Intramolecular π-stacking in copper(I) diketiminate phenanthroline complexes†

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Diketimines *N*,*N*′-dibenzyl-2-amino-4-imino-pent-2-ene (**1**), *S*,*S*-*N*,*N*′-di(phenylethyl)-2-amino-4-imino-pent-2-ene (**2**), *N*,*N*′-bis(3,4,5-trimethoxyphenylmethyl)-2-amino-4-imino-pent-2-ene (**3**), *N*,*N*′-bis(pentafluorophenylmethyl)-2-amino-4-imino-pent-2-ene (**4**) and *N*,*N*′-diisobutyl-2-amino-4-imino-pent-2-ene (**5**) react with CuO*t*Bu in the presence of 2,9-R_2-1,10-phenanthroline to give the respective neutral, tetracoordinated diketiminate copper(I) phenanthroline complexes **1a**+**2a** (R = H), **1b**, **3b**–**5b** (R = Me) and **1c**+**3c** (R = Ph). Crystal structures were obtained for all complexes except **5b** and intramolecular π-stacking between the phenanthroline ligand and one or two *N*-benzyl substituents were observed in **1a**, **2a**, **1b** and **1c**, or **3b** and **4b**, respectively. UV/vis absorption spectra show two transitions in the visible region, a diketiminate-based transition at 373–386 nm and a transition at 600–666 nm, tentatively assigned as an MLCT to phenanthroline. All complexes were weakly luminescent in the solid state at room temperature with lifetimes of less than 60 ns. Weak luminescence was also observed in solution with λ_{max} = 720–830 nm for **1b**, **1c**, **3b**, **4b** and **5b** and short luminescence lifetimes. Intramolecular π-stacking interactions, which prevent flattening distortions in the solid state, appear to have advantageous effects on luminescence intensities.

Introduction

Luminescent metal complexes find application in solar light harvesting and conversion, and complexes of second and third row metals, in particular Ru(II) polypyridines, have been among the most prominent examples.[1,2] Their widespread use is, however, limited by a notable toxicity and, in particular, high costs. There is thus interest in cheaper and more environmentally benign metal sources as alternatives.[3] Complexes with a d^{10} electron configuration, in particular Cu(I), have been considered as potential candidates, since their closed shell structure prevents the non-radiative deactivation through low-lying MC transitions, which are prevalent with other first-row transition metals.[4] Copper(I) phenanthroline complexes are among the most studied copper complexes in this regard,[4–8] following the pioneering work of McMillin and coworkers.[9,10] However, these complexes do deactivate non-radiatively after irradiation by means other than thermal equilibration of the MC and the MLCT levels. Bisphenanthroline copper(I) complexes, for example, undergo a flattening distortion in the excited state rendering them prone to nucleophilic attack by solvent molecules or counter ions to form a penta-coordinated exciplex, which deactivates *via* non-radiative relaxation (Chart 1). Substitution of the 2,9-positions of the phenanthroline ligand, avoiding coordinating solvents and excited state equilibration with organic auxiliaries have been used as strategies to avoid excited state quenching.[4–8]

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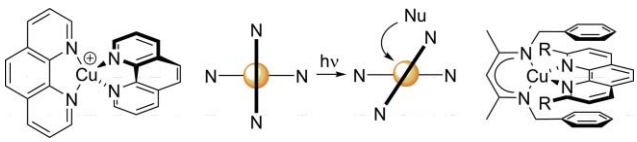


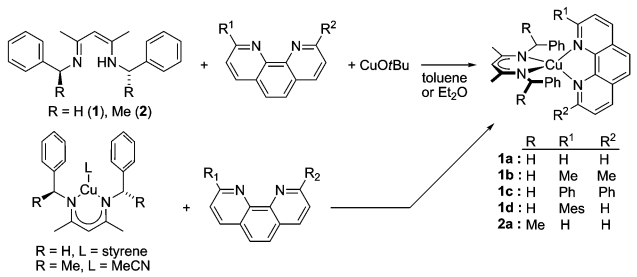
Chart 1

We have previously reported the syntheses of copper(I) complexes with *N*-alkyl substituted diketiminate ligands (*nacnac*^{R}),[11–13] in particular *nacnac*^{Bn},[12] in which π-stacking interactions are present in most of its complexes. We envisaged that this ligand would allow a "sandwiched" π-stacking arrangement of the phenanthroline ligand between the *N*-benzyl substituents, thus minimising excited state distortion (Chart 1). Due to the neutral nature of diketiminate copper complexes, exciplex quenching by the counter ion might be prevented as well. Not counting Cu(I) halogen compounds[14] and polynuclear complexes,[15] we are aware of only one report on neutral copper phenanthroline complexes,[16] although luminescent neutral copper complexes have been reported with other ligands.[17–20]

Results and discussion

Nacnac^{Bn} and *nacnac*$^{CH(Me)Ph}$ complexes

Reaction of diketimines **1** and **2** with CuO*t*Bu[21] in the presence of the appropriate phenanthroline afforded the four-coordinated copper(I) complexes **1a–d** and **2a** (Scheme 1). Complexes **1a–d** could also be obtained by displacement of styrene from *nacnac*^{Bn}Cu(styrene) with phenanthroline if liberated styrene was removed under vacuum. Analogously, phenanthroline replaced acetonitrile in *nacnac*$^{CH(Me)Ph}$CuNCMe to yield **2a**. Only



Scheme 1 Preparation of complexes **1a-1d** and **2a**.

decomposition products were observed with either method when sterically bulky 2,9-di(*tert*-butyl)phenanthroline or 2,9-dimesitylphenanthroline was employed. This mirrors common reactivity patterns of phenanthroline copper complexes: $[Cu(tbp)_2]^+$ was only synthesized indirectly by oxidation of elemental copper in the presence of tbp[22] after conventional methods had failed,[23] while copper complexes of 2,9-dimesitylphenanthroline have not been reported. The corresponding monosubstituted 2-mesitylphenanthroline, on the other hand, cleanly yielded the respective copper complex **1d**. All complexes are dark-blue in colour and sensitive to air and moisture. The complexes are soluble in dichloromethane, toluene and THF and moderately soluble in ether.[24] ^{1}H NMR spectra of **1a–c** display a singlet for the benzylic protons, indicating a C_{2v}-symmetric structure or fast rotation around the N–C_{Bn} bond. In **1d**, the benzylic protons split into two doublets due to the non-symmetric mesitylphenanthroline ligand.

Solid-state structures of **1a–d** and **2a** are displayed in Fig. 1. Cu–N bond distances and N–Cu–N bond angles for the diketiminate ligand (1.959(2)–1.981(2) Å, 98.3(2)–100.8(1)°, Table 1) and for the phenanthroline ligand (1.998(2)–2.194(1) Å, 79.3(1)–83.4(4)°) are in the usual range expected for these ligands (*nacnac*: 1.94(2) Å, 99(1)°; phenanthroline: 2.05(4) Å, 82(1)°).[25] All structures show a common motif, with one phenyl ring of the benzyl (or phenylethyl) substituent in a parallel π-stacking arrangement with phenanthroline (angles and distances between least-square planes: 5–15°, 3.0–3.8 Å), while the other is rotated out of a parallel arrangement. The symmetric NMR spectra obtained for all complexes indicate that π-stacked and non-π-stacked rings interchange easily or that in solution a C_{2v}-symmetric arrangement of both substituents is preferred. There are no evident structural reasons which would prevent the π-stacking of the second *N*-substituent. In **1a** and **1d**, slight intermolecular π-stacking between two phenanthroline ligands is observed, but it seems to be a minor structural motif and is absent in the other structures. With the exception of **1c**, N–CH_2–C_{Ph} angles of 114–116° (Table 1) for the non-π-stacked substituent (*e.g.* N1–C12–C6 in **1a**) are comparable to those observed in other *nacnac*^{Bn} metal complexes (Cu:[12] 114–116°, Zr:[26] 115°, Zn:[27] 112–113°). Corresponding angles for the π-stacked substituent (*e.g.* N2–C19–C13 in **1a**) are 3–5° smaller, indicating a bending of the phenyl substituent towards the phenanthroline ligand. Analogously, the phenanthroline ligand is either placed on the bisector of the diketiminate ligand (**1d** and **2a**, Fig. 2) or angled slightly towards the π-stacked *N*-substituent in **1a–c** (Fig. 2). π-Stacking between the benzyl and the phenanthroline substituent seems thus to require a slight deformation of the

