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Copper(II)-Hydroxide Facilitated C–C Bond Formation: Carboxamido Pyridine System versus Methylimino Pyridine System

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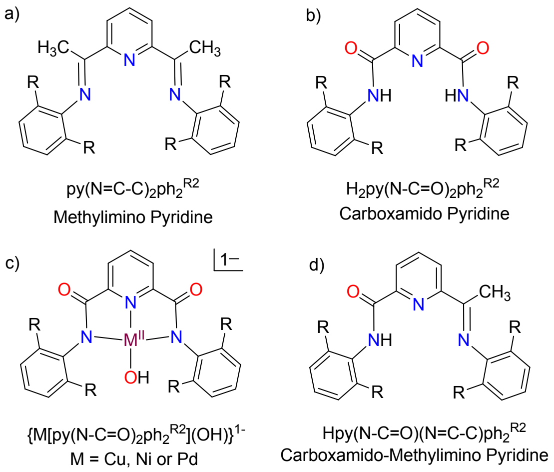
A copper(II)-hydroxide induced carbon–carbon bond formation reaction is explored with the synthesis of asymmetric carboxamido−methylimino pyridine Cu(I) complex of $[Cu^{I}(py(N-C=O)(N=C-C)ph_2^{Me2})_2]^-$ (**12**). Two imine-methyl groups are coupled to form a bridged C−C bond (N=C−C−*C*−*C*=*N*) at the methyl positions with the reduction of two Cu^{2+} center ions to Cu^+. The reaction is checked with three dicarboxamido pyridine $[Cu^{II}-OH]$ complexes, with which dinuclear Cu(I) complexes of $[Cu_2(py(N-C=O)_2ph_2^{R2})_2]^{2-}$ (R = methyl (**3**), methyl & allyl (**6**)) and trinuclear $[Cu^{II}\text{-}Cu^{I}\text{-}Cu^{II}]$ complex of $[Cu_3(\subset_{20}\text{-}py(N-C=O)_2ph_2dien^{Me3})_2]^+$ (**9**) are obtained. The reactivities of $[Cu^{II}-L]$ (L = DMF, OH^-) complexes in dicarboxamido pyridine, carboxamido−methylimino pyridine and dimethylimino pyridine systems are discussed in terms of electron delocalization properties of ligands. A cooperative metal−ligand (Cu^{2+} and enamide ligand) interaction is proposed based on the characterization of ligated Cu(II) intermediates with the techniques of X-ray crystallography, UV-Vis spectroscopy, cyclic voltammogram, EPR spectroscopy and DFT calculations.

Introduction

Transition metal-catalyzed C–C bond formation reactions are of great importance for the synthesis of natural products,[1] bioactive molecules,[2] and organic functional materials.[3] The interests in the development of new catalysts for functional group transformation keep growing,[4] and a desire for more selective and efficient method to prepare organic substances has driven efforts to make soluble catalysts for homogeneous catalysis. Meanwhile, the reactivity and selectivity of catalysts have been found widely influenced by the choice of the central metal, and most efficient catalysts are related to the precious metals such as palladium,[5] iridium,[6] platinum[7] and gold,[8] which often perform two electron oxidation-reduction to promote bond cleavage and bond formation reactions.

Base metals are often more earth-abundant and far less expensive for use in manufacturing services than precious metals. In general, base metals prefer one electron redox changes and pose challenges for controlling reactivity and/or providing unique reaction pattern.[9] The interplay of base metals and their surrounding ligands must be considered for the design of more potent catalysts with improved reaction scope.[10] Thus, the metal and the ligand can cooperate in a synergistic manner to have more energetically accessible levels for catalysis. Copper compounds are well established catalysts for various oxidation and reduction reactions.[2a,11] Ligand promoted and Cu-catalyzed coupling reactions have been described to have accelerating effect on these reactions.[12] Questions come from the understanding of the nature of catalytically active compounds, and further studies aim at exploring the particular metal-ligand interaction system which can be tuned to specific needs.

The steric and electronic properties of ligands are used to control the catalytic performance of active species. Pincer ligands have long been recognized in coordination chemistry because of the constraints of orbital symmetry and their distinctive properties in controlling of coordination sphere.[13] A



a) $py(N=C-C)_2ph_2^{R2}$ Methylimino Pyridine

b) $H_2py(N-C=O)_2ph_2^{R2}$ Carboxamido Pyridine

c) $\{M[py(N-C=O)_2ph_2^{R2}](OH)\}^{1-}$ M = Cu, Ni or Pd

d) $Hpy(N-C=O)(N=C-C)ph_2^{R2}$ Carboxamido-Methylimino Pyridine

Fig. 1 Structures and abbreviations of *NNN*-pincer ligands and complexes.

