BF$_4$) (**4**). Most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu(1)–N(1) 2.0374(11), Cu(1)–N(2) 2.0389(11), Cu(1)–N(31) 2.0559(12), Cu(1)–N(32) 2.0267(11); N(1)–Cu(1)–N(2) 81.95(5), N(1)–Cu(1)–N(31) 120.12(5), N(1)–Cu(1)–N(32) 129.81(5), N(2)–Cu(1)–N(31) 119.50(5), N(2)–Cu(1)–N(32) 128.66(5), N(31)–Cu(1)–N(32) 81.91(5).

However, the calculated τ_4 index for complex **1** was considerably lower (0.49) indicating that this geometry might be described as distorted square-planar. This difference is obvious when examining the obtained crystal structures for homoleptic

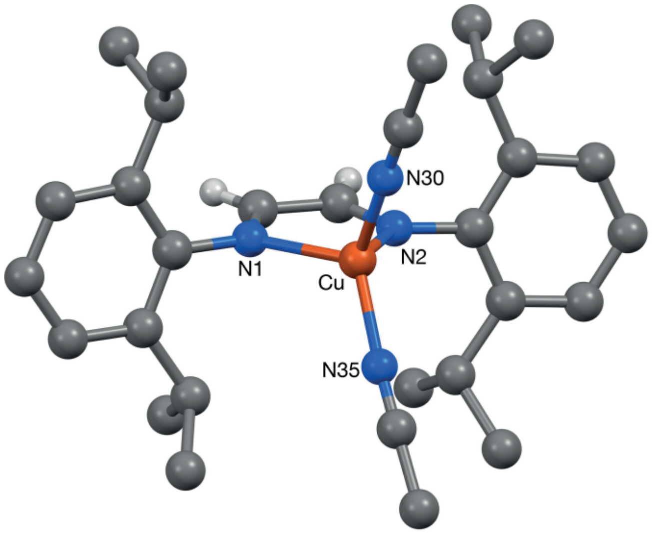


Figure 6. Structure of the cation present in the crystal of **5**. Most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu–N(1) 2.0821(12), Cu–N(2) 2.0798(12), Cu–N(30) 1.9424(15), Cu–N(35) 1.9391(14); N(1)–Cu–N(2) 78.82(5), N(1)–Cu–N(30) 112.60(6), N(1)–Cu–N(35) 117.91(5), N(2)–Cu–N(30) 110.21(6), N(2)–Cu–N(35) 117.88(5), N(30)–Cu–N(35) 114.52(6).

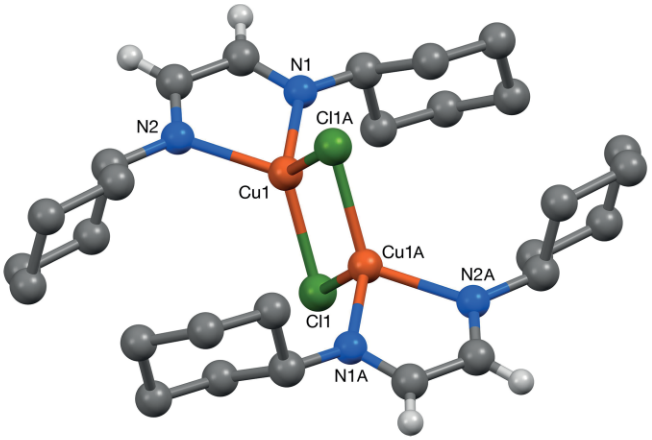


Figure 8. The crystal structure of the C_i-symmetric complex [CuCl(DAB^{Cy})] (**7**). Most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu(1)–Cl(1) 2.3625(5), Cu(1)–N(1) 2.0875(15), Cu(1)–N(2) 2.1025(15), Cu(1)–Cl(1A) 2.2909(5); Cl(1)–Cu(1)–N(1) 114.93(4), Cl(1)–Cu(1)–N(2) 112.57(4), Cl(1)–Cu(1)–Cl(1A) 101.846(17), N(1)–Cu(1)–N(2) 79.94(6), N(1)–Cu(1)–Cl(1A) 125.28(5), N(2)–Cu(1)–Cl(1A) 122.07(5), Cu(1)–Cl(1)–Cu(1A) 78.154(17).

cationic complexes (Figures 2–5). Indeed, for the monomeric bis(chelate) structures **1**–**4** the angles between the two CuN$_2$ chelate planes vary, being ca. 54, 89, 84, 81, 87, 88 and 90° for **1**, **2**, **3-A**, **3-B**, **3-C**, **3-D** and **4**, respectively. These planes are almost perpendicular except for [Cu(DAB^{Mes})$_2$](BF$_4$) (**1**). The significantly smaller angle seen in this complex is associated with a pair of intramolecular π–π contacts between the adjacent mesityl rings on the two coordinated ligands. The N(1)-bound ring overlays the N(21)-bound ring with centroid•••centroid and mean interplanar separations of ca. 3.63 and 3.53 Å, the two rings being inclined by ca. 5°, whilst the N(2)- and N(22)-bound rings overlap in a similar fashion (centroid•••centroid and mean interplanar separations of ca. 3.51 and 3.46 Å, rings inclined by ca. 1°). Overall, τ_4 clearly accounts for the intramolecular π-stacking with the mesityl rings in complex **1**. No such interaction was evidenced in [Cu(DAB^{Anis})$_2$](BF$_4$) (**2**), the other homoleptic complex bearing aromatic substituents in this study.

The diisopropylphenyl groups in mono(chelate) complex **5** adopt an almost perpendicular orientation relative to the chelate plane with torsion angles about the N(1)–C(Ar) and N(2)–C(Ar) bonds of ca. 78 and 79°, respectively. This arrangement effectively shields the copper(I) centre above and below the coordination plane, which make accommodating a second DAB ligand difficult.

Dimeric structures **6** and **7** both present central Cu_2Cl_2 rings in which the copper(I) and the chlorine ions each occupy oppo-