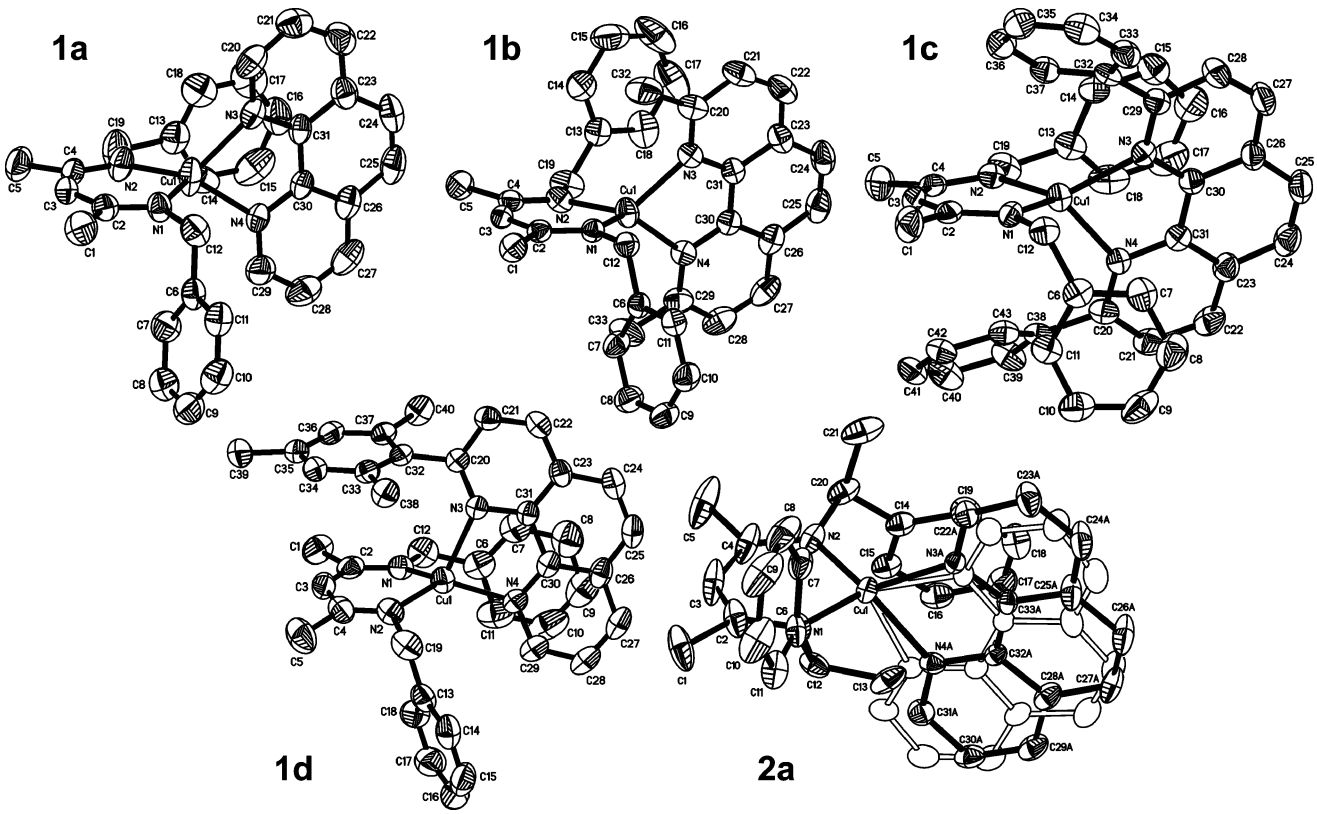


Fig. 1 X-Ray structures of **1a–d** and **2a**. Thermal ellipsoids are drawn at the 50% probability level (30% for **2a**). Hydrogen atoms were omitted for clarity.

Table 1 Selected bond distances [Å] and angles [°] for **1a–d** and **2a**

	1a	1b	1c	1d	2a
Cu–N1/2	1.959(2)/1.981(2)	1.963(4)/1.975(4)	1.961(2)/1.964(2)	1.958(2)/1.965(2)	1.962(2)/1.963(2)
Cu–N3/4	2.148(2)/2.071(2)	2.085(4)/2.092(4)	2.058(2)/2.110(2)	2.194(1)/1.998(2)	2.006(6)–2.204(6)
N1–Cu–N2	99.3(1)	98.3(2)	100.7(1)	101.4(1)	100.8(1)
N3–Cu–N4	78.7(1)	79.8(2)	81.3(1)	82.5(1)	83.4(4)[d]
N–CH_2–$C_{\pi\text{-Ph}}$ [a]	111.0(3)	111.7(4)	113.3(2)	111.0(2)	110.0(2)
N–CH_2–C_{Ph}	115.6(2)	115.1(4)	110.9(2)	113.8(2)	114.8(3)
∠ Ph–phen [b]	5	14	7	10	15
d Ph–phen[c]	3.2–3.5	3.3–3.9	3.1–3.5	3.1–3.6	3.0–3.8

[a] N–C–C angle of the π-stacked Bn substituent. [b] Angle between least-square planes of the π-stacked phenyl ring and the phenanthroline ligand. [c] Distances of the carbon atoms of the π-stacked phenyl ring to the least-square plane of the phenanthroline ligand.

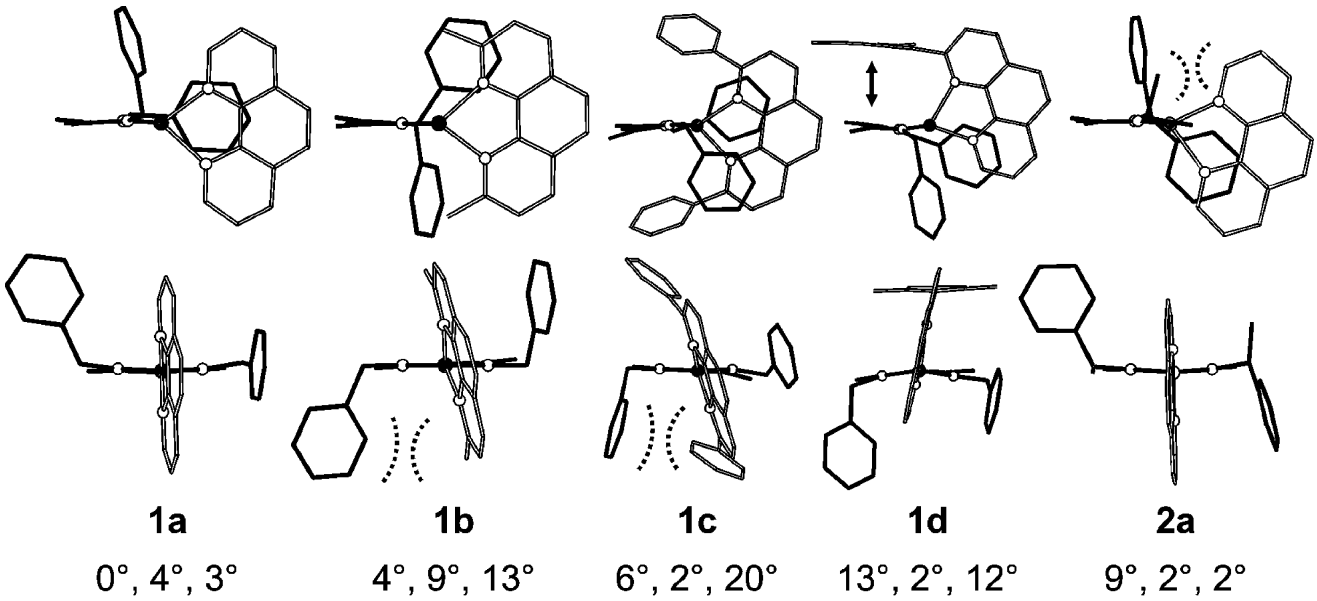


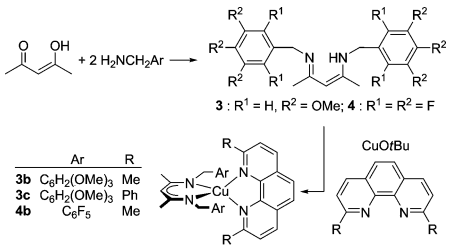
Fig. 2 Rocking (top) and flattening (bottom) distortions in **1a–d** and **2a**. Numbers indicate $\Delta\theta_x$, $\Delta\theta_y$, and $\Delta\theta_z$.