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number of pincer complexes show relatively excellent thermal stability which is particularly important for homogeneous catalysis at high temperature.[14] Much of work is derived from the first-row transition metal complexes, which are coordinated with various bis(imino)pyridine *NNN*-pincer ligands $py(N{=}C{-}C)_2ph_2^{R2}$ ($py(N{=}C{-}C)_2ph_2^{R2}$ = *N,N*′-bis(2,6-disubstitutedphenyl)-2,6-di(methylimine)pyridine, Fig. 1a). These ligands can be used as reservoirs of electrons for bond-making reactions involving oxidation/reduction of the ligand to tune the electronic properties.[10a,15] In contrast, the bis(arylcarboxamide)pyridine *NNN*-pincer ligands $H_2py(N{-}C{=}O)_2ph_2^{R2}$ ($H_2py(N{-}C{=}O)_2ph_2^{R2}$ = *N,N*′-bis(2,6-disubstitutedphenyl)-2,6-dicarboxamidepyridine, Fig. 1b) have less redox activity and their coordinated transition metal compounds were mostly presented in higher valence states such as divalence[16] and trivalence.[17] Cooperative activation of substrates by the metal complexes of bis(arylcarboxamide)pyridine ligands was much in relation to the fourth coordination donor, for example, the terminal hydroxo group in the complexes of $[M(py(N{-}C{=}O)_2ph_2^{R2})(OH)]^{1-}$ (M = Cu or Ni) (Fig. 1c),[18-23] where the hydroxide showed remarkable nucleophilic reactivity on the activation of carbon dioxide,[18] dihydroanthracene,[19] tetrahydrofuran,[20] phenols,[21] 2-phenylpropionaldehyde[22] and organonitriles.[23] The highly basic nature of the dianionic ligand $[py(N{-}C{=}O)_2ph_2^{R2}]^{2-}$ would be the other contributing factor for this reactivity. Metal, ligand and the hydroxo group worked in a collaborative manner to facilitate the chemical transformations.

To our knowledge, the reduction behavior of transition metal *NNN*-pincer complexes $[M(py(N{-}C{=}O)_2ph_2^{R2})(OH)]^{1-}$ (M = Cu or Ni) was rarely studied, and the activating abilities of metals in the bis(carboxamide)pyridine ligand system have not been investigated. As part of ongoing study of this basic ligand system, we report here a C–C bond coupling reaction facilitated by the *NNN*-pincer [Cu^{II}-OH] intermediate $[Cu(py(N{-}C{=}O)(N{=}C{-}C)ph_2^{Me2})(OH)]^{1-}$ **11a** ($Hpy(N{-}C{=}O)(N{=}C{-}C)ph_2^{Me2}$ = 6-acetyl-*N,N*′-(2,6-dimethylphenyl)-picolinamide, Fig. 2d), involving hydroxide-ligand induced reduction of central Cu(II) to Cu(I) and the extent of metal to ligand electron transfer. As a result, two coordinated ligands are coupled to generate a new C–C bond at the enamide positions forming a bridged bis(arylimino)pyridine ligand.

Results and Discussion

The deprotonation of the *NNN*-pincer ligand $H_2py(N{-}C{=}O)_2ph_2^{Me2}$ with two equivalents of Et_4NOH in the presence of $Cu(OTf)_2$ in DMF affords the solvent ligated

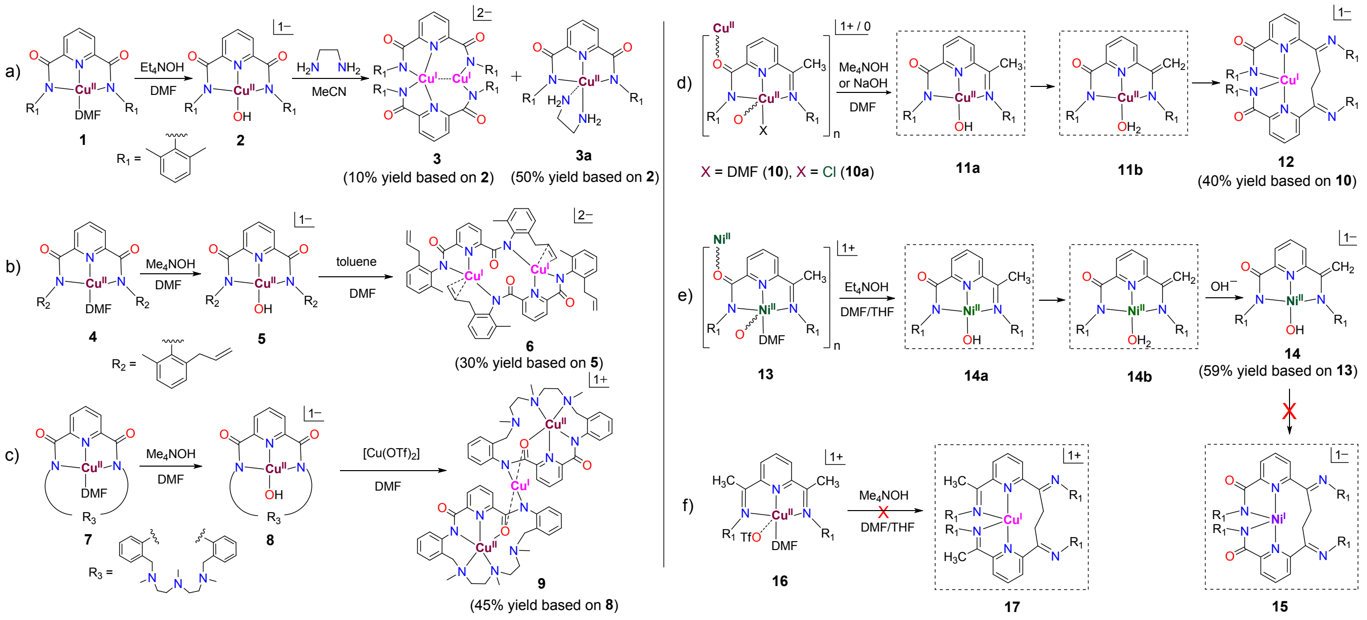

Fig. 2 The examination of *NNN*-pincer complexes Cu(II) to Cu(I) *via* [Cu^{II}–OH] intermediates: a) The generation of *NNN*-pincer Cu(I) by mixing of [Cu^{II}–OH] complex and ethylenediamine; b) The investigation of the transformation of Cu(II) to Cu(I) without the presence of ethylenediamine; c) The investigation of the reduction of free Cu^{2+} to Cu^{+} by [Cu^{II}–OH] complex; d) The exploration of the C-C bond formation of carboxamido–methylimino pyridine ligand *via* [Cu^{II}–OH] intermediate; e) The exploration of the configuration of carboxamido–enamide pyridine [M^{II}–OH] intermediate by nickel; f) The investigation of the stability of [Cu^{II}–OH] complex in dimethylimino pyridine system.

