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A Bifunctional Diketimine Ligand for Secondary Building Blocks: Formation of a 2D Copper–Zinc Coordination Polymer

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Condensation of 3-(aminomethyl)pyridine with acetylacetone in the presence of 2 equiv. of HCl afforded *N*,*N*′-bis(3-pyridylmethyl)-2-amino-4-imino-pent-2-ene, *nacnac*^{CH2Py}H, a diketimine with pendant pyridine donors. Under the same conditions, 2- and 4-(aminomethyl)pyridine afforded the respective 1-(2-pyridyl)- and 1-(4-pyridyl)-2,4-dimethylpyrrol. The heteroleptic complex (*nacnac*^{CH2Py})(*nacnac*^{Bn})Zn was obtained upon reaction of *nacnac*^{CH2Py}H with *nacnac*^{Bn}ZnEt. Combining 2 equiv. of this ligand with $ZnEt_2$ afforded the homoleptic complex *nacnac*$^{CH2Py}{}_2$Zn. The latter forms a 2D coordination polymer upon reaction with $[Cu(NCMe)_4][PF_6]$, which shows short-lived luminescence at ambient temperature. The coordination polymer and complex (*nacnac*^{CH2Py})(*nacnac*^{Bn})Zn were characterised by single-crystal X-ray diffraction.

Introduction

The preparation of secondary building blocks for the construction of metal–organic frameworks[1] or polynuclear complexes[2] requires bifunctional ligands that form geometrically and chemically inert metal complexes with pendant donor substituents for further supramolecular assembly. In the course of our recent investigations into the coordination chemistry of *N*-alkyl-substituted β-diketimine ligands (*nacnac*^{R}), we found that they form (in contrast to their *N*-aryl counterparts) highly symmetric homoleptic bis(diketiminate) complexes *nacnac*$^R{}_2$M with tetrahedral (Zn, Mg)[3,4] or square-planar (Cr)[5,6] geometry. We thus undertook to introduce pendant donor groups into the diketiminate framework and to investigate their potential as secondary building blocks. These ligands would contain a chelating anionic coordination site, which would be responsible for the formation of the geometrically inert building block, and secondary coordination sites, which allow the extension of the building block into defined or infinite polynuclear assemblies (Figure 1).

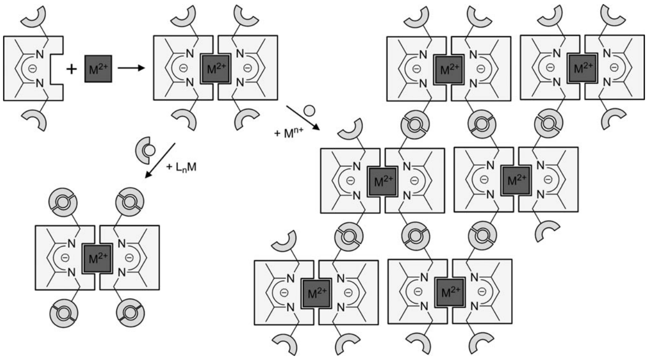

Figure 1. Bis(diketiminate) complexes as secondary building blocks.

Here we report the preparation of *nacnac*$^{CH2Py}{}_2$Zn and its coordination polymer with Cu^I. Coordination polymers or metal–organic frameworks have attracted interest as solid-state materials for luminescence applications.[7] While luminescent coordination polymers have been reported with zinc(II) (mostly LMCT transitions) or copper(I) (mostly MLCT transitions) as central metals, there are few reports of luminescent coordination polymers that combine both metals.[8]

Results and Discussion

Ligand and Complex Synthesis

N-Alkyl-substituted β-diketimines can be prepared by simple condensation of acetylacetone with 2 equiv. of amine in the presence of 1 equiv. of acid (HCl or TsOH) and azeotropic removal of water.[9] Reaction of 3-(aminomethyl)pyridine with acetylacetone under these conditions afforded, however, only the monocondensation product *acnac*^{CH2Py} (Scheme 1), which was identified by independent synthesis. In the presence of 2 equiv. of HCl, ligand **1** could be prepared in 40–55% yield. Further increase of the acid concen-