N–C–C_{Ph} angle from its equilibrium position, but appears to be a stabilizing interaction.

Distortions from an ideal geometry can be described using the θ_x, θ_y, and θ_z angles, introduced by White and coworkers.[28] Perfect C_{2v} symmetry yields $\theta_x = \theta_y = \theta_z = 90°$. A rocking distortion of the phenanthroline ligand causes a deviation in θ_x and can be expressed in the form of $\Delta\theta_x = |90° - \theta_x|$ (Fig. 2). Analogously, a flattening of the complex can be expressed by θ_z and $\Delta\theta_z = |90° - \theta_z|$, where θ_z is roughly equivalent to the angle between the mean planes of the ligands. Of the investigated complexes, sterically least encumbered **1a** and **2a** display the most symmetrical coordination. Symmetrical substitution of the phenanthroline ligand in **1b** and **1c** resulted in small rocking distortions, but significant complex flattening of 13° and 20°, respectively. Complex **1d** shows the highest rocking deformation (13°), probably due to attractive π-stacking between the mesityl substituent and the diketiminate ligand. Despite the high flexibility of the benzyl substituents and the unsymmetrical conformation with one π-stacked phenyl ring, the complexes do not deviate significantly from ideal geometry. The dmp-coordinated complex **1b**, for example, shows deviations of $\Delta\theta_{x,y,z} = 4°$, 9° and 13°, while values of $\Delta\theta_{x,y,z} = 0$–12°, 1–16°, and 2–18° were found for the symmetric $[Cu(dmp)_2]^+$ cation with different anions.[28,29]

Copper dmp complexes with different diketiminate ligands

In an attempt to stabilize the planar, π-stacked arrangement of the phenanthroline ligand with both *N*-benzyl substituents depicted in Chart 1, we prepared diketimines **3** and **4** with trimethoxybenzyl or pentafluorobenzyl *N*-substituents, following the protocol established elsewhere (Scheme 2).[12,30] Ligand **3** could be further characterized by an X-ray diffraction study (Fig. 3, ESI†). Ligand **4** was obtained only in purities of 85–90%, which were however sufficient for subsequent reactions.



Scheme 2 Preparation of complexes **1b**, **3c** and **4b**.

Reaction of **3** or **4** with CuO*t*Bu in the presence of the corresponding phenanthroline yielded the respective copper complexes

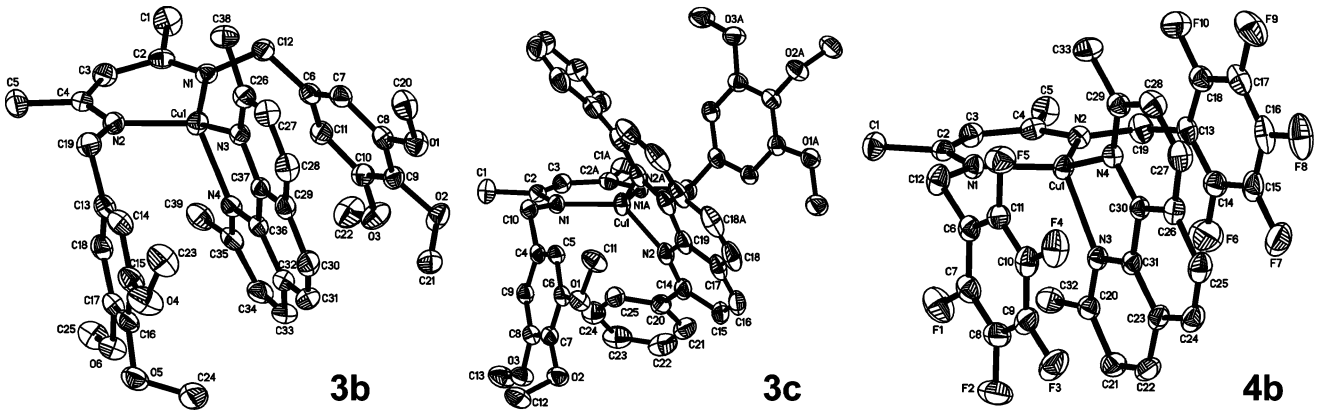


Fig. 3 Crystal structures of **3b**, **3c** and **4b**. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Table 2 Selected bond distances [Å] and angles [°] for **3b**, **3c** and **4b**

	3b	3c	4b
Cu–N1/2	1.948(1)	1.959(1)	1.984(2)
	1.961(1)	1.959(1)	1.982(2)
Cu–N3/4	1.985(1)	2.060(1)	2.148(2)
	2.136(1)	2.060(1)	2.052(2)
N1–Cu–N2	100.3(1)	101.4(1)	99.3(1)
N3–Cu–N4	111.2(1)	82.5(1)	79.6(1)
N–CH_2–C_{Ph}	111.6(1)	112.5(1)	110.6(2)
	113.0(1)		109.9(2)
∠ Ph–phen[a]	13, 20	40	5, 4
d (Ph–phen)[b]	3.4–4.0,	3.4–5.0	3.0–3.3,
	3.0–3.8		3.0 –3.3

[a] Angle between least-square planes of π-stacked phenyl rings and the phenanthroline ligand. [b] Distances of the carbon atoms of π-stacked phenyl rings to the least-square plane of the phenanthroline ligand.

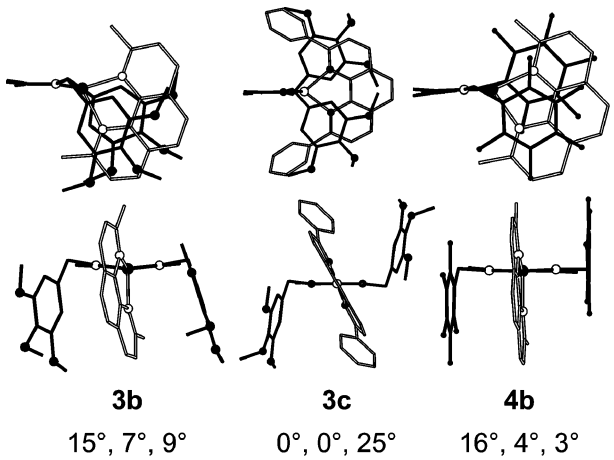


Fig. 4 Rocking (top) and flattening (bottom) distortions in **3b**, **3c** and **4b**. Numbers indicate $\Delta\theta_x$, $\Delta\theta_y$, and $\Delta\theta_z$.