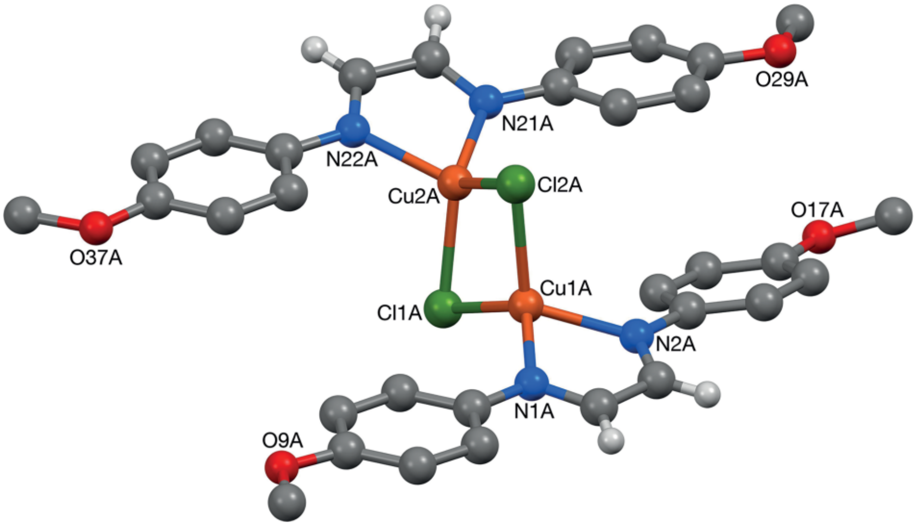


Figure 7. Structure of one (**6-A**) of the four independent complexes present in the crystal of [CuCl(DAB^{Anis})] (**6**). Most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu(1A)–Cl(1A) 2.2773(7), Cu(1A)–N(1A) 2.073(2), Cu(1A)–N(2A) 2.0641(19), Cu(1A)–Cl(2A) 2.3534(7); Cl(1A)–Cu(1A)–N(1A) 125.29(6), Cl(1A)–Cu(1A)–N(2A) 123.56(6), Cl(1A)–Cu(1A)–Cl(2A) 105.29(2), N(1A)–Cu(1A)–N(2A) 80.53(8), N(1A)–Cu(1A)–Cl(2A) 109.85(6), N(2A)–Cu(1A)–Cl(2A) 110.54(6), Cu(1A)–Cl(1A)–Cu(2A) 73.58(2).

site corners. This ring is perfectly flat in **7** as a consequence of the centre of symmetry in the middle of the ring, but distinct folds of ca. 21, 13, 16 and 26°, respectively, are seen between the two $CuCl_2$ planes for the four independent complexes (**6-A**–**6-D**) in structure **6**. The observed Cu•••Cu distances in each independent unit (2.74–2.83 Å) are just around the sum of their van der Waals radii (2.80 Å),[14] which might be indicative of a weak attractive interaction between the two closed-shell d^{10} metal ions. No such interaction can be postulated in **7** as the observed Cu•••Cu separation of 2.934 Å is too long.

The sp^2 character of the C and N atoms in the chelate ring of complexes **1**–**7** is confirmed by imine bond lengths of 1.286(2)–1.296(3) Å for cationic **2**, or 1.280(3) Å for neutral complex **7**, for instance. These values are very similar to standard $N(sp^2){=}C(sp^2)$ double bonds (1.27 Å).[15]

In an attempt to better understand the steric environment imposed by these diimine ligands in the solid state, and maybe also the specific stoichiometries obtained for the prepared complexes, we quantified such effect of DAB^R using the percent buried volume ($\%V_B$) method, originally developed by Cavallo and co-workers as a steric probe of N-heterocyclic carbene ligands.[16] A simple online tool calculates the percentage of the volume of a metal-centred sphere of defined radius that is occupied by a given ligand.[17] For these calculations we used the crystallographic data obtained for cationic complexes **1**–**5**, and according to the obtained $\%V_B$ values (41.4–47.5),[18] the steric demand of the diimine ligands used in this study follows the sequence: $DAB^{Anis} \approx DAB^{Cy} < DAB^{Ad} < DAB^{Dipp} < DAB^{Mes}$. It was surprising to find that the sterically most hindered ligand was DAB^{Mes} and not DAB^{Dipp} as the isolation of heteroleptic complex **5** would suggest. These values clearly show both steric and electronic factors determine the nature of the accessible complexes for these ligands.

UV/Vis Studies

All the complexes prepared are red, with shades ranging from dark pink to almost black. As ligand dissociation had been observed in related complexes,[6] even in noncoordinating solvents, UV/Vis studies were carried out to determine the behaviour in solution. We focused our efforts on the homoleptic cationic complexes as there is some precedent in the literature for $[CuCl(DAB^R)]$[9a] complexes, and also the low solubility of CuCl in organic solvents would impede any titration experiments.

In a first stage, we studied $[Cu(DAB^{Anis})_2](BF_4)$ (**2**), whose absorption spectrum recorded in DCM (15 µM) showed an intense broad band between 420 and 452 nm (ε = 35280 ± 697 L mol^{-1} cm^{-1}), as well as a much weaker band at lower energy (593 nm, 5100 ± 70 L mol^{-1} cm^{-1}). Both bands were attributed to $d\pi$–π^* metal-to-ligand charge transfer (MLCT) absorptions as the free ligand, DAB^{Anis}, in DCM displays a band at 375 nm (24810 ± 293 L mol^{-1} cm^{-1}).

Titration experiments were then carried out with $[Cu(NCMe)_4](BF_4)$ solutions in degassed DCM (15 µM) and increasing amounts of free ligand DAB^{Anis} (0.2–3 equiv.). Between 0.2 and 1.6 equiv. of ligand, a constant increase of both bands was observed (Figure 9). At higher ligand concentrations, a band at 425 nm appeared and progressively shifted towards the wavelength of DAB^{Anis}.

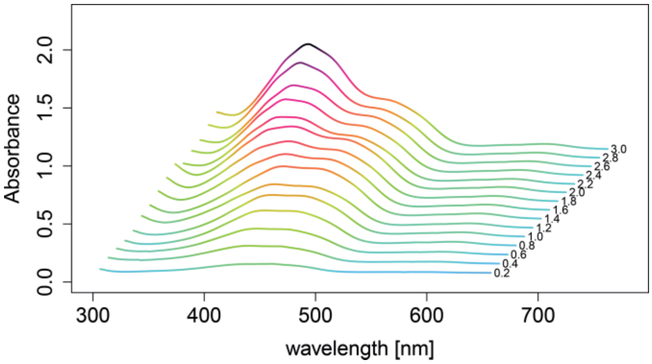
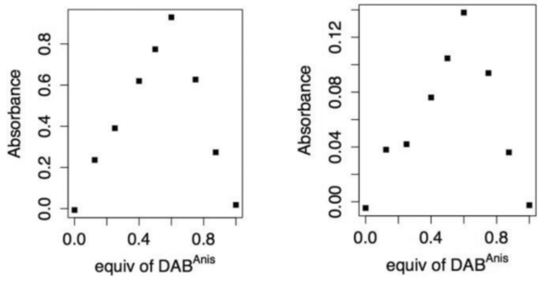


Figure 9. UV/Vis spectra for the titration experiments with $[Cu(NCMe)_4](BF_4)$ (15 µM) and different equivalents of DAB^{Anis} in DCM.

Plotting of the intensity of each absorption against the equivalents of ligand used evidenced that the intensity of both bands increases up to 1.5 equiv. of ligand, and remains constant at higher concentrations.[18] Furthermore, Jobs plots for these two bands indicate a mol fraction of 0.64 and 0.62 for DAB^{Anis}, with both values very close to a 2:3 Cu/L ratio for the species in solution (Figure 10).



(A) 454 nm (B) 593 nm

Figure 10. Jobs plot for the titration experiments with DAB^{Anis} in DCM.

This points towards a different stoichiometry of the species in solution when compared to isolated $[Cu(DAB^{Anis})_2](BF_4)$ (**2**). It is important to note that the UV/Vis spectrum recorded for **2** was found to be virtually identical to that from a titration experiment with a 2:3 and not a 1:2 Cu/L ratio as it could have been expected (Figure 11).