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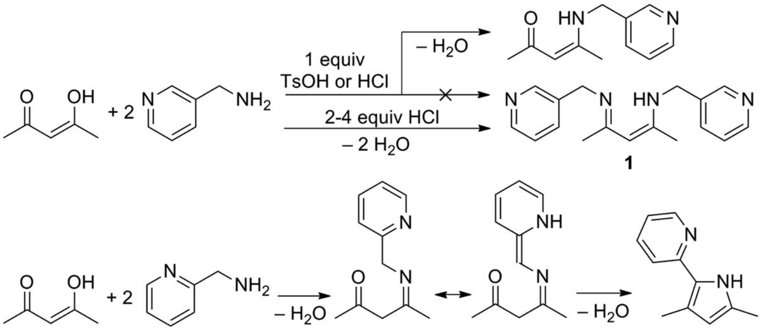
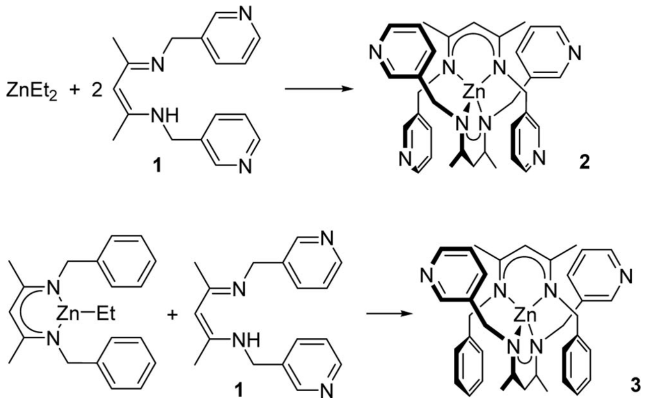


Scheme 1.

tration did not affect the reaction outcome. When 2- and 4-(aminomethyl)pyridine are reacted under the same conditions, 1-(2-pyridyl)- and 1-(4-pyridyl)-2,4-dimethylpyrrol, respectively, were obtained, most likely due to the more accessible enimine tautomer in those compounds (Scheme 1). Preparation of pyrrols from acetylacetone and 2- or 4-(aminomethyl)pyridine has been reported before, albeit under slightly more forcing conditions.[10]

Reaction of 2 equiv. of **1** with diethylzinc generated the homoleptic complex *nacnac*$^{\mathrm{CH2Py}}{}_2$Zn (**2**) (Scheme 2). A heteroleptic complex could be obtained by stepwise reaction, and addition of **1** to *nacnac*$^{\mathrm{Bn}}$ZnEt afforded (*nacnac*$^{\mathrm{CH2Py}}$)(*nacnac*$^{\mathrm{Bn}}$)Zn, **3**. Compounds **1** and **2** were obtained in high yields as slightly coloured oils, which show no or only very minor impurities in ^{1}H NMR, and could be further purified by crystallisation if desired. In crystalline form **2** could be handled in air for short times. Complex **3** did not show any signs of decomposition after heating to reflux in C_6D_6 for several hours. Only one singlet is observed for the CH_2 group in ^{1}H NMR spectra of **2** and two singlets for the CH_2Py and CH_2Ph groups in **3**, indicating that rotations around the N–CH_2 and CH_2–Ar bonds are fast on the NMR time scale.



Scheme 2.

To test for the ability of **2** to act as a secondary building block, we investigated its reactions with metal complexes containing labile ligands. Reaction of **2** with $PdCl_2(NCPh)_2$ in various ratios, concentrations and temperatures consistently yielded brown precipitates, most likely a coordination polymer containing *trans*-Py_2PdCl_2 units. We were, however, unable to obtain X-ray quality crystals from these reactions. On the other hand, slow diffusion of $[Cu(NCMe)_4][PF_6]$ in acetonitrile into a solution of **2** in toluene cleanly afforded yellow crystals of the heterometallic coordination polymer $[\mathbf{2}\mathrm{Cu}]_n[\mathrm{PF}_6]_n$ (**4**).