3b, **3c** and **4b** (Scheme 2). Their crystal structures showed indeed more symmetrical conformations (Fig. 3 and 4, Table 2). In **3c**, π-stacking between both benzyl substituents and the dpp ligand is lost. In **3b**, on the other hand, the second phenyl ring is now found in a more planar arrangement with the dmp ligand (Ph–dmp angle: **3b**: 20°, **1b**: 79°). Complex **4b**, carrying perfluorinated benzyl substituents, shows the targeted sandwich-like π-stacking of both phenyl rings, characterized by small angles between the phenyl and phenanthroline planes (4° and 5°) and small distance variations (0.3 Å). Both N–C–C_{Ph} angles are now reduced to 109.9(2)° and 110.6(2)°, respectively, a deformation apparently required for a planar arrangement. The more planar conformation of the second phenyl ring in **3b** compared to **1b** is mirrored by a decrease of $\Delta\theta_z$ (13° in **1b**, 9° in **3b**) and the close planar arrangement of all aromatic rings in **4b** resulted in a very small $\Delta\theta_z$ of 3°. Increased π-stacking thus seems to reduce the flattening distortion in the ground state, while slightly increasing rocking distortions (Fig. 4). Complex **3c**, which is the only compound not showing any intramolecular π-stacking interactions in the solid state, displayed the highest flattening distortion observed for all complexes (25°). Since **3c** crystallized on a crystallographic C_2 axis, rocking and wagging distortions are consequently absent (Fig. 4).

UV/vis spectroscopy

For the sake of comparison, we prepared *nacnac*$^{i\mathrm{Bu}}$Cu(dmp), **5b**, where the benzyl substituents were replaced by sterically comparable isobutyl groups, which, however, cannot undergo π-stacking interactions. UV/vis absorption and emission spectra were recorded in toluene and, for selected complexes, in diethyl ether at room temperature (Table 3). UV/vis absorption spectra of all compounds show two distinct peaks above 350 nm with ε = 1200–12000 $M^{-1}cm^{-1}$ (Fig. 5). One transition is located at λ_{max} = 373–386 nm and appears as a shoulder on more intense π–π* transitions for several complexes (Table 3). A second transition of lower intensity, showing a distinctively asymmetric peak profile, is found at λ_{max} = 600–667 nm. Both transitions are weaker than π–π* transitions located below 350 nm in these compounds and might be associated with charge-transfer transitions. The transition at λ_{max} = 373–386 nm is found at shorter wavelengths than the MLCT in $[CuL_2]^+$ complexes (L = phen,[31,32] dmp,[32–35] dpp:[31–33,36,37] $\lambda_{max}(CH_2Cl_2)$ = 440–460 nm, with occasional shoulders at longer wavelengths around 540–580 nm). Replacing an electron-poor phenanthroline ligand with an anionic, electron-rich diketiminate would not be expected to result in a hypsochromic shift of the metal-phenanthroline CT. *N*-substituent effects also argue against

Table 3 Longest wavelength absorption and luminescence maxima for *nacnac*^{R}Cu(L)

					Toluene, λ_{max}/nm (ε·M cm)		Diethyl ether, λ_{max}/nm (ε·M cm)	
	R	L	$\Delta\theta_z$	π-stacking	Absorption	Emission	Absorption	Emission
1a	Bn	phen	3°	Moderate	382 (4448), 666 (2070)	None		
2a	CH(Me)Ph	phen	2°	Moderate	377sh, 665 (1870)	None		
1b	Bn	dmp	13°	Moderate	375sh, 662 (2460)	820	386 (6247), 646 (3017)	785
3b	$CH_2C_6H_2(OMe)_3$	dmp	9°	Strong	376sh, 656 (1720)	801	385 (7721), 645 (3652)	825
4b	$CH_2C_6F_5$	dmp	3°	Very strong	386 (9560), 605 (5270)	735	384 (13469), 600 (7458)	722
5b	*i*Bu	dmp	n.d.	None	373 (7163), 667 (1830)	822	370 (2836), 661 (1407)	814
1c	Bn	dpp	20°	Moderate	376 (3786), 646 (1429)	805		
3c	$CH_2C_6H_2(OMe)_3$	dpp	25°	None	377sh, 661 (1670)	None		
1d	Bn	phen^{Mes}	12°	Moderate	378sh, 661 (1340)	None		

Emission wavelengths are given for excitation at λ_{max} of the longest wavelength transition.

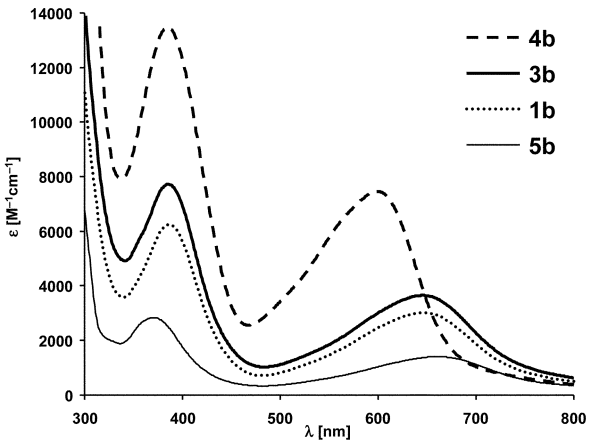


Fig. 5 UV/vis absorption spectra of **1b** and **3b–5b** in diethyl ether at room temperature.

an assignment of the transition around 380 nm as a charge transfer transition towards phenanthroline: in the series **1b–5b**, isobutyl-substituted **5b** displays the highest-energy transition (373 and 370 nm in toluene and diethyl ether, respectively), while **4b**, carrying pentafluorobenzyl substituents, is found at the low-energy end of the observed range (386 and 384 nm). We assign transitions around 380 nm thus to diketiminate-based transitions, not involving a phenanthroline acceptor orbital. In agreement with this, *nacnac*^{Bn}Cu(styrene) and (*nacnac*^{Bn})$_2$Zn show comparable transitions at 349 nm (ε = 2.2 × 10^4 M^{-1}cm^{-1}) and 362 nm (ε = 2.1 × 10^4 M^{-1}cm^{-1}, ESI†). Intense transitions in copper diketiminate complexes around 350 nm have been previously assigned to diketiminate π–π* transitions,[38,39] but relatively low molar absorption coefficients (2800–15000 M^{-1}cm^{-1}), line widths of ≈80 nm at half maximum, and the effect on the *N*-substituent on λ_{max} for **2b–5b** would also be in agreement with a metal to diketiminate CT, normally hidden below π–π* transitions in this region.

Room temperature luminescence in the solid state (λ_{exc} = 514.5 nm) was observed for all complexes, with emission wavelengths of 715–740 nm. Luminescence was weak and short-lived (τ < 60 ns). Overlapping emission peaks from decomposition of the air-sensitive compounds on the surface caused high errors in the determination of λ_{max} and we refrain from reporting λ_{max} values for solid state emission (ESI†).

Luminescence in solution was generally very weak (an exception seems to be **4b**) and again short-lived (τ < 60 ns). While other reasons cannot be excluded, a contributing factor to the low luminescence intensities is certainly the low energy of the emission, which makes non-radiative deactivation pathways more probable. Complexes **1a**, **2a**, **1c** and **1d** were not luminescent in solution. Qualitative luminescence intensity did not seem to correlate with the observed distortions in the solid state: undistorted complexes **1a** and **2a**, carrying an unsubstituted phenanthroline ligand, did not show any luminescence in solution. Analogous to [Cu(phen^{R})$_2$]$^+$, lack of luminescence in **1a** and **2a** might be related to distortions in the excited state rather than to ground-state distortions:[4–8,40] despite their symmetrical structures, both **1a** and **2a** show evidence for easy thermal motions following a rocking distortion mode in their crystal structures.

Luminescence spectra in toluene or diethyl ether solution showed the same general features for all luminescent complexes, which will be discussed in detail for **3b** in diethyl ether. Excitation at different wavelengths across the longest-wavelength transition in **3b** yielded a weak emission peak at 825 nm (Fig. 6). Excitation of the higher-energy transition at 385 nm did not lead to any observable luminescence (Fig. 7), in agreement with its assignment as a diketiminate-based transition, not involving a phenanthroline acceptor orbital.