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[Cu$^{\mathrm{II}}$-DMF] complex [Cu$^{\mathrm{II}}$(py(N−C=O)$_2$ph$_2^{\mathrm{Me2}}$)(DMF)] (**1**) (Fig. 3a), which is easily convert to complex (Et$_4$N)[Cu$^{\mathrm{II}}$(py(N−C=O)$_2$ph$_2^{\mathrm{Me2}}$)(OH)] (**2**) by an addition of Et$_4$NOH. The stirring of **2** with ethylenediamine (EDA) in MeCN under dinitrogen atmosphere generates a mixture of complexes (Et$_4$N)$_2$[Cu$^{\mathrm{I}}$(py(N−C=O)$_2$ph$_2^{\mathrm{Me2}}$)]$_2$ (**3**) (Fig. 2a & 3b) and [Cu$^{\mathrm{II}}$(py(N−C=O)$_2$ph$_2^{\mathrm{Me2}}$)(EDA)] (**3a**) (Fig. S1a). The monovalent dicopper complex **3** is isolated unexpectly, in which the two Cu(I) centers are bonded in different modes. One is two-coordinated with a linear geometry, and the other is four-coordinated with distorted tetrahedron geometry. The characters of bond lengths (Cu−N: 1.854(1)−2.092(1) Å) and bond angles (N−Cu−N: 108.5(1)−173.3(1)°) indicate the formation of Cu(I) complex **3** with a short Cu$^{\mathrm{I}}\cdots$Cu$^{\mathrm{I}}$ distance of 2.805(1) Å. Interestingly, this reaction does not generate the cyanomethide complex of [Cu$^{\mathrm{II}}$-CH$_2$CN] and/or its related Cu(II)/Cu(I) species,[23] probably due to the quick substitution of OH$^-$ ligand with EDA, following by the release of OH$^-$ anion into the solution. Moreover, the recrystalization of **3a** in MeCN does NOT generate the Cu(I) complex **3**. In order to validate this reaction, a dicarboxamido *NNN*-pincer ligand with two allyl groups located on the two phenyl rings is synthesized to examine the redox reaction (Scheme S1). The allyl group is designed to enable the coordination ability of ligand to Cu$^+$ ion. Layer diffusion of toluene into a solution of [Cu$^{\mathrm{II}}$−OH] complex of (Me$_4$N)[Cu$^{\mathrm{II}}$(py(N−C=O)$_2$ph$_2^{\mathrm{Me/Allyl}}$)(OH)] (**5**) in DMF under N$_2$ produces a monovalent dicopper(I) complex of (Me$_4$N)$_2$[Cu$^{\mathrm{I}}$(py(N−C=O)$_2$ph$_2^{\mathrm{Me/Allyl}}$)]$_2$ (**6**) spontaneously (Fig. 2b & 3d). The complex **6** presents a symmetric coordination configuration with each of Cu$^+$ ion coordinated by three nitrogen donors and one vinyl group, displaying a distorted tetrahedron geometry. The above two reactions are checked with analogous [Cu$^{\mathrm{II}}$-Cl] complexes of (Et$_4$N)[Cu$^{\mathrm{II}}$(py(N−C=O)$_2$ph$_2^{\mathrm{Me2}}$)(Cl)] and/or (Et$_4$N)[Cu$^{\mathrm{II}}$(py(N−C=O)$_2$ph$_2^{\mathrm{Me/Allyl}}$)(Cl)], respectively. No Cu(I) product is obtained with the recovery of [Cu$^{\mathrm{II}}$-Cl] starting materials. This result supports the participation of hydroxo group in the oxidation-reduction process, probably as a nucleophilic reagent for the deprotonation of organic species, as well as regulating the basicity of solution in favour of reduction of Cu^{2+} to Cu$^+$. The basic nature of the dianionic *NNN*-pincer ligand would help to improve the nucleophilic reactivity of hydroxo group on the deprotonation of organic substrates. Beyond that, the hydroxo-group induced reduction of free Cu^{2+} ion is also investigated by the analogous [Cu$^{\mathrm{II}}$−OH] compound. A solution of (Me$_4$N)[Cu$^{\mathrm{II}}$($\subset_{20}$-py(N−C=O)$_2$ph$_2$dien$^{\mathrm{Me3}}$)(OH)] (**8**) (Fig. S1b) in DMF is treated with one equivalent of solid Cu(OTf)$_2$. The reaction affords the mixed-valence trinuclear [Cu$^{\mathrm{II}}$-Cu$^{\mathrm{I}}$-Cu$^{\mathrm{II}}$] complex [Cu$_3$($\subset_{20}$-py(N−C=O)$_2$ph$_2$dien$^{\mathrm{Me3}}$)$_2$](OTf) (**9**) smoothly (Fig. 2c & 3e). Each of the Cu(II) ion in the side core of **9** has a distorted pyramid geometry, while the central Cu(I) ion holds a distorted linear geometry with Cu$^{\mathrm{I}}$−N bond lengths of 1.880(2)-1.882(2) Å and Cu$^{\mathrm{I}}$-O of 2.683(2)-2.743(1) Å. This result is consistent with the conclusion presented above; the hydroxo group in the [Cu$^{\mathrm{II}}$−OH] compounds facilitates the reduction of Cu^{2+} to Cu$^+$. It is currently unclear as to the fate of the hydroxide ligand. By comparison, free Cu^{2+} ion works better than the coordinated Cu^{2+} ion in the reduction process according to the reaction time and yields in our system (Free Cu^{2+} ion: complex **9**, 15 mins, yield 45%; Coordinated Cu^{2+} ion: complexes **3** and **6**, one week, yields 10% and 30%, respectively). All the yields of Cu(I) and [Ni$^{\mathrm{II}}$-OH] are calculated in reference to reactants [Cu$^{\mathrm{II}}$-OH], [Cu$^{\mathrm{II}}$-DMF]$_n$ and [Ni$^{\mathrm{II}}$-DMF]$_n$ respectively (see Fig. 2).