Crystal Structures

Apart from minor differences in unit cell parameters and torsion angles, the crystal structure of **3** (Figure 2, Table 1) is isostructural to that of the homoleptic complex *nac-*

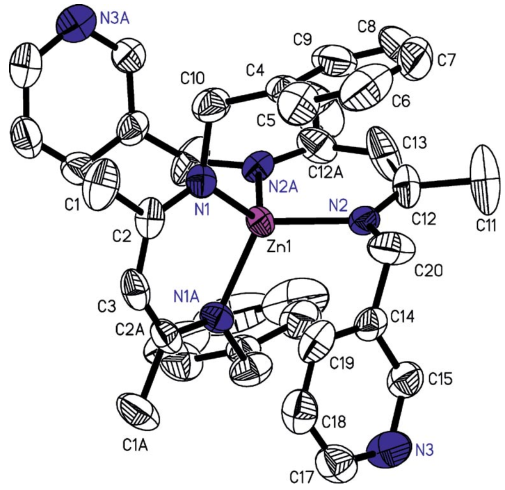


Figure 2. X-ray structure of **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Bond lengths [Å] and angles [°] in the X-ray structures of complex **3** and coordination polymer **4**.

	3	4	*nacnac*$^{\mathrm{Bn}}{}_2$Zn[3]
Zn1–N	1.988(2), 1.991(2)	1.982(2)–1.991(2)	1.983(1), 1.989(1)
Cu1–N		2.048(2)–2.136(2)	
N–Zn1–N[a]	97.71(11), 98.49(11)	97.54(7), 97.91(7)	97.93(7), 98.27(7)
N–Cu1–N		97.25(7)–135.22(8)	
nacnac-nacnac[b]	89	89	89
nacnac-Ph[c]	71, 73	66–74	69, 88

[a] Diketiminate bite angle. [b] Angle between the mean planes of diketiminate ligands. [c] Angles between the mean planes of Ph substituents and the respective diketiminate ligand.

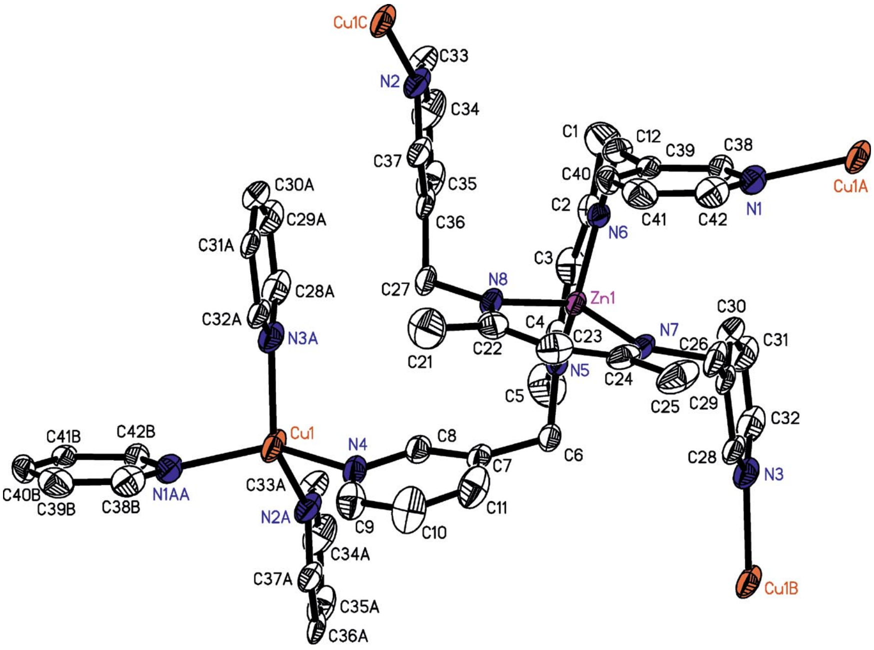


Figure 3. Repeating unit of coordination polymer **4** (pyridyl ligands at Cu1 and Cu1A-Cu1C added for clarity). Hydrogen atoms and the anion were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Colour coding: N: blue, Cu: brown, Zn: magenta.

nac$^{Bn}{}_2$Zn.[3] As in *nacnac*$^{Bn}{}_2$Zn, the molecule is located on a crystallographic C_2 axis and CH–π interactions between CH_2 and phenyl groups (2.8 Å) stabilise a regular geometry close to S_4 symmetry. Given the absence of inter- or intramolecular hydrogen bonding involving the pyridyl nitrogen, this structural similarity is not surprising. Indeed, from the structural data we cannot exclude that the nitrogen position might be disordered between N3 and C8.