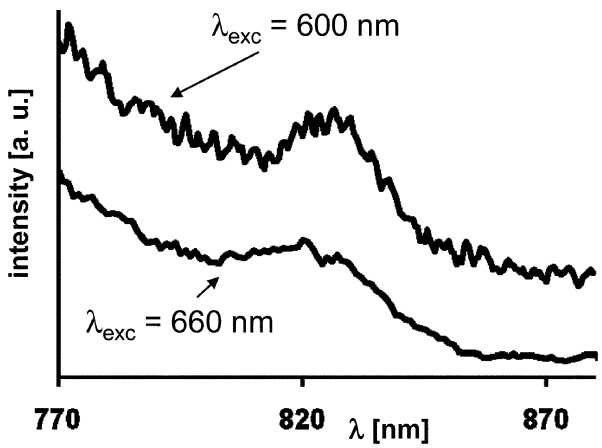


Fig. 6 Emission spectra of **3b** in diethyl ether with λ_{exc} = 600 nm (above) and 660 nm (below).

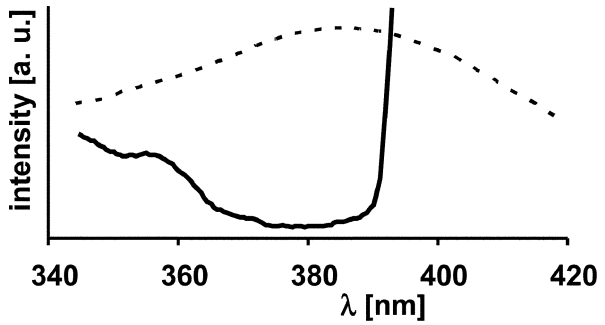


Fig. 7 Absorption spectrum (dashed line) and excitation spectrum (λ_{em} = 825 nm, solid line) of **3b** in diethyl ether. The increase of intensity in the excitation spectrum around 390 nm is due to stray light from the 2λ fraction in the excitation beam.

Based on the results above, the lower-energy transition in the obtained absorption spectra is most likely an MLCT transition to the phenanthroline ligand or a mixture of LLCT and MLCT transitions. Stokes shifts of 129–159 nm in toluene and 122–166 nm in diethyl ether solution are intermediate between those of $[CuL_2]^+$ (250–260 nm in CH_2Cl_2, L = dmp, dpp)[31–37] and those observed in neutral amidophosphine copper complexes (65–110 nm in C_6H_6), for which LLCT transitions have been proposed.[18] Substitution of a phenanthroline in cationic diphenanthroline copper complexes $[CuL_2]^+$ (L = phen, dmp, dpp),[22] which show maxima of the longest wavelength absorption at λ_{max} = 440–460 nm (in CH_2Cl_2),[31–37] with a diketiminate ligand thus led to a significant bathochromic shift of approx. 200 nm. Although reduction of complex symmetry from D_{2d} to D_2 is considered to be responsible for the formation of shoulders around 540–580 nm for bisphenanthroline copper complexes,[41–43] reduction to C_{2v} symmetry does not seem to be the cause for the displacement of the MLCT here. Related C_{2v}-symmetric complexes (acac)Cu(dmp) (acac = acetylacetonate or derivatives), for example, display longest wavelength absorption maxima around 460 nm,[44] very comparable to those of cationic bisphenanthroline complexes. Copper dmp complexes with neutral or anionic diphosphinesulfide ligands also display absorption maxima between 420–460 nm, which were again accompanied by shoulders at longer wavelengths (500–550 nm).[16] The bathochromic shift of the longest wavelength transition is thus most likely due to the electron-donating nature of the *N*-alkyl substituted diketiminate ligand. The high electron-donor characteristics of β-diketiminate ligands have been described previously.[21,45–52] In particular for copper complexes, π back-bonding to ancillary ligands is significantly increased in the presence of *N*-alkyl substituted diketiminate ligands.[12,53,54] A hypsochromic shift in λ_{max} of 60 nm when the isobutyl substituent in **5b** is replaced with pentafluorobenzyl (**4b**) further supports a strong influence of the diketiminate ligand on the position of the absorption maximum.

Complexes **1a–d** and **2a** do not display any correlation of flattening or rocking distortions with λ_{max} in their absorption spectra. The difference in π-stacking interactions observed in the crystal structures of **1b/c**, **3b/c**, and **4b** and its correlation with $\Delta\theta_z$ make it interesting to compare the presence of these interactions with photophysical properties. Some qualitative indications argue that π-stacking of the *N*-benzyl substituent and the phenanthroline ligand might indeed increase luminescence intensity. Thus no luminescence in solution is observed for the dpp complex **3c**, where π-stacking was lost in the crystal structure, while complexes **1c** or **3b**, which show moderate π-stacking interactions, are both luminescent in solution. Complex **4b**, which displays the targeted sandwich-like arrangement of all aryl rings, shows the highest luminescence intensity. However, even for **4b** luminescence is weak and short-lived, and the increased intensity might simply be a result of its high absorption coefficient.

While π-stacking was only shown in the solid state, observed changes in λ_{max} values of absorption spectra of **1b** and **3b**, when the solvent was changed from toluene to diethyl ether, are in agreement with an increase of intramolecular π-stacking in the non-aromatic solvent: the MLCT/LLCT is displaced slightly hypsochromically, the diketiminate-based transition around 380 nm slightly bathochromically, and π–π* transitions of the benzyl substituent, which were present above 350 nm in toluene, are now found below 350 nm. On the other hand, complexes **4b** and **5b** with very strong or no possible π-stacking interactions, respectively, show only minor changes in their absorption maxima between toluene and diethyl ether solution. In comparison to **5b**, ^{13}C NMR spectra of **1b–4b** in benzene-d_6 show a high-field shift of C10A/C10B (C30 and C31 in the crystal structure of **4b**, Fig. 3), which qualitatively correlates with the observed π-stacking and might be attributed to the ring current effect of the π-stacked benzyl substituent. The effect is however minor ($\Delta\delta$ < 2 ppm) and could not be reliably reproduced in diethyl ether/acetone-d_6 mixtures.

Conclusions

Heteroleptic diketiminate copper phenanthroline complexes can be prepared readily through protonation of CuO*t*Bu by diketimines in the presence of the desired phenanthroline ligand. The complexes are stable and show no evidence of undergoing ligand redistribution reactions. Intramolecular π-stacking interactions between the *N*-benzyl substituents and the phenanthroline ligand suppress complex flattening in the ground state and reduced Stokes shifts in solution (compared to copper bisphenanthroline complexes) are indicative of reduced distortions in the excited states. Comparatively sharp luminescence peaks with full-width-at-half-maximum (FWHM) values well below 100 nm (Fig. 6) also support the notion that the investigated complexes do not undergo extensive exited state distortions. For comparison, typical FWHM values for $[Cu(dmp_2]^+$ complexes in solution range from 120–240 nm.[29,32,34]

Luminescence intensities, however, were low and lifetimes were shorter than 60 ns for all complexes, which might be partly due to the low energies of the emission (up to 830 nm). We are currently investigating if luminescence properties can be improved by shifting the emission to shorter wavelengths or by further increasing π-stacking interactions between *N*-substituents and phenanthroline.