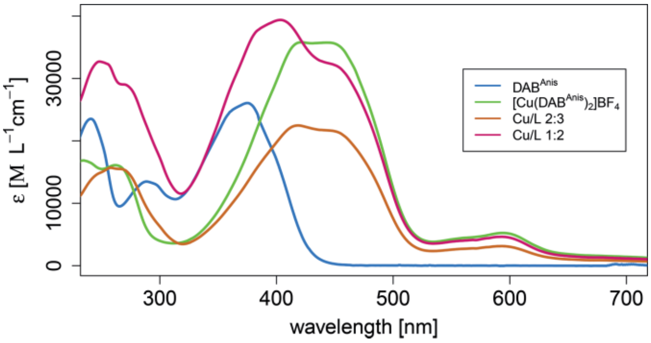


Figure 11. Comparison of UV/Vis spectra in DCM for the Cu/DAB^{Anis} system ([Cu] = 15 µM).

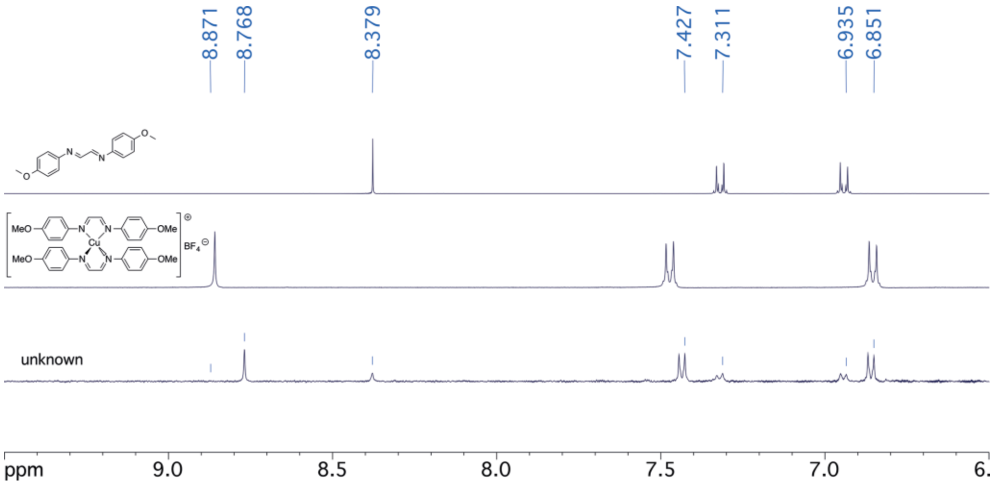


Figure 12. Comparison of ^{1}H NMR spectra for the Cu/DAB^{Anis} system in CD_2Cl_2.

In order to further validate these observations, the ^{1}H NMR spectrum of a 15 μm solution of **2** in CD_2Cl_2 was recorded. Indeed, no signals corresponding to $[Cu(DAB^{Anis})_2](BF_4)$ were found at this low concentration. Instead, the signals corresponding to free DAB^{Anis} were observed, together with those corresponding to a new ligated species with a single chemical environment for all diimine hydrogen atoms present (Figure 12). Based on these results, a structure is proposed for the copper complex formed in the titration experiments, featuring a dicopper complex with three bridging diimine ligands (Figure 13).[19]

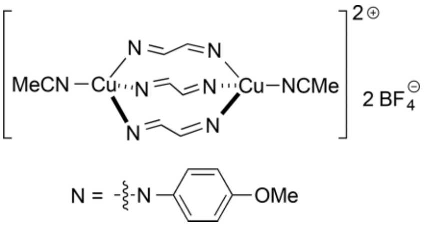


Figure 13. Plausible structure for the species formed by the Cu/DAB^{Anis} system in DCM.

Pre-formed $[Cu(DAB^{Anis})_2](BF_4)$ (**2**) might rearrange into a similar species at low concentrations in non-coordinating solvents. Measurements at higher concentrations could not be carried out due to the strong absorbance of this system, which also prevented the use of MeCN as solvent.

In order to obtain more information about these homoleptic complexes, $[Cu(DAB^{Ad})_2](BF_4)$ (**4**) was investigated next. DAB^{Ad} has the advantage of not having any absorptions in the visible region, and in DCM only a band at 228 nm (14450 ± 503 L mol^{-1} cm^{-1}) is observed. In this case all measurements were carried out at higher concentrations (typically 300 μm) as both the complex and the ligand are significantly less absorbent than in the previous case. However, it is important to note that identical UV/Vis bands were recorded at lower concentrations, down to 40 μm. The absorption spectrum of **4** recorded in DCM showed a small absorption at 430 nm and a much stronger band at 530 nm attributed to $d\pi$–π^* metal-to-ligand charge transfer (MLCT) absorptions.

The titration experiments were performed in degassed DCM with a constant concentration in $[Cu(NCMe)_4](BF_4)$ (300 μm) and an increasing amount of DAB^{Ad} (60–900 μm, 0.2–5 equiv., Figure 14). When 0.2 to 1 equiv. of ligand was used, the band at 530 nm (together with a very small absorption at 326 nm) was observed. Between 1 and 2 equiv. of ligand, the band at 326 nm gradually decreased in intensity, whereas the ones at 430 and 530 nm steadily increased. The spectra remained unchanged when larger excesses of ligand, up to 5 equiv., were employed. Plots of the intensity of each band against the equivalents of ligand can be found in the Supporting Information.

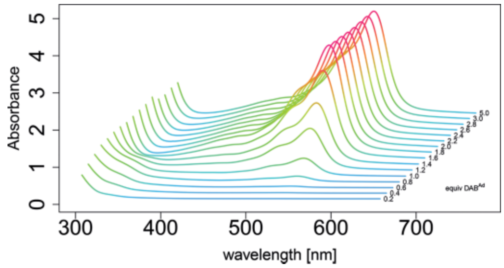


Figure 14. UV/Vis spectra for the titration experiments with $[Cu(NCMe)_4](BF_4)$ (300 μm) and different equivalents of DAB^{Ad} in DCM.

Significantly, the UV/Vis spectrum of $[Cu(DAB^{Ad})_2](BF_4)$ (**4**) and the one obtained for the titration experiment with a Cu/L ratio of 1:2 are identical.[14] These results led us to tentatively assign the band at 326 nm to a heteroleptic complex $[Cu(DAB^{Ad})(NCMe)_2](BF_4)$.