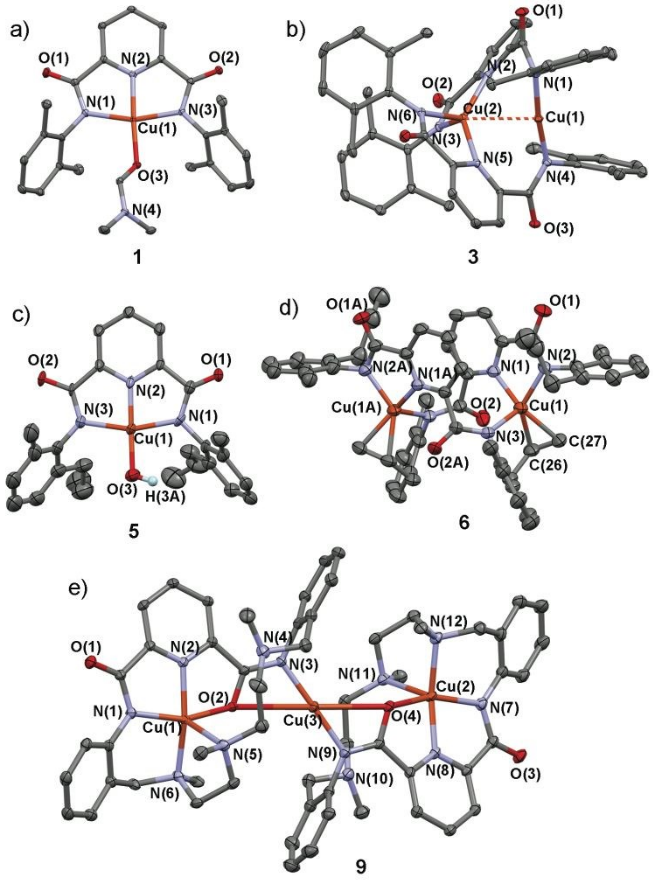

Fig. 3 Crystal structures of [Cu$^{\mathrm{II}}$(py(N−C=O)$_2$ph$_2^{\mathrm{Me2}}$)(DMF)] (**1**), [Cu$^{\mathrm{I}}$(py(N−C=O)$_2$ph$_2^{\mathrm{Me2}}$)]$_2^{2-}$ (**3**), [Cu$^{\mathrm{II}}$(py(N−C=O)$_2$ph$_2^{\mathrm{Me/Allyl}}$)(OH)]$^-$ (**5**), [Cu$^{\mathrm{I}}$(py(N−C=O)$_2$ph$_2^{\mathrm{Me/Allyl}}$)]$_2^{2-}$ (**6**) and [Cu$_3$($\subset_{20}$-py(N−C=O)$_2$ph$_2$dien$^{\mathrm{Me3}}$)$_2$]$^+$ (**9**) with all non-hydrogen atoms shown as 40% probability ellipsoids.

The cooperative metal−ligand interaction is examined by the design of copper(II) complexes of [Cu$^{\mathrm{II}}$(py(N−C=O)(N=C−C)ph$_2^{\mathrm{Me2}}$)(X)]$^{+/0}$ (X = DMF, OH) (Fig. 2d). The asymmetric mixed 2,6-disubstituted arylcarboxamido-arylimino pyridine ligand was supposed to have the characteristics of both strong base quality of diarylcarboxamido pyridine (H$_2$py(N−C=O)$_2$ph$_2^{\mathrm{Me2}}$) and good electron delocalization property of diarylimino pyridine (py(N=C−C)ph$_2^{\mathrm{Me2}}$).[24] The latter has been usually used as π-accepting ligand to support first-row transition metal complexes that exhibit novel reactivity with the ligand skeleton getting involved in chemical reactions.[10a] Two synthetic routes are developed for the preparation of ligand