Experimental section

All operations, except ligand synthesis, were carried out under nitrogen atmosphere using Schlenk or glove box techniques. Solvents were dried by passage through activated aluminium oxide (MBraun SPS) and de-oxygenated by repeated extraction with nitrogen. C_6D_6 was distilled from Na and de-oxygenated

Table 4 Details of X-ray diffraction studies

	3	1a	2a	1c	1b	1d	3c	3b
Formula	$C_{25}H_{34}N_2O_6$	$C_{31}H_{29}N_4Cu$	$C_{33}H_{33}N_4Cu$	$C_{43}H_{37}N_4Cu$	$C_{33}H_{33}N_4Cu$	$C_{40}H_{39}N_4Cu$	$C_{49}H_{49}N_4O_6Cu$	$C_{39}H_{45}N_4O_6Cu$
Mw (g mol^{-1}); d_c (g cm^{-3})	458.54; 1.291	521.12; 1.342	549.17; 1.317	673.31; 1.312	549.17; 1.328	639.29; 1.292	853.47; 1.377	729.33; 1.361
T/K; F(000)	175; 984	200; 1088	150; 1152	150; 1408	150; 1152	200; 672	150; 1792	150; 1528
Crystal System	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space Group	Pbcn	$P2_1/n$	$P2_12_12_1$	$Pca2_1$	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/c$
Unit Cell: a/Å	14.865(2)	12.9479(5)	11.9865(3)	19.4278(5)	14.3783(7)	10.6782(2)	24.122(2)	15.9441(3)
b/Å	21.753(2)	13.3925(6)	13.2064(4)	9.2147(2)	8.7026(4)	12.4794(2)	14.137(1)	13.4855(3)
c/Å	7.2959(9)	15.6737(6)	17.4969(5)	19.0384(5)	22.2668(10)	12.8421(2)	14.689(1)	16.8628(3)
α (°)	90	90	90	90	90	104.773(1)	90	90
β (°)	90	108.18(2)	90	90	98.534(2)	92.322(1)	124.751(4)	101.081(1)
γ (°)	90	90	90	90	90	94.659(1)	90	90
V/Å^3; Z	2359.2(5)	2578.95(18); 4	2769.73(13); 4	3408(15); 4	2755.4(2); 4	1643.63(5); 2	4115.7; 4	3558.1(1); 4
θ range (°); completeness	3.60–73.39; 0.984	3.88–72.42; 0.994	4.19–72.51; 0.990	4.55–63.67; 0.980	3.11–67.83; 0.991	3.57–68.26; 0.976	3.84–67.85; 0.992	2.82–68.30; 0.998
Refl.: collec./indep.; R_{int}	30741/2347; 0.071	33584/5068; 0.045	36033/4712; 0.044	45919/5514; 0.057	54048/4961; 0.064	20597/5875; 0.032	43433/3707; 0.068	45237/6505; 0.048
μ/mm^{-1}	0.753	1.391	1.321	1.180		1.190	1.207	1.295
R_1(F); wR(F^2); GoF(F^2)^a	0.053; 0.157; 1.06	0.056; 0.155; 1.02	0.038; 0.098; 1.04	0.030; 0.056; 0.89	0.034; 0.96; 1.12	0.039; 0.118; 1.11	0.034; 0.099; 1.07	0.034; 0.103; 1.07
Residual electron density	0.23	0.78	0.29	0.20	0.32	0.23	0.26	0.31

^{a} R1(F) based on observed reflections with $I > 2s(I)$, wR(F^2) and GoF(F^2) based on all data.

by three freeze-pump-thaw cycles. CuO*t*Bu,[55] dpp,[56] monomesityl phenanthroline,[57] **1**,[12,30] **2**,[11,30] *nacnac*$^{i\text{Bu}}$H,[30] *nacnac*$^{\text{Bn}}$Cu(styrene),[12] and *nacnac*$^{\text{CH(Me)Ph}}$Cu(NCMe)[11] were synthesized according literature procedures. Dmp was purchased as the hemihydrate and dried by allowing a solution in dry toluene to stand overnight over activated molecular sieves (4 Å), followed by decantation and evaporation of the solvent. All other chemicals were obtained from commercial suppliers and used as received. Elemental analyses were performed by the Laboratoire d'Analyse Elémentaire (Université de Montréal). NMR spectra were recorded on a Bruker ARX 400 MHz spectrometer and referenced to residual solvent (C_6D_5H: δ 7.15, C_6D_6: δ 128.02, $CHCl_3$: δ 7.26, $CDCl_3$: δ 77.0). NMR coupling constants are provided in Hz. UV/vis spectra were recorded on a Cary 500i UV/vis/NIR spectrometer in dry and oxygen-free diethyl ether or toluene using a sealable UV cell. Emission and excitation spectra in solution were obtained on a Cary Eclipse Fluorescence spectrometer. The luminescence spectra of the solid state samples were measured using a Renishaw 3000 imaging microscope system equipped with a CCD detector. The excitation source was the 514.5 nm line of an Argon ion laser. All measurements were undertaken at ambient temperature.

Nacnac$^{\text{Bn}}$Cu(phen), 1a

A flask was charged with **1** (100 mg, 0.36 mmol), CuO*t*Bu (44 mg, 0.33 mmol) and 1,10-phenanthroline (58 mg, 0.33 mmol). Toluene (15 mL) was added and the mixture was stirred for 1 h to give a dark-blue suspension. The suspension was filtered and the resulting dark blue solution was evaporated to dryness. The residue was washed twice with hexane (6 mL). Residual solvent was removed under vacuum to obtain dark-blue powder (104 mg, 60%). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 8.84 (d, J = 4 Hz, 2H, phen), 7.36 (d, J = 8, 2H, phen), 7.05 (s, 2H, phen), 6.91 (d, J = 6, 4H, Bn), 6.85 (dd, J = 4, 8, 2H, phen), 6.73–6.76 (m, 6H, Bn), 4.83 (s, 1H, CH(C=N)$_2$), 4.53 (s, 4H, Bn CH_2), 2.16 (s, 6H, C(=N)Me).^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 162.5 (C=N), 146.7, 144.1, 142.9, 131.4, 128.6, 128.3, 127.0, 125.8, 125.0, 124.0, 94.3 (*C*H(C=N)$_2$), 57.5 (Bn CH_2), 22.4 (C(=N)*Me*). Anal. Calcd for $C_{31}H_{29}N_4Cu$: C, 71.45; H, 5.61; N, 10.75. Found: C, 70.80; H, 5.74; N, 10.43. X-Ray quality crystals were obtained by slow evaporation of a diethyl ether solution (20 mg, 1 mL).

Nacnac$^{\text{Bn}}$Cu(dmp), 1b

Preparation analogous to **1a** from **1** (100 mg, 0.36 mmol), CuO*t*Bu (49 mg, 0.36 mmol), 2,9-dimethyl-1,10-phenanthroline (84 mg, 0.36 mmol) and ether (10 mL) gave a crude product, which was recrystallised from diethyl ether (5 mL) at –30 °C. Dark-blue plates formed after 1 day (72 mg, 35%). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.48 (d, J = 8 Hz, 2H, dmp 4/7), 7.18 (s, 2H, dmp 5/6), 6.94 (d, J = 8 Hz, 2H, dmp 3/8), 6.65 (d, J = 6 Hz, 4H, Bn), 6.36–6.37 (m, 6H, Bn), 4.78 (s, 1H, CH(C=N)$_2$), 4.38 (s, 4H, Bn CH_2), 2.79 (s, 6H, dmp Me), 2.16 (s, 6H, C(=N)Me).^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 161.7 (C=N), 155.5 (dmp 2/9), 143.5 (*ipso* Bn), 142.6 (dmp 10A/10B), 132.1 (dmp 4/7), 128.2 (*meta* Bn), 126.8 (dmp 4A/6A), 126.7 (*ortho* Bn), 124.9 (*para* Bn), 124.7 (dmp 5/6), 124.2 (dmp 3/8), 94.0 (*C*H(C=N)$_2$), 57.8 (Bn CH_2),

25.7 (dmp Me), 22.4 (C(=N)*Me*). Anal. Calcd for $C_{33}H_{33}N_4Cu$: C, 71.45; H, 5.61; N, 10.75. Found: C, 70.80; H, 5.74; N, 10.43.

Nacnac^{Bn}Cu(dpp), 1c

Preparation analogous to **1a** from **1** (100 mg, 0.36 mmol), CuO*t*Bu (49 mg, 0.36 mmol), 2,9-diphenyl-1,10-phenanthroline (128 mg, 0.36 mmol) and ether (10 mL) afforded a dark-blue solid (143 mg, 59%). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 8.68 (d, $J = 8$, 2H, phen Ph), 7.22–7.65 (m, 16H), 6.45 (d, $J = 4$, 2H), 6.20–6.22 (m, 6H), 4.66 (s, 1H, CH(C=N)$_2$), 3.84 (s, 4H, Bn CH_2), 1.91 (s, 6H, C(=N)Me).^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 161.5 (C=N), 142.9, 140.3, 133.0, 129.9, 129.1, 129.0, 128.6, 128.5, 128.4, 127.8, 127.5, 126.4, 124.6, 124.1, 94.0 (*C*H(C=N)$_2$), 56.8 (Bn *C*H$_2$), 22.9 (C(=N)*Me*). Anal. Calcd for $C_{43}H_{37}N_4Cu$: C, 76.70; H, 5.54; N, 8.32. Found: C, 77.17; H, 5.44; N, 8.24. Crystals suitable for an X-ray diffraction study were obtained by slow evaporation of a diethyl ether solution (20 mg, 1 mL).