In order to gather additional evidence, we next carried out UV/Vis studies in MeCN, a coordinating solvent. In this case, two main bands were observed in the spectrum of **4**, one at 398 nm and a more intense one at 525 nm. When this spectrum was recorded at different concentrations (0.15–1.2 mm), it became clear that as the concentration was reduced, the band at 525 nm decreased in intensity at a faster rate than the band at 398 nm (Figure 15). A plot of the bands' intensity vs. the concentration of **4**, showed that both lines eventually cross each other, giving evidence that these two bands do not belong to the same species in solution. Further proof comes from

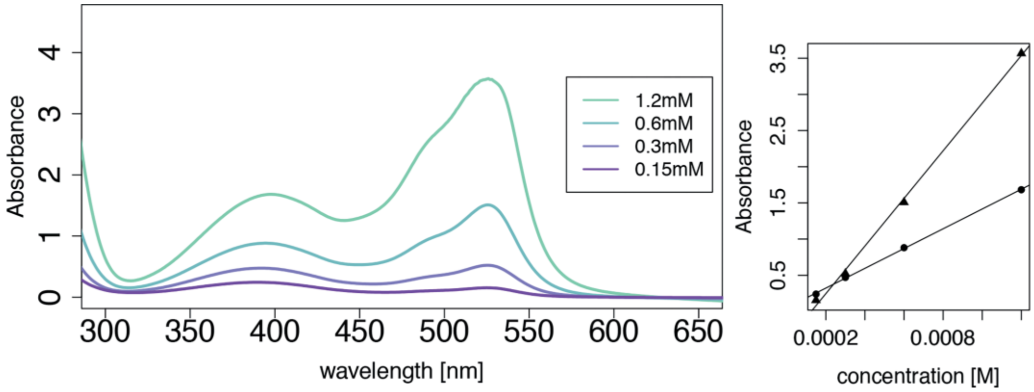
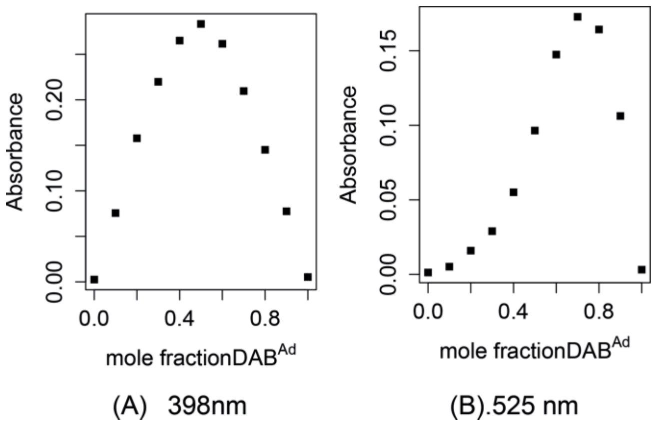


Figure 15. UV/Vis spectra for the titration experiments with $[Cu(NCMe)_4](BF_4)$ (300 μM) and different equivalents of DAB^{Ad} in DCM.

a vastly different shape of normalised spectra recorded at different concentrations.[18] These results indicate that MeCN can in fact displace diimine ligands at low concentrations, possibly forming $[Cu(DAB^{Ad})(NCMe)_2](BF_4)$ in situ.

Titration experiments in degassed MeCN with $[Cu(NCMe)_4](BF_4)$ and DAB^{Ad} led to results very similar to those obtained in DCM.[18] The Jobs plot derived from this data showed that the maximum for the 398 nm band lays within 0.5 mol fraction of the ligand, pointing towards a 1:1 Cu/L ratio (Figure 16). For the band at 525 nm, the maximum absorbance was between 0.6 and 0.7, which could be attributed to a 1:2 or a 2:3 copper/ligand ratio. Considering the NMR and X-ray crystallography data previously collected, a 1:2 stoichiometry for the copper complex was favoured.



(A) 398nm

(B).525 nm

Figure 16. Jobs plot for the titration experiments with DAB^{Ad} in MeCN.

The extinction coefficient for the absorption band at 398 nm, attributed to heteroleptic $[Cu(DAB^{Ad})(NCMe)_2](BF_4)$, could be calculated from titration experiments with a large excess of $[Cu(NCMe)_4](BF_4)$ (up to 1000 equiv.) to prevent the formation of the bis(DAB) complex.[18] Under these conditions, no band at 525 nm was observed and an extinction coefficient of 2191 ± 22 $L\,mol^{-1}\,cm^{-1}$ was obtained. On the other hand, the dilution of **4** (0.06–0.6 mM) in solutions of acetonitrile saturated in DAB^{Ad} led to UV/Vis spectra with only the 525 nm band, and the extinction coefficient found for this species was 7448 ± 255 $L\,mol^{-1}$. With this data in hand, the equilibrium constant for the reaction depicted in Scheme 4 was found to be 1.3×10^3. It is important to note that only data obtained at copper concentrations between 0 and 0.3 mM could be used in these calculations, since at higher concentrations the Beer–Lambert law is not fulfilled anymore, most probably because of additional equilibria present in the system.

$$[Cu(DAB^{Ad})_2]BF_4 + MeCN_{sol} \xrightleftharpoons{k} [Cu(DAB^{Ad})(NCMe)_2]BF_4 + DAB^{Ad}$$

Scheme 4. Proposed equilibrium.

All attempts to isolate the proposed heteroleptic $[Cu(DAB^{Ad})(NCMe)_2](BF_4)$ failed. No crystals suitable for X-ray analysis could be grown, and upon concentration, only homoleptic complex **4** was observed by NMR spectroscopy. However, further evidenced could be obtained by ^1H NMR analysis. The spectrum of $[Cu(DAB^{Ad})_2](BF_4)$ (**4**) was recorded in CD_3CN at different concentrations. As it can be seen in Figure 17, as the concentration decreased from 12 to 0.3 mM, the resonance of the imine hydrogen atoms in the copper complex shifted upfield from $\delta = 8.3$ ppm to $\delta = 8.0$ ppm. This signal also became very broad with dilution, indicating a quick exchange process of the diimine ligands on the NMR time scale. When the same spectrum was recorded at –40 °C, three imine environments were evidenced, homoleptic complex **4** ($\delta = 8.3$ ppm), free DAB^{Ad} ligand ($\delta = 7.8$ ppm), and a new signal ($\delta = 8.0$ ppm). Next, a mixture 1:0.2 $[Cu(NCMe)_4](BF_4)/DAB^{Ad}$ was considered as only the band at 398 nm was observed under these conditions during the titration experiments (see Figure 14). Significantly, a single resonance at $\delta = 8.0$ ppm was obtained at room temperature for this experiment. Overall, these results show that even if they might not be isolable, $[Cu(DAB^R)(NCMe)_2](BF_4)$ complexes can be formed as diluted solutions either by dilution of pre-isolated $[Cu(DAB^R)_2](BF_4)$ complexes or by the reaction of the ligand with a large excess (i.e. 5 equiv.) of the copper source.

Importantly, the only heteroleptic cationic complex of this kind we could prepare during our synthetic studies, $[Cu(DAB^{Dipp})(NCMe)_2](BF_4)$ (**5**), has a similar UV/Vis spectrum, and the band of the lowest energy for **5** appeared at 353 nm (1709 ± 4 $L\,mol^{-1}\,cm^{-1}$) in MeCN. Quite surprisingly, this particular compound is as stable as the rest of the complexes reported in this work.