In the coordination polymer **4** (Figure 3, Table 1), the coordination geometry around the Zn atom remains close to S_4 symmetry. Zn–N distances [1.982(2)–1.991(2) Å] are identical to those in *nacnac*$^{Bn}{}_2$Zn[3] and **3** (Table 1). The copper(I) centre has a distorted tetrahedral coordination geometry with N–Cu–N angles ranging from 97° to 135°. Cu–N distances (Table 1) are comparable to those in other $[CuPy^R{}_4]^+$ cations (1.99–2.11 Å).[11,12]

Each *nacnac*$_2$Zn unit is connected to four different copper centres. The pyridyl rings are perpendicular to the mean plane of the diketiminate ligand and thus form ladder-like one-dimensional chains of copper and zinc centres (Figure 4). Those are interconnected by the same type of chains formed by the remaining diketiminate ligands, resulting in a two-dimensional grid of alternating copper and zinc centres. The 2D coordination polymers are stacked along the crystallographic *c*-axis in alternation with the $[PF_6]^-$ anions (Figure 5). Steric constraints introduced by the formation of the two-dimensional network exclusively affect the $CuPy_4$ fragment, which displays two N–Cu–N angles widened to 130° and 135° and a bending of the Cu–N bonds of 7–14° out of the mean planes of the pyridine li-

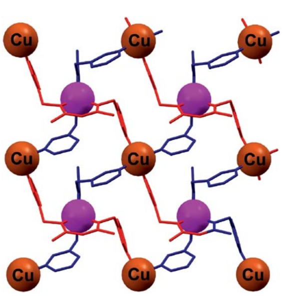


Figure 4. Grid-like structure formed by alternating zinc (magenta) and copper atoms (brown) in the crystallographic *a*,*b*-plane. The two interconnected 1D coordination polymers formed by the diketimine ligands are indicated in red and blue, respectively.

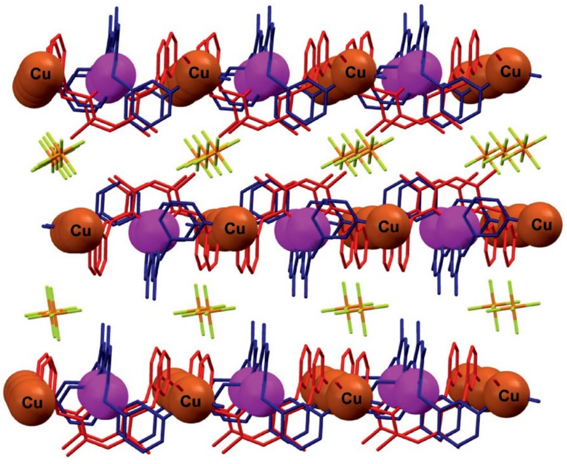


Figure 5. Stacking of the 2D Zn–Cu coordination polymers along the *c*-axis. Zn: magenta spheres, Cu: brown spheres, F: green, P: orange. Atoms in red and blue indicate the two interconnected 1D coordination polymers (see Figure 4).

gands. The *nacnac*$_2$Zn fragment, on the other hand, displays a coordination geometry essentially identical to that of *nacnac*$^{Bn}{}_2$Zn[3] and **3**, serving as desired as a geometrically inert building block. Use of metalloligands in the construction of metal–organic frameworks is a subject of continuing interest,[13,14] and the use of *N*-alkyl-functionalised diketiminate ligands in the secondary building block **4** presents a more easily accessible and more readily adaptable alternative to back-bone-functionalised acetylacetonates used for this purpose.[15–21]