Nacnac^{Bn}Cu(monomesityl phenanthroline), 1d

Diketimine **1** (44 mg, 0.16 mmol) and CuO*t*Bu (24 mg, 0.18 mmol) were dissolved in toluene (2 mL) to afford a yellow solution. A solution of 2-mesityl-1,10-phenanthroline (47 mg, 0.16 mmol) in toluene (2 mL) was added drop-wise to give a dark-blue suspension. After stirring for 1 h, the suspension was filtered and the resulting dark blue–green solution was evaporated to dryness. The crude product was dissolved in diethyl ether (3 mL) and kept at −30 °C. Dark-blue crystals (20 mg, 20%) formed after 2 months. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 8.20 (d, $J = 4$, 1H), 7.64 (d, $J = 8$, 1H), 7.32 (d, $J = 8$, 1H), 7.28 (d, $J = 8$, 1H), 6.89–7.19 (m, 12H), 6.59 (dd, $J = 4$, 8, 1H), 4.55 (d, $J = 15$, 2H, Bn CH_2), 4.27 (s, 1H, HC(C=N)$_2$), 3.93 (d, 2H, $J = 15$, Bn CH_2), 2.36 (s, 3H, Mes *p*-CH_3), 2.17 (s, 6H, Mes *o*-CH_3), 1.86 (s, 6H, Me(C=N)$_2$).^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 161.8 (C=N), 158.8, 146.1, 145.0, 144.2, 142.3, 138.4, 137.3, 135.8, 129.9, 129.4, 128.6, 127.4 126.9, 126.8, 125.9, 125.8, 125.6, 125.4, 124.6, 105.4, 94.3 (H*C*(C=N)$_2$), 57.1 (Bn *C*H$_2$), 22.0 (Mes *o*-*C*H$_3$), 21.3 (Mes *p*-*C*H$_3$), 20.6 (*Me*(C=N)$_2$). Anal. Calcd for $C_{40}H_{39}N_4Cu$: C, 75.15; H, 6.15; N, 8.76. Found: C, 74.82; H, 6.12; N, 8.67.

SS-*nacnac*$^{CH(Me)Ph}$Cu(phen), 2a

A flask was charged with *SS*-**2** (100 mg, 330 μmol), CuO*t*Bu (45 mg, 0.33 mmol) and 1,10-phenanthroline (60 mg, 0.33 mmol). Toluene (15 mL) was added and the mixture was stirred to give a dark-blue solution. After stirring for 1 h, the solution was concentrated to 1/5th of its volume and layered with hexane (3 mL). Dark-blue crystals (80 mg, 44%) formed after 3 days. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 8.70 (d, $J = 4$, 2H, phen), 7.36 (d, $J = 8$, 2H, phen), 7.03 (s, 1H, phen), 6.91 (d, $J = 6$, 4H, Ph), 6.85 (dd, $J = 4$, 8, 2H, phen), 6.55–6.57 (m, 6H, Ph), 4.98 (q, $J = 6$, 2H, C*H*(Me)Ph), 4.73 (s, 1H, CH(C=N)$_2$), 2.17 (s, 6H, C(=N)Me), 1.03 (d, $J = 6$, 6H, CH(*Me*)Ph).^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 161.5 (C=N), 149.0, 147.5, 142.6, 132.0, 129.1, 127.3, 127.1, 126.1, 125.1, 124.2, 94.6 (*C*H(C=N)$_2$), 59.0 (*C*HMePh), 24.0 (C(=N)*Me*), 23.2 (CH*Me*Ph). Anal. Calcd for $C_{33}H_{33}N_4Cu$: C, 72.17; H, 6.06; N, 10.20. Found: C, 71.75; H, 6.19; N, 10.24.

N,*N*′-Bis(3,4,5-trimethoxyphenylmethyl)-2-amino-4-imino-pent-2-ene, 3

Acetylacetone (0.4 mL, 4 mmol), *p*-toluenesulfonic acid monohydrate (0.7 g, 4 mmol) and 3,4,5-trimethoxybenzylamine (1.5 g, 7.6 mmol) were suspended in toluene (175 mL) and refluxed under azeotropic removal of water (Dean–Stark apparatus). A white suspension formed immediately, which turned yellow after 6 h and finally became orange after 5 days. The reaction mixture was cooled to room temperature and then transferred to a solution of KOH (0.4 g in 150 mL H_2O). The organic layer was separated and the aqueous phase was extracted with 2 × 100 mL of toluene. The combined organic phases were dried over Na_2SO_4, filtered and evaporated to give a yellow solid. Washing of the yellow solid with MeOH (15 mL) afforded 900 mg (65%) of a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ 6.50 (s, 4H, C$_6H_2$(OMe)$_3$), 4.68 (s, 1H, HC(C=N)$_2$), 4.43 (s, 4H, *CH*$_2$Ar), 3.80 (s, 6H, *p*-C$_6H_2$(O*Me*)$_3$), 3.68 (s, 6H, *m*-C$_6H_2$(O*Me*)$_3$), 1.96 (s, 6H, Me(C=N)$_2$). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 161.3 (C=N), 153.1, 138.8, 136.3, 103.6 (*o*-*C*$_6H_2$(OMe)$_3$), 95.7 (H*C*(C=N)$_2$), 60.7 (*p*-C$_6H_2$(O*Me*)$_3$), 55.7 (*m*-C$_6H_2$(O*Me*)$_3$), 50.8 (*C*H$_2$Ar), 19.6 (*Me*(C=N)$_2$). Anal. Calcd. for $C_{25}H_{34}N_2O_6$: C, 65.48; H, 7.47; N, 6.11. Found C, 65.20; H, 7.48; N, 6.14. X-Ray quality crystals were obtained by slow evaporation of a CH_2Cl_2 solution.

N,*N*′-Bis(C$_6H_2$(OMe)$_3$)-*nacnac*Cu(dmp), 3b

Diketimine **3** (70 mg, 0.15 mmol) and 2,9-dimethyl-1,10-phenanthroline (45 mg, 0.15 mmol) were dissolved in toluene (5 mL) to give a colourless solution. A solution of CuO*t*Bu (26 mg, 0.15 mmol) in toluene 2 (mL) was added, affording a dark-green solution, which was stirred for 1 h, filtered and evaporated to dryness (109 mg, 98%). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.54 (d, $J = 8$, 2H, dmp), 7.20 (s, 2H, dmp 5/6), 7.01 (d, $J = 8$, 2H, dmp), 5.88 (s, 4H, C$_6H_2$(OMe)$_3$), 4.78 (s, 1H, CH(C=N)$_2$), 4.36 (s, 4H, N*CH*$_2$), 3.54 (s, 6H, *para* OMe), 2.96 (s, 12H, *meta* OMe), 2.85 (s, 6H, dmp Me), 2.23 (s, 6H, C(=N)Me).^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 161.3 (C=N), 155.3 (dmp 2/9), 152.7 (*meta* Ar), 142.4 (dmp 10A/10B), 139.1 (Ar), 136.6 (Ar), 132.4 (dmp 4/7), 126.8 (dmp 4A/6A), 125.0 (dmp), 124.3 (dmp), 105.6 (*ortho* Ar), 93.9 (*C*H(C=N)$_2$), 60.1 (*para* OMe), 58.2 (N*C*H$_2$), 55.0 (*meta* OMe), 25.8 (dmp Me), 22.5 (C(=N)*Me*). Anal. Calcd for $C_{39}H_{45}N_4O_6Cu$: C, 64.22; H, 6.22; N, 7.68. Found: C, 64.22; H, 6.17; N, 7.56. X-ray quality crystals were obtained by layering a toluene solution (20 mg, 1 mL) with an equal amount of hexane and keeping the mixture at −30 °C for 3 days.