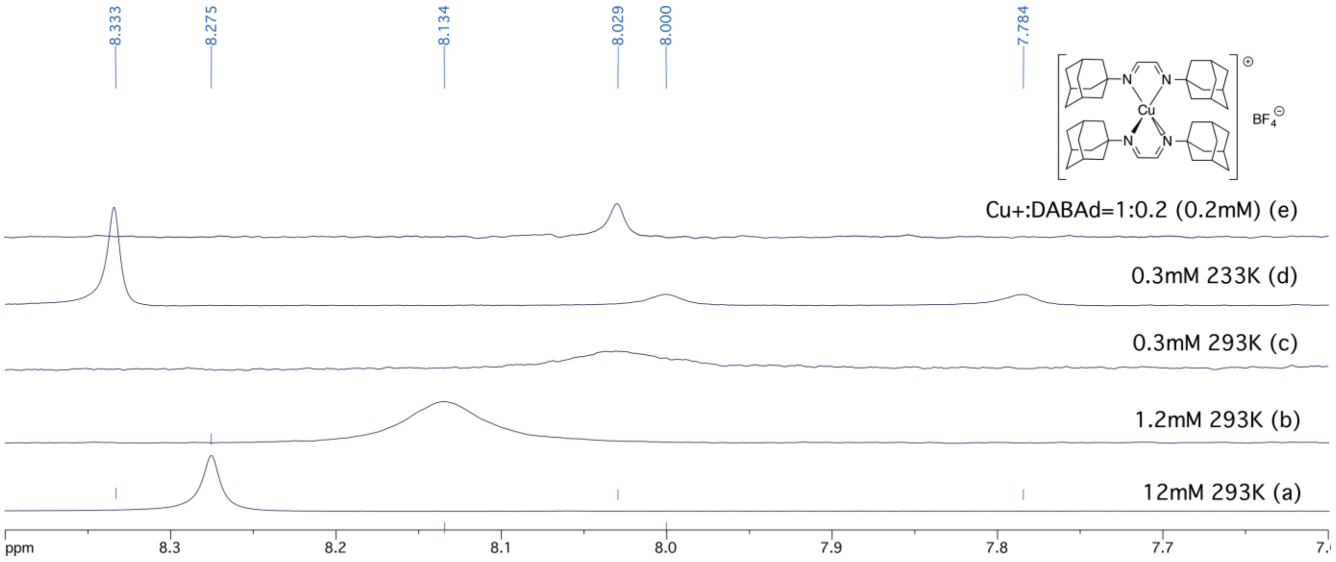


Figure 17. Comparison of ^{1}H NMR spectra for the Cu/DAB^{Ad} system in CD_3CN.

Finally, in order to study the possible fluorescence emission of the prepared compounds, $[Cu(DAB^{Anis})_2](BF_4)$, $[Cu(DAB^{Ad})_2](BF_4)$, as well as $[CuCl(DAB^{Anis})]$ and $[CuCl(DAB^{Ad})]$ complexes were excited in the MLCT or the π–π* bands, but no fluorescence emissions were observed at room temperature in DCM or MeOH, neither in the presence of oxygen nor in degassed solutions.

Conclusions

Three related families of copper(I) complexes bearing diazabutadiene ligands have been prepared and fully characterised: homoleptic $[Cu(DAB^{R})_2](BF_4)$, heteroleptic $[Cu(DAB^{R})(NCMe)_2](BF_4)$ and neutral $[CuCl(DAB^{R})]$ complexes. Interestingly, the Cu/L ratio in these complexes is dictated by the chosen copper source and the diimine ligand, but not the stoichiometry of the reactions. All of these can be easily handled with no particular precautions to exclude oxygen or moisture, and – with the exception of **5** – they are indefinitely stable in the solid state. The prepared complexes displayed a tetracoordinate copper centre in the solid state, with different degrees of distortion from the expected tetrahedral geometry. Furthermore, the behaviour in solution was studied by means of UV/Vis and NMR spectroscopy. The obtained results show that even if they might only be stable under diluted conditions, heteroleptic cations $[Cu(DAB^{R})(NCMe)_2]^+$ appear to be intermediates in the formation of the isolated homoleptic $[Cu(DAB^{R})_2](BF_4)$ complexes. Moreover, in diluted solutions one of the diimine ligands in the homoleptic complexes can be displaced by a coordinating solvent, or the initial complex might rearrange into dinuclear species. This is in line with the known lability of copper–diimine complexes in solution. While this feature is often regarded as a drawback for the exploitation of the photochemical properties of these compounds, it can also be regarded as a very easy activation mode for catalytic applications. Hence, by simply adding a sub-stoichiometric amount of such copper complexes to a solution, the copper complex will evolve to a new coordinatively unsaturated species prone to act as a catalyst. In fact, we recently reported that these complexes are competent catalysts for the copper(I)-catalysed Click azide-alkyne cycloaddition reaction,[20] with $[Cu(DAB^{Cy})_2](BF_4)$ (**3**) as the best performing catalyst. Further studies on the application of these complexes are currently ongoing in our laboratory.

Experimental Section

General Considerations: All reagents were used without any further purification. DCM was dried by passing it through columns of molecular sieves in a solvent purification system. All reactions were carried out in anhydrous solvent under nitrogen using oven-dried glassware. Melting points (uncorrected) were determined with an Electrothermal Gallenhamp apparatus. NMR spectra were recorded with Bruker AVANCE 400 spectrometers at room temperature. ^{1}H NMR shifts in δ (ppm) are referenced to tetramethylsilane (δ = 0.00 ppm). ^{13}C NMR shifts are referenced to the central peak of the $CDCl_3$ triplet, the $(CD_3)_2SO$ septuplet or the CD_3CN septuplet, set at δ = 77.00, 39.50 or 1.32 ppm, respectively. ^{19}F NMR shifts are referenced to the monofluorobenzene singlet, set at δ = –113.15 ppm. IR spectra were recorded with a Perkin–Elmer 100 series FT-IR spectrometer, equipped with a beam-condensing accessory (samples were sandwiched between diamond compressor cells). Single-crystal X-ray diffraction was performed with Oxford Diffraction Xcalibur PX Ultra (λ = 1.54184 Å) (**1**, **2**, **3**, **6** and **7**) and Xcalibur 3 (λ = 0.71073 Å) (**4** and **5**) diffractometers, and the structures were refined using the SHELXTL, SHELX-97, and SHELX-2013 program systems.[21] The absolute structure of **1** was determined by a combination of R-factor tests ($R_1^+ = 0.0315$, $R_1^- = 0.0393$) and by use of the Flack parameter [$x^+ = 0.000(17)$, $x^- = 1.030(17)$]. CCDC 1409952 (for **1**), 1409953 (for **2**), 1409954 (for **3**), 1409955 (for **4**), 1409956 (for **5**), 1409957 (for **6**), and 1409958 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. UV/Vis spectra were recorded with a Perkin–Elmer Lambda 20 spectrometer in nondegassed DCM or MeCN solutions. Mass spectra were recorded with a Micromass Autospec Premier, Micromass LCT Premier or a VG Platform II spectrometer using EI, CI or ESI techniques. Elemental analyses were carried out by the Science Technical Support Unit at London Metropolitan University.