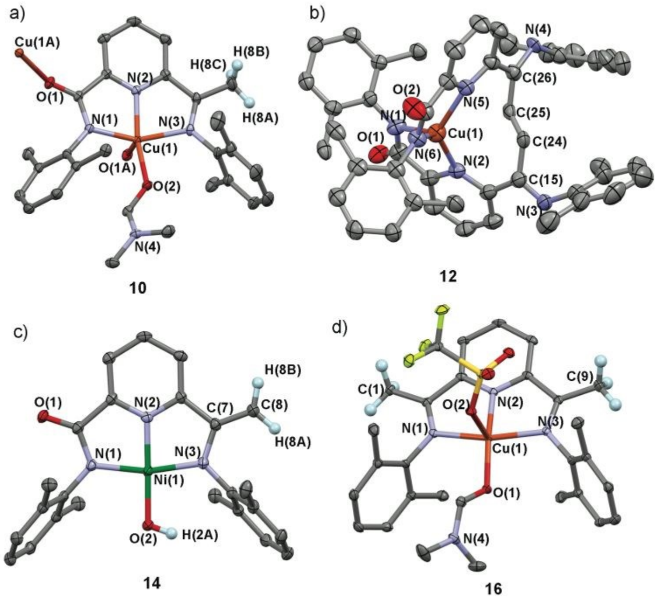

Fig. 4 Crystal structures of {[Cu^{II}(py(N−C=O)(N=C−C)ph$_2^{Me2}$)(DMF)](OTf)}$_n$ (**10**), [Cu^I(py(N−C=O)(N=C−C)ph$_2^{Me2}$)$_2$]$^-$ (**12**), [Ni^{II}(py(N−C=O)(N=C−C)ph$_2^{Me2}$)(OH)]$^-$ (**14**) and [Cu^{II}(py(N=C−C)$_2$ph$_2^{Me2}$)(DMF)(OTf)]$^+$ (**16**) with all non-hydrogen atoms shown as 40% probability ellipsoids. The structures of complexes **14** and **16** were solved by fast-data collections with the crystallographic data shown in Table S3.

Hpy(N−C=O)(N=C−C)ph$_2^{Me2}$ (Scheme S2). Addition of one equivalent of Me$_4$NOH to the complex of {[Cu^{II}(py(N−C=O)(N=C−C)ph$_2^{Me2}$)(DMF)](OTf)}$_n$ (**10**) (Fig. 4a) in DMF results in a light brown solution immediately under N$_2$ atmosphere. Crystallization of the resultant solid from DMF/Et$_2$O affords the product (Me$_4$N)[Cu^I(py(N−C=O)(N=C−C)ph$_2^{Me2}$)$_2$]·1.5Et$_2$O·0.5H$_2$O (**12**) as light brown crystals (Fig. 2d & 4b). The structure of **12** shows that the Cu(I) center has a strongly distorted tetrahedral geometry defined by four nitrogen donors from two anionic arylcarboxamidopyridine ligands. The two ligands are coupled to form a new C−C bond (C$_{24}$−C$_{25}$ = 1.45(3) Å, C$_{24}$'−C$_{25}$' = 1.49(4) Å) at the imino-methyl position. No restraint of bond length is applied to the C$_{24}$−C$_{25}$ bond in the solution of the structure of complex **12**. The distance of the new C−C bond is shorter than those of analogous diaryliminopyridine compounds with the alkylation of ligands on the peripheral methyl atoms of N=C−C groups, in which the coupled C−C bonds showed distinct single bond characteristics with bond lengths between 1.523 Å and 1.562 Å.[15a,15e] Strongly disordered structure of **12** is perceived as contributing to the short C−C bond distance. HR-MS characterization supports the formation of a C−C single bond rather than a C=C double bond in complex **12** (Fig. S2). The driving force of the carbon−carbon bond coupling reaction in complex **12** is investigated by the reaction of analogous complex of [Cu^{II}(py(N−C=O)(N=C−C)ph$_2^{Me2}$)(Cl)] (**10a**) with one equivalent of Me$_4$NOH. The starting material of complex **10a** is recovered from reaction without the generation of new species, which implies that the reaction of complex **10** to **12** is induced by the hydroxo group, probably *via* intermediates of [Cu(py(N−C=O)(N=C−C)ph$_2^{Me2}$)(OH)] (**11a**) and [Cu(py(N−C=O)(N−C=C)ph$_2^{Me2}$)(OH$_2$)] (**11b**) (Fig. 2d). The substitution of solvated DMF with OH$^-$ anion runs faster than the deprotonation of methyl group, and the added Et$_4$NOH would be used preferentially for coordination. In literature, the formation of enamide ligands from deprotonation of diaryliminopyridines has been well-precedented among complexes of Cr(II),[15c] Mn(II),[15a] Fe(II),[15b] Co(II)[15e] and Ni(II)[15d].

This is the first example of C−C bond formation of methylimino pyridine through the reduction of Cu(II) to Cu(I), which implies a formal elimination of one proton from the methyl group of intermediate species of **11a**. Unfortunately, all the efforts to isolate the intermediates of **11a** and/or **11b** are unsuccessful. A analogous [Ni^{II}−OH] complex of (Et$_4$N)[Ni^{II}(py(N−C=O)(N=C−C)ph$_2^{Me2}$)(OH)] (**14**) is prepared for the examination of the coordination pattern and electronic structure of likely complex **11a** and/or its de-protonated complex **11b**. The latter would be the key compound in the reaction of formation of C−C bond (Fig. 2e). X-ray crystallography analysis of **14** reveals that the nickel(II) ion has a square planar geometry with three nitrogen donors from ligand and one oxygen donor from the hydroxo group lying in the equatorial plane (Fig. 4c). The imine-methyl group in the [Ni^{II}-OH] complex of **14a** is attacked to lose a proton by the hydroxide ligand, forming a conjugated enamide group (N$_3$−C$_7$ 1.374(3) Å, C$_7$=C$_8$ 1.357(4) Å). The dianionic carboxamido-enamide pyridine ligand [py(N−C=O)(N−C=C)ph$_2^{Me2}$]$^-$ is energetically strong enough to support the transformation of complex **14b** to **14**. In complex **11b**, the cooperative metal−ligand interaction would occur between Cu^{2+} and *NNN*-pincer ligand, after deprotonation of imine-methyl group with hydroxide ligand. With the aim to check the stability of imino group for the Cu^{2+} ion under base condition, the diimino pyridine [Cu^{II}−DMF] complex of [Cu^{II}(py(N=C−C)$_2$ph$_2^{Me2}$)(DMF)(OTf)](OTf) (**16**) is prepared and the compound is treated with one equivalent of Me$_4$NOH or Et$_4$NOH. No product is obtained with the colour of solution changing to light yellow-green (Fig. 2f). It seems that the diimino compound would suffer from decomposition in the presence of hydroxide ligand. A certain amount of brown-black precipitate is found deposited at the bottom. That is to say, the carboxamido group in complex **11a** helps to hold the [Cu^{II}−OH] unit, which triggers the deprotonation reaction thereafter C−C bond coupling reaction.