Luminescence

Coordination polymer **4** is luminescent in the solid state at room temperature with an intense and broad emission band centred at 670 nm (full width at half maximum = 200 nm). The emission is short-lived and excited-state lifetimes are shorter than 30 ns (instrumental limit). Emission from **4** in the solid state occurs at significantly lower energy than that reported for $[CuPy_4]^+$ cations (525 nm)[22] or for other coordination polymers based on $[CuPy^R{}_4]$-units (540 nm).[23] The zinc complex **2**, on the other hand, shows a weak absorption band (λ_{max} = 510 nm) in toluene solution, the excitation of which leads to a weak emission band at 550 nm. In the solid state **2** shows emission around 615 nm. We thus assign the emission in **4** to be centred on the zinc bis(diketiminate) fragment, while the Cu cation acts only as a structural element.

Conclusions

Incorporation of pendant donor groups into *N*-alkyl-substituted diketiminate complexes afforded geometrically stable zinc complexes that are suitable for application as secondary building blocks. Coordination of **2** to four different metal centres in **4** indicates that their chemistry might be further extended to polynuclear complexes.

Experimental Section

General: All reactions, except ligand synthesis, were carried out under nitrogen 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 by three freeze–pump–thaw cycles. *Nacnac*^{Bn}ZnEt was prepared according to literature procedures.[3] All other chemicals were obtained from commercial suppliers and used as received. Elemental analyses were performed by the Laboratoire d'Analyse Élémentaire (Université de Montréal). NMR spectra were recorded with a Bruker DRX 400 MHz spectrometer and referenced to residual solvent (C_6D_6, ^{1}H: δ = 7.15, ^{13}C: δ = 128.02. $CDCl_3$, ^{1}H: δ = 7.26, ^{13}C: δ = 77.0 ppm). Emission spectra in solution were obtained with a Cary Eclipse Fluorescence spectrometer. The luminescence spectrum of **4** in the solid state was measured using a Renishaw "inVia" Raman microscope system equipped with a CCD detector at ambient temperature. The excitation source was the 488 nm line of an Argon ion laser. Samples were prepared under nujol in the glove box.

2-[(3-Pyridylmethyl)amino]-4-[(3-pyridylmethyl)imino]pent-2-ene (1): A mixture of acetylacetone (5.0 g, 50 mmol) and concentrated hydrochloric acid (12 M, 16.6 mL, 0.20 mol) in toluene (50 mL) was stirred for 10 min, resulting in a pale yellow solution. 3-(Aminomethyl)pyridine (10.8 g, 0.10 mol) was added slowly under agitation (exothermic), the mixture stirred for another 10 min and finally refluxed with a Dean–Stark apparatus for azeotropic water removal for 2 d. After cooling to room temperature a brown precipitate appeared. Toluene was discarded by decantation and the obtained solid treated with excess aqueous KOH. The aqueous phase was extracted with toluene until the organic phase remained colourless. The combined organic phases were dried with Na_2SO_4 and the solvent evaporated to yield **1** as a brown oil of sufficient purity for subsequent reactions (12.2 g, 43%). An analytically pure sample was obtained by recrystallisation from toluene at –30 °C to yield orange crystals. ^{1}H NMR ($CDCl_3$): δ = 11.36 (s, 1 H, NH), 8.49 (br. s, 4 H, Py C2, C6), 7.47 (d, J = 7.5 Hz, 2 H, Py C4), 7.14 (m, 2 H, Py C5), 4.68 [s, 1 H, HC(C=N)$_2$], 4.44 (s, 4 H, CH_2), 1.96 (s, 6 H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 161.4 (*C*=N), 148.8 (Py C2/C6), 148.0 (Py C2/C6), 135.9 (Py C3/C4), 134.8 (Py C3/C4), 123.3 (Py C5), 95.5 [H*C*(C=N)$_2$], 48.0 (CH_2), 19.6 (Me) ppm. $C_{17}H_{20}N_4$ (280.37): calcd. C 72.83, H 7.19, N 19.98; found C 72.71, H 7.57, N 19.76.