Complex 1: A mixture of $[Cu(NCMe)_4](BF_4)$ (108 mg, 0.34 mmol) and *N,N′*-bis(mesityl)-1,4-diaza-1,3-butadiene (209 mg, 0.72 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature overnight. This resulted in a dark green solution that was concentrated to ca. 5 mL, and pentane (ca. 30 mL) was added, which led to the precipitation of a nearly black solid. This was collected by filtration, washed with pentane (3 × 10 mL) and dried under reduced pressure (yield 179 mg, 71 %). Single crystals for X-ray diffraction were grown from DCM/hexane. M.p. 297 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.30 (s, 4 H, H–C=N), 6.61 (s, 8 H, H^{Ar}), 2.28 (s, 12 H, 4-Me), 1.97 (s, 24 H, 2,6-Me) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 159.3 (CH, CH=N), 144.3 (C, *i*-C^{Ar}), 136.7 (C, *o*-C^{Ar}), 129.3 (CH, *m*-C^{Ar}), 129.1 (C, *p*-C^{Ar}), 20.8 (CH_3, *p*-Me), 18.8 (CH_3, *o*-Me) ppm. ^{19}F NMR (377 MHz, $CDCl_3$): δ = –153.4 (BF_4^-) ppm. IR: $\tilde{\nu}$ = 2947, 2910, 1610 (C=N), 1475, 1455, 1379, 1299, 1206, 1087, 1048 (BF_4^-), 886, 850, 723, 650, 587, 519, 418, 336 cm^{-1}. UV/Vis: λ_{max}/nm (ε/M^{-1} cm^{-1}) = 228 (31170 ± 150), 398 (13600 ± 20), 727 (3150 ± 60). HRMS: calcd. for $C_{40}H_{48}CuN_4$ $[Cu(DAB^{Mes})_2]^+$ 647.3175, found 647.3150. $C_{40}H_{48}BCuF_4N_4$ (735.19): calcd. C 74.10, H 7.46, N 8.64; found C 74.03, H 7.51, N 8.59.

Complex 2: A mixture of $[Cu(NCMe)_4](BF_4)$ (206 mg, 0.65 mmol) and *N,N′*-bis(4-methoxylphenyl)-1,4-diaza-1,3-butadiene (354 mg, 1.32 mmol) in DCM (30 mL) was stirred at room temperature for 4 h. After filtration of the dark solution, the solution was concentrated to ca. 5 mL, and petroleum ether (40 mL) was added, which led to the precipitation of a black solid. This was collected by filtration, washed with petroleum ether (8 × 3 mL) and dried under reduced pressure (yield 367 mg, 82 %). Single crystals for X-ray diffraction were grown from DCM/hexane. M.p. 205–207 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.99 (s, 4 H, H–C=N), 7.50 (d, *J* = 9.0 Hz, 8 H, H^{Ar}), 6.85 (d, *J* = 9.0 Hz, 8 H, H^{Ar}), 3.79 (s, 12 H, OMe) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 161.5 (CH, CH=N), 150.8 (C, *p*-C^{Ar}), 139.1 (C, *i*-C^{Ar}), 124.6 (CH, C^{Ar}), 115.2 (CH, C^{Ar}), 55.6 (CH_3, OMe) ppm. ^{19}F NMR (377 MHz, $CDCl_3$): δ = –152.5 (BF_4^-) ppm. IR: $\tilde{\nu}$ = 2836, 1599 (C=N), 1562, 1503, 1455, 1438, 1253, 1164, 1096, 1058, 1021, 939, 885, 841, 826, 799, 658, 639, 550, 519, 426, 389 cm^{-1}. UV/Vis: λ_{max}/nm (ε/M^{-1} cm^{-1}) = 251 (22100 ± 500), 451 (36100 ± 500), 593 (5100 ± 70). LRMS (ES^+): 599 $[Cu(DAB^{Anis})_2]^+$. $C_{32}H_{32}BCuF_4N_4O_4$ (686.98): calcd. C 55.95, H 4.70, N 8.16; found C 55.85, H 4.60, N 8.05.

Complex 3: A mixture of $[Cu(NCMe)_4](BF_4)$ (174 mg, 0.55 mmol) and *N,N′*-bis(cyclohexyl)-1,4-diaza-1,3-butadiene (240 g, 1.09 mmol) was stirred in DCM (30 mL) at room temperature overnight. After filtration of the resulting dark red solution, the solvent was evaporated to dryness, the residue dissolved in THF (10 mL) and petroleum ether (40 mL) added leading to the precipitation of a red brownish solid, which was collected by filtration, washed with a mixture of DCM/petroleum ether (1:4, 10 × 5 mL) and dried under reduced pressure (yield 208 mg, 64 %). Single crystals for X-ray diffraction were grown from DCM/hexane. M.p. 150–153 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 4 H, H–C=N), 3.60 (br., 4 H, CH^{Cy}), 1.88–1.68 (m, 20 H, CH_2), 1.41–1.08 (m, 20 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 157.2 (CH, CH=N), 67.1 (CH), 34.9 (CH_2), 25.1 (CH_2), 24.7 (CH_2) ppm. ^{19}F NMR (377 MHz, $CDCl_3$): δ = –153.3 (BF_4^-) ppm. IR: $\tilde{\nu}$ = 2928, 2854, 1627 (C=N), 1541, 1450, 1348, 1257, 1063 (BF_4^-), 1026, 873, 855, 520, 465, 412 cm^{-1}. UV/Vis: λ_{max}/nm (ε/M^{-1} cm^{-1}) = 241 (7250 ± 130), 516 (4360 ± 10). HRMS: calcd. for $C_{28}H_{48}CuN_4$ $[Cu(DAB^{Cy})_2]^+$ 503.3175, found 503.3180. $C_{28}H_{48}BCuF_4N_4$ (591.06): calcd. C 56.90, H 8.19, N 9.48; found C 56.86, H 8.17, N 9.39.

Complex 4: A mixture of $[Cu(NCMe)_4](BF_4)$ (400 mg, 1.50 mmol) and *N,N′*-bis(adamantyl)-1,4-diaza-1,3-butadiene (427 mg, 0.79 mmol) was stirred in DCM (15 mL) at room temperature overnight. The resulting dark red solution was then concentrated to dryness and the precipitate dissolved in the minimum amount of DCM. Addition of diethyl ether led to the precipitation of a dark red solid. This was washed with diethyl ether and hexane, dried under reduced pressure and recrystallised from DCM and diethyl ether (yield 580 mg, 80 %). Single crystals for X-ray diffraction were grown from acetone/pentane. M.p. 325 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.51 (s, 4 H, H–C=N), 2.18 (s, 12 H, CH^{Ad}), 184–1.53 (m, 48 H, CH_2^{Ad}) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 155.6 (CH, CH=N), 59.9 (C, C^{Ad}), 44.3 (CH_2, C^{Ad}), 35.9 (CH_2, C^{Ad}), 29.5 (CH, C^{Ad}) ppm. ^{19}F NMR (377 MHz, $CDCl_3$): δ = –151.6 (BF_4^-) ppm. IR: $\tilde{\nu}$ = 2902, 2847, 1621 (C=N), 1558, 1531, 1453, 1378, 1304, 1191, 1040, 1090, 1048, 896, 813, 735, 695 cm^{-1}. UV/Vis: λ_{max}/nm (ε/M^{-1} cm^{-1}) = 230 (7100 ± 160), 252 (8960 ± 1540), 532 (9560 ± 60). HRMS: calcd. for $C_{44}H_{64}CuN_4$ $[Cu(DAB^{Ad})_2]^+$ 711.4427, found 711.4431. $C_{45}H_{68}BCuF_4N_4$ (815.41): calcd. C 66.28, H 8.41, N 6.87; found C 66.18, H 8.62, N 6.73.