Considering the different oxidative ability and reactivity of Cu^{II} complexes in our systems, we set out to analyze the structural characteristics of carboxamido-methylimino ligands with conjugated π-electron system. The examination of the influence of ligand types on the activation of copper(II) pincer complexes is carried out by the techniques of UV-vis spectroscopy, cyclic voltammetry and EPR spectroscopy. The absorption bands of *d-d* transition show blue shifting and widening with the increase of absorption coefficient in order of complexes **1** > **10** > **16** (Fig. 5), which implies that the complex **1** possesses larger *d*-orbital splitting energy than

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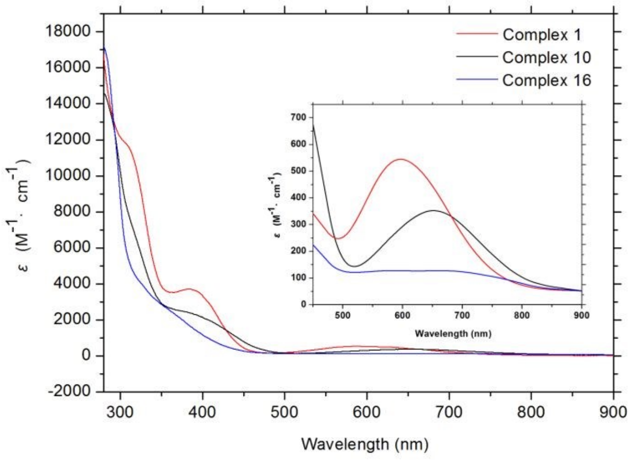

Fig. 5 UV-vis spectra of the complexes **1, 10** and **16** in DMF solution.

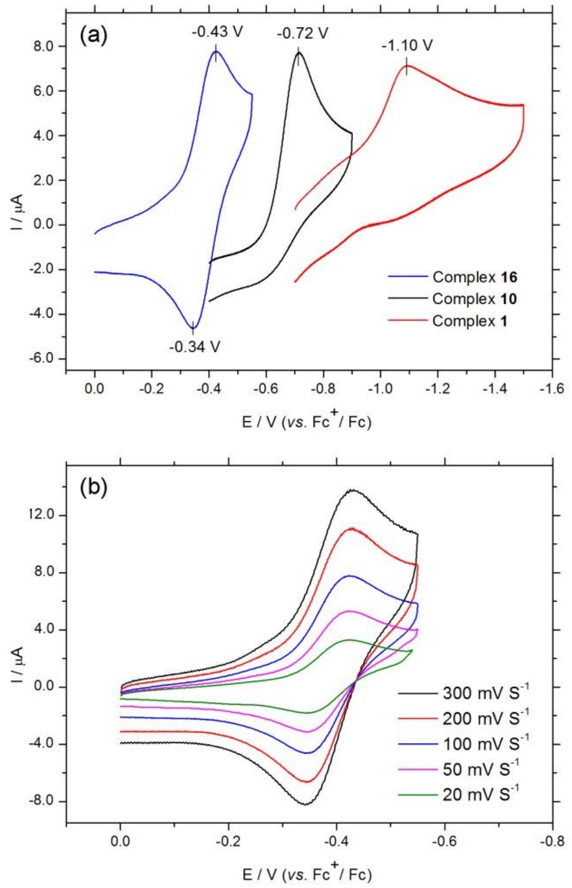

Fig. 6 (a) Cyclic voltammogram of complexes **1**, **10** and **16** in DMF (0.1 M NBu_4PF_6) at 298 K; (b) Examination of the reversible reduction process of complex **16** at variable scan rates.

complex **10** and **16** associating with the electron-donating ability of the ligands. The dianionic carboxamido-pyridine ligand donates more electron density to the Cu(II) center than the imino pyridine ligand, and for this reason, it is only necessary for the coordinated hydroxo groups in the [Cu^{II}–OH] complexes of **2**, **5** and **8** donating minor electron density to the metal centers. As a result, the coordination interaction between Cu^{2+} ion and the OH^- group decreases, and the hydroxo group would tend to show good nucleophilic reactivity on the deprotonation of organic species.