2-[(3-Pyridylmethyl)amino]pent-2-en-4-one (*acnac*^{CH2Py}H): A solution of acetylacetone (0.5 g, 5 mmol) and 3-(aminomethyl)pyridine (0.54 g, 5 mmol) in toluene (5 mL) was stirred for 24 h. The yellow oil formed was isolated by decantation and dried under vacuum (0.89 g, 94%, >90% purity according to NMR). An analytically pure sample was obtained by recrystallisation from toluene at –25 °C. ^{1}H NMR ($CDCl_3$): δ = 11.02 (s, 1 H, NH), 8.39 (br. s, 2 H, Py C2, C6), 7.47 (d, J = 8 Hz, 1 H, Py C4), 7.15 (m, 1 H, Py C5), 4.94 [s, 1 H, HC(C=N)(C=O)], 4.34 (d, J = 6 Hz, 2 H, CH_2), 1.89 (s, 3 H, Me), 1.79 (s, 3 H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 195.3 (C=O), 162.2 (C=N), 148.6 (Py C2/C6), 148.1 (Py C2/C6), 134.0 (Py C3/4), 133.3 (Py C3/4), 123.3 (Py C5), 96.0 (CH), 43.8 (CH_2), 28.6 (Me), 18.5 (Me) ppm. $C_{11}H_{14}N_{20}$ (426.37): calcd. C 69.45, N 14.72, H 7.42; found C 69.07, N 14.88, H 7.42.

***nacnac*$^{CH2Py}{}_2$Zn (2):** To zinc diethyl (92 µL, 0.9 mmol) in toluene (0.5 mL) was added a solution of **1** (487 mg, 1.7 mmol) in toluene (1 mL). Ethane evolution was observed and the solution stirred for 30 min at ambient temperature. Evaporation of toluene afforded **2** as a brown oil (0.51 g, 94%). Purity according to NMR: >5%. Recrystallisation by diffusion of hexane into a toluene solution of **2** afforded dark-yellow microcrystals. ^{1}H NMR (C_6D_6): δ = 8.45 (br. s, 4 H, Py C2), 8.36 (d, J = 4 Hz, 4 H, Py C6), 6.97 (d, J = 7.5 Hz, 4 H, Py C4), 6.59 (m, Py C5), 4.31 [s, 2 H, HC(C=N)$_2$], 3.77 (s, 8 H, CH_2), 1.61 (s, 12 H, Me) ppm. ^{13}C NMR (C_6D_6): δ = 168.1 (C=N), 150.1 (Py C2/6), 148.6 (Py C2/6), 136.4 (Py C3/4), 134.7 (Py C3/4), 123.2 (Py C5), 94.9 [H*C*(C=N)$_2$], 52.0 (CH_2), 22.4 (Me) ppm. $C_{34}H_{38}N_8Zn$ (624.11): calcd. C 65.43, N 17.95, H 6.14; found C 65.43, N 17.56, H 6.61.

(*nacnac*^{CH2Py})(*nacnac*^{Bn})Zn (3): To a solution of *nacnac*^{Bn}ZnEt (0.44 g, 1.2 mmol) in toluene (1 mL) was added a solution of **1** (0.33 g, 1.2 mmol) in toluene (1 mL). The mixture was heated to 60 °C for 1 h. The solvent was evaporated, the resulting yellow oil was re-dissolved in a minimum of toluene and crystallised at –30 °C by slow diffusion of hexane into this solution to yield **3** in the form of orange crystals (40%). ^{1}H NMR (C_6D_6): δ = 8.53 (s, 2 H, Py C2), 8.40 (d, J = 4 Hz, 2 H, Py C6), 6.90–7.15 (m, 12 H, Py C4, Ph), 6.63 (m, 2 H, Py C5), 4.40 (s, 1 H, CH), 4.34 (s, 1 H, CH), 4.04 (s, 4 H, CH_2), 3.88 (s, 4 H, CH_2), 1.73 (s, 6 H, Me), 1.59 (s, 6 H, Me) ppm. ^{13}C NMR (C_6D_6): δ = 167.8 (C=N), 167.7 (C=N), 149.8 (Py C2/6), 148.1 (Py C2/6), 141.5 (ipso Ph), 136.6 (Py C3/4), 134.3 (Py C3/4), 127.4 (Ph), 126.5 (Ph), 122.8 (Py C5), 105.8 (Ph), 94.4 (CH), 94.3 (CH), 54.1 (CH_2Ph), 51.7 (CH_2Py), 22.0 (Me), 21.0 (Me) ppm. $C_{36}H_{40}N_6Zn$ (622.11): calcd. C 69.50, N 13.51, H 6.48; found C 69.25, N 13.08, H 6.58.