Complex 5: A mixture of $[Cu(NCMe)_4](BF_4)$ (250 mg, 0.79 mmol) and *N,N′*-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene (299 mg, 0.79 mmol) was stirred in DCM (30 mL) at room temperature for 4 h. After filtration of the resulting dark solution, the filtrate was concentrated to ca. 5 mL, and hexane (20 mL) was added, leading to the precipitation of a dark brown solid. This was collected by filtration, washed with pentane (5 × 3 mL) and dried under reduced pressure product as a dark red powder (yield 463 mg, 96 %). Single crystal for X-ray diffraction were grown from DCM/hexane. M.p. 123 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 2 H, H–C=N), 7.34–7.26 (m, 6 H, H^{Ar}), 2.95 (sept, *J* = 6.8 Hz, 4 H, C*H*Me_2), 2.20 (s, 6 H, NCMe), 1.26 (d, *J* = 6.8 Hz, 24 H, CH*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 160.0 (CH, CH=N), 144.9 (C, *i*-C^{Ar}), 138.4 (C, *o*-C^{Ar}), 127.1 (CH, *p*-CH^{Ar}), 123.8 (CH, *m*-CH^{Ar}), 28.2 (CH, C*H*Me_2), 23.9 (CH_3, CH*Me*$_2$) ppm. ^{19}F NMR (377 MHz, $CDCl_3$): δ = –153.1 (BF_4^-) ppm. IR: $\tilde{\nu}$ = 2965, 2871, 2277 (C≡N), 1634 (C=N), 1591 (C=N), 1466, 1435, 1365, 1334, 1256, 1186, 1050 (BF_4^-), 797, 753, 699 cm^{-1}. UV/Vis: λ_{max}/nm (ε/M^{-1} cm^{-1}) = 342 (2630 ± 70) 565 (256 ± 5); 353 (1709 ± 4), 464 (357 ± 22), 524 (265 ± 19) (MeCN). LRMS (ES^+): *m/z* = 480 $[Cu(DAB^{DIPP})(NCMe)]^+$. $C_{30}H_{42}BCuF_4N_4$ (609.04): calcd. C 59.16, H 6.95, N 9.20; found C 59.07, H 6.67, N 9.38.

Complex 6: A mixture of CuCl (123 mg, 1.24 mmol) and *N,N′*-bis(4-methoxyphenyl)-1,4-diaza-1,3-butadiene (364 g, 1.39 mmol) in DCM (30 mL) was stirred at room temperature overnight. The resulting black suspension was filtered through anhydrous $MgSO_4$, and the resultant dark filtrate was concentrated to 15 mL. Addition of petroleum ether (40 mL) led to the precipitation of a nearly black powder, which was collected by filtration, washed with petroleum ether, and dried under reduced pressure (yield 378 mg, 83 %). Single crystals for X-ray diffraction were grown from DCM/hexane. M.p. 220–223 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.79 (br. s, 2 H, H–C=N), 7.48–7.46 (m, 4 H, H^{Ar}), 6.98–6.96 (m, 4 H, H^{Ar}), 3.87 (s, 6 H, OMe) ppm. $^{13}C\{^1H\}$ NMR: could not be recorded due to the low solubility of **6**. IR: $\tilde{\nu}$ = 2835, 1611 (C=N), 1586, 1503, 1436, 1297, 1253, 1165, 1111, 1026, 825, 798, 636, 528, 406 cm^{-1}. UV/Vis: λ_{max}/nm (ε/M^{-1} cm^{-1}) = 232 (12900 ± 360), 393 (14300 ± 300), 589 (1250 ± 90). HRMS: calcd. for $C_{18}H_{19}CuN_3O_2$ $[Cu(DAB^{Anis}) + MeCN]^+$ 372.0773, found 372.0788. $C_{16}H_{16}ClCuN_2O_2$ (367.31): calcd. C 52.32, H 4.39, N 7.63; found C 52.55, H 4.60, N 7.85.

Complex 7: A mixture of CuCl (133 mg, 1.34 mmol) and *N,N′*-bis(cyclohexyl)-1,4-diaza-1,3-butadiene (296 mg, 1.34 mmol) was stirred in DCM (30 mL) at room temperature overnight. The resulting mixture was filtered through anhydrous $MgSO_4$, the dark red filtrate was concentrated to 5 mL, and petroleum ether (50 mL) was added to precipitate a dark red solid, which was collected by filtration, washed with a mixture of Et_2O/*n*-hexane (1:3) and vacuum-dried (yield 220 mg, 86 %). Single crystals for X-ray diffraction were grown from DCM/hexane. M.p. 166–170 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.36 (br. s, 2 H, H–C=N), 3.63 (br. t, 2 H, CH^{Cy}), 2.20–1.51 (m, 10 H CH_2), 1.51–1.12 (m, 10 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR: could not be recorded due to the low solubility of **7**. IR: $\tilde{\nu}$ = 2926, 2852, 1644 (C=N), 1569, 1456, 1441, 1393, 1379, 1155, 1102, 956, 869, 854, 584, 464, 406 cm^{-1}. UV/Vis: λ_{max}/nm (ε/M^{-1} cm^{-1}) = 230 (7060 ± 50), 382 (856 ± 9), 515 (1830 ± 20). HRMS: calcd. for $C_{16}H_{27}CuN_3$ $[Cu(DAB^{Cy}) + MeCN]^+$ 324.1501, found 324.1494. $C_{14}H_{24}ClCuN_2$ (319.36): calcd. C 52.99, H 6.99, N 8.83; found C 52.88, H 6.78, N 8.73.

Complex 8: A mixture of CuCl (75.3 mg, 0.761 mmol) and *N*,*N*′-bis(adamantyl)-1,4-diaza-1,3-butadiene (241.0 mg, 0.743 mmol) in DCM (20 mL) was stirred at room temperature overnight resulting in a red mixture. This was concentrated to ca. 5 mL, and pentane (30 mL) was added, which led to the precipitation of a dark red solid, which was filtered, washed with pentane and dried under vacuum (yield 176 mg, 56 %). M.p. 237 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.56 (br. s, 2 H, H–C=N), 2.26 (br. s, 6 H, H^{Ad}), 1.90–1.72 (m, 24 H, H^{Ad}) ppm. $^{13}C\{^1H\}$ NMR: could not be recorded due to the low solubility of **8**. IR: $\tilde{\nu}$ = 2901, 2848, 1624 (C=N), 1581, 1538, 1451, 1367, 1343, 1306, 1090, 981, 890, 813 cm^{-1}. UV/Vis: λ_{max}/nm (ε/M^{-1} cm^{-1}) = 232 (6900 ± 200), 384 (900 ± 11), 530 (1290 ± 50). HRMS: calcd. for $C_{24}H_{35}CuN_3$ $[Cu(DAB^{Ad}) + MeCN]^+$ 428.2127, found 428.2132. $C_{22}H_{328}ClCuN_2$ (721.85): calcd. C 62.39, H 7.62, N 6.61; found C 62.23, H 7.65, N 6.59.