The basic nature of the dianionic carboxamido-pyridine ligands is also investigated by the study of reduction potentials of Cu(II) complexes. The cyclic voltammograms of complexes **1**, **10** and **16** in DMF (0.1 M NBu_4PF_6, 298 K) at a scan rate of 100 mVs^{-1} shows reduction processes at E_p^c = -1.10 V, -0.72 V and -0.43 V versus Fc^+/Fc, which are assigned to the Cu^{II}/Cu^I couple of complexes (Fig. 6a), respectively. The reduction process of complex **16** at -0.43 V is associated with an oxidation process at -0.34 V. The examination of this reduction-oxidation process at variable scan rates reveals that the reduction of complex **16** to Cu(I) species is a reversible process in solution at 298 K (Fig. 6b). It indicates that the imino group has superior structural characteristic with conjugated π-electron system, which is beneficial to electron delocalization and enhancement of reduction response of Cu(II) complex.

The above result is consistent with the analysis of EPR spectra of complexes **1**, **10** and **16** in DMF solution. The fluid X-band spectra of **1**, **10** and **16** (Fig. 7a-7c) show similar EPR signals with a major quadruplets that results from hyperfine coupling to $^{63,65}Cu$ nuclei (I = 3/2, 100% combined natural abundance). The seven-line super-hyperfine coupling on the high-filed feature is assigned to the hyperfine coupling involving three equivalent ^{14}N nuclei ($2nI+1$, I = 1). Simulation of these spectra gives g_{iso} = 2.101 and $|A_{iso}|$ = 71 × 10^{-4} cm^{-1} for **1**, g_{iso} = 2.111 and $|A_{iso}|$ = 67 × 10^{-4} cm^{-1} for **10**, g_{iso} = 2.128, $|A_{iso}|$ = 65 × 10^{-4} cm^{-1} for **16**, with a Gaussian line width W_{iso} = 1G for all of them. The frozen solution X-band spectra of **1**, **10** and **16** (Fig. 7d-7f) are approximately axial with $^{63,65}Cu$ hyperfine, and the simulated spin-Hamiltonian parameters are given in Table 1. The quasi-axial EPR spectra of complexes are consistent with the approximate square-planar structures of complexes **1**, **10** and **16** determined by X-ray crystallography. Thus, g_{xx} and g_{yy} are assigned to orientations lying in the equatorial CuN_3O plane, with g_{zz} (the largest g-value) perpendicular to this plane. Crystal field theory predicts a $3d_{xy}$-based SOMO in the above Cu(II) complexes consistent with the observed $g_{\parallel} > g_{\perp} > g_e$ pattern. Analysis of the simulated g and A-values of these three complexes gave α^2 = 67.8 % for **1**, 67.6 % for **10** and 64.3 % for **16** (see Supporting Information) with reference to the interpretation of spin Hamiltonian parameters developed for the analogous Cu(II), Ag(II) and Au(II) complexes.[23b,25] Thus, the contributions of $3d_{xy}$ metal orbital to the SOMO are 67.8 % for complex **1**, 67.6 % for complex **10** and 64.3 % for complex **16**, which indicates the larger ligand contributions to the SOMO for **16** than **1** and **10** in the diimino-pyridine system. The complexes of **1** and **10** have similar ligand contributions to the SOMO with one or two anionic carboxamido group participated in the system.

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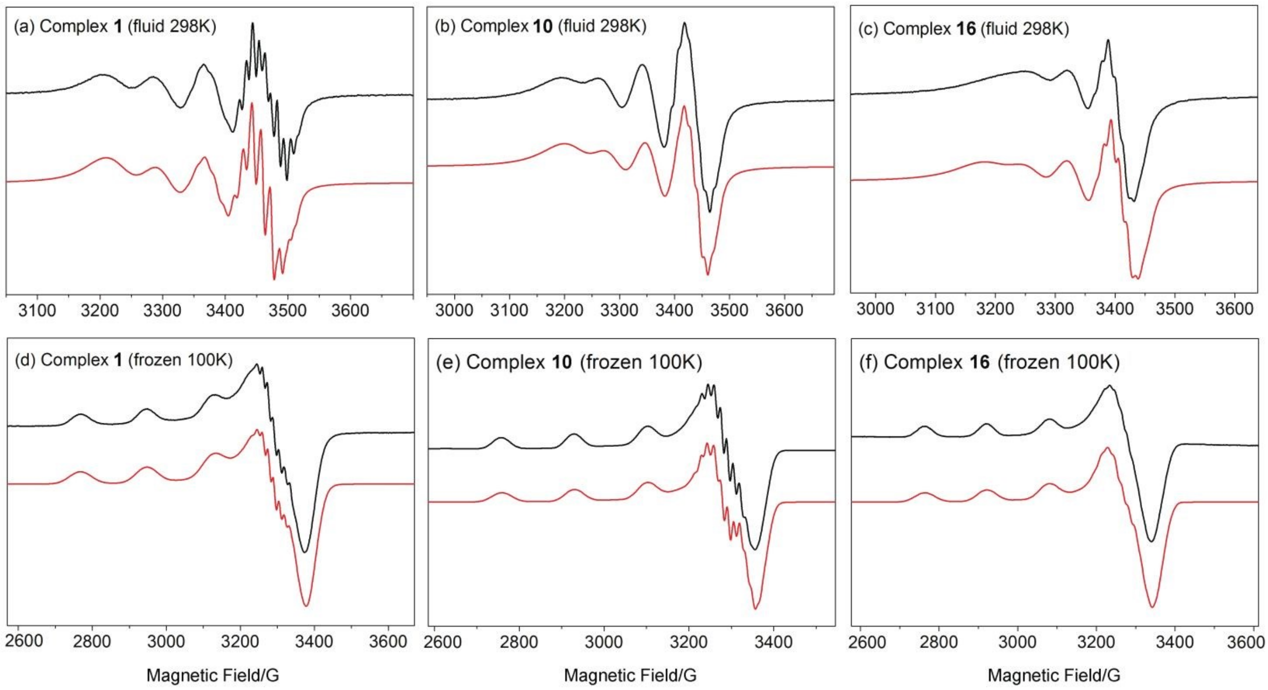

Fig. 7 X-band fluid EPR spectra (a)-(c) and frozen EPR spectra (d)-(f) of complexes **1**, **10** and **16** in DMF solution (top). Their simulations are presented at the bottom. The simulated spin-Hamiltonian parameters are listed in Table 1.