[(*nacnac*$^{\mathbf{CH2Py}}$$_{\mathbf{2}}$Zn)Cu]$_n$[PF$_6$]$_n$ (4): With care, the following phases were layered in a Schlenk flask: (i) **2** (0.30 g, 0.4 mmol) in toluene (2 mL), (ii) toluene (1 mL), (iii) acetonitrile (1 mL), and (iv) $[Cu(NCMe)_4][PF_6]$ (0.163 g, 0.4 mmol) in acetonitrile (2 mL). After 36 h yellow crystals formed at the interface. $C_{34}H_{38}CuF_6N_8PZn$ (832.60): calcd. C 49.05, H 4.60, N 13.46; found C 48.64, H 3.81, N 13.10.

X-ray Diffraction Studies: All data sets were recorded on a Bruker SMART 6000 diffractometer with optics, equipped with a rotating anode source for Cu-K_α radiation (λ = 1.54178 Å). Cell refinement and data reduction were performed using APEX2.[24] Absorption corrections were applied using SADABS.[25] Structures were solved by direct methods using SHELXS97 and refined on F^2 by full-matrix least-squares using SHELXL97.[26] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined on calculated positions using a riding model.

Comparison of thermal parameters and analysis of the electron density map did not reveal any indication for the position of the nitrogen atom in **3**. Slightly shorter bond lengths in the aromatic cycle (1.36 vs. 1.38 Å) indicated that the nitrogen is most likely located at N3 or C8 and it was finally assigned to N3 due to slightly better agreement factors in this position. Given the absence of any intermolecular hydrogen bonding and the overall symmetry of the structure, it is possible that the nitrogen might be disordered at least over the positions N3 and C8, if not over all four possible positions. For further details see Table 2 and Supporting Information.

Table 2. Details of X-ray structure studies.

	3	**4**
Formula	$C_{36}H_{40}N_6Zn$	$C_{34}H_{38}CuN_8Zn{\cdot}PF_6$
Mw [g mol^{-1}]; $d_{calcd.}$ [g cm^{-3}]	622.11; 1.304	832.60; 1.552
T [K]; F(000)	200; 1312	200; 852
Crystal system	monoclinic	triclinic
Space group	$C2/c$	$P\bar{1}$
a [Å]	14.7946(4)	9.4348(2)
b [Å]	15.2285(4)	9.7075(2)
c [Å]	14.0689(4)	19.9335(5)
α [°]	90	77.795(1)
β [°]	90.739(2)	87.103(1)
γ [°]	90	88.567(1)
V [Å^3]; Z	3169.45(15); 4	1781.94(7); 2
θ range [°]; completeness	4.2–72.1; 0.99	2.2–72.1; 0.96
Collected refl.; R_{sigma}	20757; 0.019	23586; 0.026
Independent refl.; R_{int}	3105; 0.069	6770; 0.035
μ [mm^{-1}]	1.337	2.592
$I > 2\sigma(I)$: $R_1(F)$; $wR(F^2)$	0.056; 0.145	0.037; 0.105
All data: $R_1(F)$; $wR(F^2)$; GoF(F^2)	0.056; 0.145; 1.050	0.042; 0.108; 1.062
Residual electron density	0.40, –0.77	0.42, –0.50

CCDC-796290 (for **3**) and -796291 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Emission spectrum of **4**, absorption and emission spectrum of **3**, details of the X-ray diffraction studies (CIF).

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