Acknowledgments

This research was financially supported by the Imperial College London. The Royal Society (RG140579) and the Engineering and Physical Sciences Research Council (EPSRC) (EP/K030760/1) are acknowledged for further funding. R. F. P. and E. V. I. thank the Ministerio de Educación (Spain) for funding, J. M. B. thanks the Universidad de Barcelona (Spain) for an Erasmus scholarship. Dr. Marina Kuimova is acknowledged for helpful discussions.

Keywords: Charge transfer · Copper · N ligands · Schiff bases · Transition metals

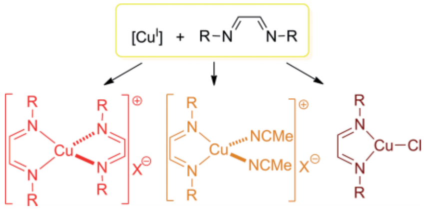
[1] K. C. Gupta, A. K. Sutar, *Coord. Chem. Rev.* **2008**, *252*, 1420–1450.
[2] a) I. Kostova, L. Saso, *Curr. Med. Chem.* **2013**, *20*, 4609–4632; b) S. R. Collinson, D. E. Fenton, *Coord. Chem. Rev.* **1996**, *148*, 19–40.
[3] B. Champin, P. Mobian, J.-P. Sauvage, *Chem. Soc. Rev.* **2007**, *36*, 358–366.
[4] For selected recent examples, see: a) Z. Gonda, S. Kovacs, C. Weber, T. Gati, A. Meszaros, A. Kotschy, Z. Noval, *Org. Lett.* **2014**, *16*, 4268–4271; b) B. L. Tran, B. Li, M. Driess, J. F. Hartwig, *J. Am. Chem. Soc.* **2014**, *136*, 2555–2563; c) D.-L. Mo, L. L. Anderson, *Angew. Chem. Int. Ed.* **2014**, *53*, 5816–5820; *Angew. Chem.* **2014**, *126*, 5925–5830; d) J. E. Steves, S. S. Stahl, *J. Am. Chem. Soc.* **2013**, *135*, 15742–15745; e) Y.-F. Wang, H. Chen, X. Zhu, S. Chiba, *J. Am. Chem. Soc.* **2012**, *134*, 11980–11983.
[5] a) A. Lavie-Cambot, M. Cantuel, Y. Leydet, G. Jonusauskas, D. M. Bassani, N. D. McClenaghan, *Coord. Chem. Rev.* **2008**, *252*, 2572–2584; b) N. Armaroli, *Chem. Soc. Rev.* **2001**, *30*, 113–124; c) O. Horváth, *Coord. Chem. Rev.* **1994**, *135/136*, 303–324.
[6] A. Kaeser, M. Mohankumar, J. Mohanraj, F. Monti, M. Holler, J.-J. Cid, O. Moudam, I. Nierengarten, L. Karmazin-Brelot, C. Duhayon, B. Delavaux-Nicot, N. Armaroli, J.-F. Nierengarten, *Inorg. Chem.* **2013**, *52*, 12140–12151.
[7] a) U. El-Ayaan, A. Paulovicova, Y. Fukuda, *J. Mol. Struct.* **2003**, *645*, 205–212; b) K. V. Vasudevan, M. Findlater, A. H. Cowley, *Chem. Commun.* **2008**, 1918–1919; c) T. Kern, U. Monkowius, M. Zabel, G. Knör, *Eur. J. Inorg. Chem.* **2010**, 4148–4156; d) V. Rosa, C. I. Santos, R. Welter, G. Aullón, C. Lodeiro, T. Avilés, *Inorg. Chem.* **2010**, *49*, 8699–8708.
[8] I. Andrés-Tomé, J. Fyson, F. Baiao Dias, A. P. Monkman, G. Iacobellis, P. Coppo, *Dalton Trans.* **2012**, *41*, 8669–8674.
[9] a) H. tom Dieck, I. W. Renk, *Chem. Ber.* **1971**, *104*, 92–109; b) H. Ayranci, C. Daul, M. Zobrist, M. von Zelewsky, *Helv. Chim. Acta* **1975**, *58*, 1732–1735; c) H. tom Dieck, L. Z. Stamp, *Z. Naturforsch. B* **1990**, *45*, 1369–1382; d) L. Stamp, H. tom Dieck, *Inorg. Chim. Acta* **1987**, *129*, 107–114.
[10] a) J. Reinhold, R. Benedix, P. Birner, H. Henning, *Inorg. Chim. Acta* **1979**, *33*, 209–213; b) J. Reinhold, R. Benedix, P. Birner, H. Z. Hennig, *Z. Chem.* **1977**, *17*, 115–116; for a review, see: G. Van Koten, K. Vrieze, *Adv. Organomet. Chem.* **1982**, *21*, 151–239.
[11] C. L. Foster, C. A. Kilner, M. Thornton-Pett, M. A. Halcrow, *Acta Crystallogr., Sect. C* **2000**, *56*, 319–320.
[12] S. Anga, R. K. Kottalanka, T. Pal, T. K. Panda, *J. Mol. Struct.* **2013**, *1040*, 129–138.
[13] L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* **2007**, 955–964.
[14] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.
[15] M. Burke-Laing, M. Laing, *Acta Crystallogr., Sect. B* **1976**, *32*, 3216–3224.
[16] a) A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano, L. Cavallo, *Eur. J. Inorg. Chem.* **2009**, 1759–1766; b) H. Clavier, S. P. Nolan, *Chem. Commun.* **2010**, *46*, 841–861.
[17] www.molnac.unisa.it/OMtools/sambvca.php.
[18] See the Supporting Information for further details.
[19] For relevant examples of bridging DAB ligands with transition metals, see: a) H. Van der Poel, G. Van Koten, K. Vrieze, *J. Organomet. Chem.* **1977**, *135*, C63–C65; b) K. J. Cavell, P. Stufkens, K. Vrieze, *Inorg. Chim. Acta* **1981**, *47*, 67–76; c) H. Van der Poel, G. Van Koten, K. Vrieze, *Inorg. Chim. Acta* **1981**, *51*, 253–262; d) H. tom Dieck, J. Klaus, *J. Organomet. Chem.* **1983**, *246*, 301–308.
[20] J. Markalain Barta, S. Díez-González, *Molecules* **2013**, *18*, 8919–8928.
[21] a) *SHELXTL*, Bruker AXS, Madison, WI; b) SHELX-97: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122; c) SHELX-201: http://shelx.uni-ac.gwdg.de/SHELX/index.php.

Received: May 24, 2016

Copper(I) Complexes

*B. Zelenay, R. Frutos-Pedreño, J. Markalain-Barta, E. Vega-Isa, A. J. P. White, S. Díez-González** 1–11

Homo- and Heteroleptic Copper(I) Complexes with Diazabutadiene Ligands: Synthesis, Solution- and Solid-State Structural Studies



The preparation of novel copper(I) complexes with aliphatic diazabutadiene (DAB) ligands is reported. [Cu(DAB^R)$_2$](BF$_4$), [Cu(DAB^R)(NCMe)$_4$](BF$_4$) and [CuCl(DAB^R)] are easily synthesised and air-stable. These complexes, which remain scarce in the literature, were fully characterised, and their behaviour both in the solid state as well as in solution has been studied by means of X-ray crystallography and UV/Vis spectroscopy.

DOI: 10.1002/ejic.201600620