Table 1. EPR parameters derived from simulations of experimental X-band spectra[a]

Fluid	g_{xx}	g_{yy}	g_{zz}	$\|A_{xx}\|_{(Cu)}$	$\|A_{yy}\|_{(Cu)}$	$\|A_{zz}\|_{(Cu)}$	$\|A_{xx}\|_{(N)}$	$\|A_{yy}\|_{(N)}$	$\|A_{zz}\|_{(N)}$	W_{iso} (G)		
1	1.960	2.172	2.172	13	100	100	12	15	15	1 G		
10	1.945	2.194	2.194	1	100	100	5	16	16	1 G		
16	1.988	2.198	2.198	1	97	97	13	13	13	1 G		
Frozen	g_{xx}	g_{yy}	g_{zz}	$\|A_{xx}\|_{(Cu)}$	$\|A_{yy}\|_{(Cu)}$	$\|A_{zz}\|_{(Cu)}$	$\|A_{xx}\|_{(N)}$	$\|A_{yy}\|_{(N)}$	$\|A_{zz}\|_{(N)}$	W_{xx}	W_{yy}	W_{zz}
1	2.048	2.060	2.223	10	15	182	14	15	16	9	70	40
10	2.048	2.057	2.234	12	12	175	13.5	13.5	13.5	25	11	20
16	2.050	2.069	2.250	17	17	162	15	15	15	20	17	20

[a] units of $|A|$ are in 10^{-4} cm^{-1}.

Since the attempts to isolate the [Cu^{II}-OH] intermediates of **11a** and **11b** are failed, the structures of them are optimized by density functional theory (DFT) calculations (Fig. 8). The imine-methyl group in complex **11a** is shown as [N=C−C] unit with the N=C bond length of 1.291 Å and the C−C bond length of 1.483 Å. The Cu−O$_{(OH)}$ bond length of 1.864 Å is comparable to those of bond lengths in the analogous complexes of **2**, **5** and **8**. In the state of **11b**, the [N=C−C] unit changes to [N⎓C⎓C] with the N⎓C, C⎓C and Cu−O$_{(H2O)}$ bond lengths shown as 1.374 Å, 1.360 Å and 2.069 Å, respectively. The conjugated enamide group is similar to that of the analogous [Ni^{II}-OH] complex **14**, which is obtained by deprotonation of methyl group with hydroxo group from [Ni^{II}-OH] moiety. However, it is still not clear to us how the carbon-carbon formation reaction works.

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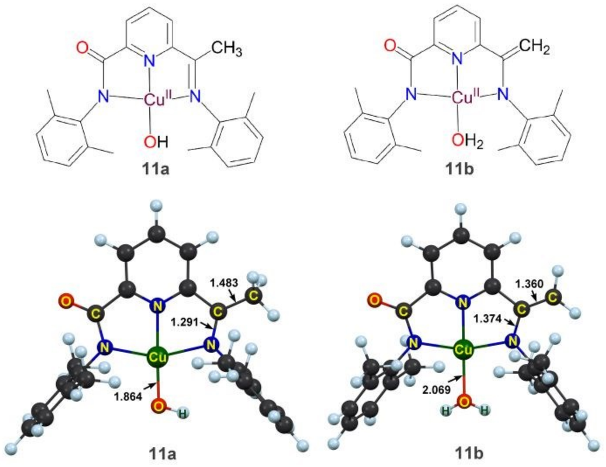

Fig. 8 Optimized structures of **11a** and **11b** using M06-L functional and 6-311G** basis set for C, H, N, and O atoms and SDD basis set for Cu atom.

Conclusions

In summary, we have described a [Cu^{II}–OH] species facilitated carbon–carbon bond formation *via* cooperative metal–ligand (enamide ligand) interaction. Two imine-methyl groups (N=C–C) are coupled to form a new C–C bond (N=C–C–*C*–*C*=*N*) at the methyl positions. The two-electron oxidation coupling is accompanied with the reduction of two Cu^{2+} center ions to Cu^{+}. The techniques of X-ray crystallography, UV-vis spectroscopy, cyclic voltammogram, EPR spectroscopy and DFT calculations are used to check the intermediate species with the discovery of structural characteristics of carboxamido-pyridine and imino-pyridine ligands. Experimental and theoretical results reveal that the hydroxide ligand in the [Cu^{II}-OH] complexes works as a nucleophilic reagent for the deprotonation of methyl group, as well as regulating the basicity of solution in favour of reduction of Cu^{2+} to Cu^{+}. The formation of conjugated enamide Cu(II) intermediate would be the key point for the carbon-carbon coupling reaction. This work discovers the potential of carboxamido [Cu^{II}–OH] complexes in catalysis, organic transformation and energy conversion. It might provide a clue to access copper mediated C–C bond formation, and open up a new synthetic protocol to develop new reactants and catalysts for further organic synthesis.

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