N,*N*′-Bis(C$_6H_2$(OMe)$_3$)-*nacnac*Cu(dpp), 3c

Preparation analogous to **3b** afforded 118 mg (90%) of **3c**, which contained approximately 15% of dpp. Recrystallisation from toluene–hexane at −30 °C yielded crystalline material, still contaminated however with dpp and elemental analyses were not satisfactory. Hand picking of a suitable crystal allowed an X-ray diffraction study. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 8.86 (d, $J = 8$, 2H, dpp), 7.29–7.75 (m, 12H, dpp), 7.28 (s, 2H, dpp), 5.71 (s, 4H, C$_6H_2$(OMe)$_3$), 4.69 (s, 1H, CH(C=N)$_2$), 3.77 (s, 4H, N*CH*$_2$), 3.34 (s, 6H, *para* OMe), 2.89 (s, 12H, *meta* OMe), 2.85 (s, 6H, dmp Me), 1.98 (s, 6H, C(=N)Me).^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 161.4 (C=N), 154.2 (*meta* Ar), 152.3, 143.4, 139.9, 138.4,

136.4, 133.5, 129.9, 128.6, 128.2, 127.9, 127.5, 126.0, 123.7, 119.8, 111.3 (*o*-$C_6H_2(OMe)_3$), 93.9 ($CH(C{=}N)_2$), 60.0 (*para* OMe), 57.2 (NCH_2), 54.9 (*meta* OMe), 23.0 (C(=N)*Me*).

N,*N*′-Bis(pentafluorophenylmethyl)-2-amino-4-imino-pent-2-ene, 4

To a flask containing pentafluorobenzylamine (310 mg, 1.6 mmol) in toluene (5 mL) were added acetylacetone (80 μL, 0.8 mmol) and HCl (196 μL, 12 M, 2.4 mmol) to give white precipitate. The mixture was refluxed under azeotropic removal of water for 5 days during which the reaction mixture turned yellow. By cooling to room temperature, yellow precipitate formed. The solvent was decanted and KOH solution (1.5 g in 5 mL of water) was added to the solid, followed by toluene (5 mL). After stirring for 15 min, the mixture was separated and the aqueous phase was extracted with toluene (5 mL). The combined organic phases were dried over Na_2SO_4, filtered and evaporated to afford 40 mg (6%) of a beige solid in 85–90% purity. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ 11.08 (bs, 1H, NH), 4.58 (s, 1H, $HC(C{=}N)_2$), 4.44 (s, 4H, $CH_2C_6F_5$), 1.98 (s, 6H, Me$(C{=}N)_2$). ^{13}CNMR ($CDCl_3$, 101 MHz): δ 161.2 (C=N), 145.1 (dm, $^1J_{CF} = 250$, *ortho*), 140.5 (dm, $^1J_{CF} = 250$), 137.5 (dm, $^1J_{CF} = 250$), 113.7 (t, $^2J_{CF} = 2$, *ipso*), 95.9 ($HC(C{=}N)_2$), 37.9 ($CH_2C_6F_5$), 19.3 ($Me(C{=}N)_2$). Three aromatic peaks are missing. ^{19}F NMR ($CDCl_3$, 377 MHz, 298 K) δ –144.9 (dd, $J = 9, 22$), –156.5 (t, $J = 22$), –162.9 (td, $J = 9, 22$). Anal. Calcd for $C_{19}H_{12}N_2F_{10}$: C, 49.79; H, 2.64; N, 6.11. Found: C, 50.58; H, 2.76; N, 6.13. MS ESI-HRMS (hexane) (*m*/*z*): $[M+H]^+$ for $C_{19}H_{12}N_2F_{10}$ calcd. 459.0919; found 459.0915.

N,*N*′-Bis(pentafluorophenylmethyl)-*nacnac*Cu(dmp), 4b

Preparation analogous to **3b** and recrystallisation in diethyl ether at –30 °C afforded black crystals after 1 day (18 mg, 56%). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.56 (d, $J = 8$, 2H, dmp), 7.22 (s, 2H, dmp 5/6), 7.04 (d, $J = 8$, 2H, dmp), 4.73 (s, 1H, $CH(C{=}N)_2$), 4.20 (s, 4H, NCH_2), 2.92 (s, 6H, dmp Me), 2.06 (s, 6H, C(=N)Me).^{19}F NMR (C_6D_6, 377 MHz, 298 K) δ –144.6 (dd, $J = 9, 22$), –160.5 (t, $J = 22$), –165.7 (td, $J = 9, 22$). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 162.7 (C=N), 156.5 (dmp 2/9), 145.0 (dm, $^1J_{CF} = 240$, *ortho* C_6F_5), 141.2 (dmp 10A/10B), 140.4 (dm, $^1J_{CF} = 180$, *para* C_6F_5), 135.9 (dm, $^1J_{CF} = 240$, *meta* C_6F_5), 133.6 (dmp 4/7), 126.3 (dmp 4A/6A), 125.2 (dmp), 124.4 (dmp), 116.0 (t, $^2J_{CF} = 2$, *ipso* C_6F_5), 94.5 ($CH(C{=}N)_2$), 43.7 (CH_2), 25.4 (dmp Me), 22.8 (C(=N)*Me*). Anal. Calcd for $C_{33}H_{23}N_4F_{10}Cu$: C, 54.36; H, 3.18; N, 7.68. Found: C, 54.73; H, 3.53; N, 7.65.

Nacnac$^{i\mathrm{Bu}}$Cu(dmp), 5b

Nacnac$^{i\mathrm{Bu}}$H (60 mg, 0.29 mmol), CuO*t*Bu (39 mg, 0.29 mmol) and 2,9-dimethyl-1,10-phenanthroline (66 mg, 0.29 mmol) were dissolved in diethyl ether (4 mL) to give a dark-green solution. After stirring for 10 min, the solvent was evaporated and the residue was washed with hexane (2 × 2 mL) and dried under vacuum to yield 109 mg (84%) of a dark-blue solid. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.55 (d, $J = 8$, 2H, dmp), 7.17 (s, 2H, dmp 5/6), 7.07 (d, $J = 8$, 2H, dmp), 4.67 (s, 1H, $CH(C{=}N)_2$), 3.12 (m, 4H, NCH_2) 3.08 (s, 6H, dmp Me), 2.16 (s, 6H, C(=N)Me), 1.24 (sp, $J = 7$, 2H, $CHMe_2$), 0.58 (d, $J = 7$, 12H, $CHMe_2$). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 161.1 (C=N), 155.8 (dmp 2/9), 142.6 (dmp 10A/10B), 132.4 (dmp 4/7), 127.8 (dmp 4A/6A), 125.2 (dmp), 124.7(dmp), 93.8 ($CH(C{=}N)_2$), 61.7 (NCH_2), 30.8 ($CHMe_2$), 25.8 (dmp Me), 22.9 (C(=N)*Me*), 20.6 ($CHMe_2$). Anal. Calcd for $C_{27}H_{37}N_4Cu$: C, 67.40; H, 7.75; N, 11.64. Found: C, 67.70; H, 7.96; N, 11.32.

X-Ray diffraction studies

All data sets were recorded on a Bruker SMART 6000 with Montel 200 monochromator, except that of compound **1b** which was collected on a Bruker Microstar-Proteum with Helios optics, both equipped with a rotating anode source for Cu-Kα radiation (λ = 1.54178 nm). Cell refinement and data reduction were performed using APEX2.[58] Absorption corrections were applied using SADABS.[59] Structures were solved by direct methods using SHELXS97 and refined on F^2 by full-matrix least squares using SHELXL97.[60] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined on calculated positions using a riding model. Additional details are provided in Table 4.

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