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Synthesis of triisocyanomesitylene β diketiminato copper(I) complexes and evaluation of isocyanide π-back bonding

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ABSTRACT

A new 2,4,6-triisocyanomesitylene ligand was synthesized and along with 1,4-isocyanobenzene utilized to prepare unique *N*-aryl-*N'*-alkylpyridyl β-diketiminato copper(I) complexes. Crystallographic characterization of 2,4,6-triisocyanomesitylene, dinuclear and trinuclear copper isocyanide complexes were carried out to elucidate their structural features. The FT-IR spectroscopic analysis of the prepared copper (I) isocyanide complexes show the CN stretching frequencies experience a significant red shift relative to those of the free ligands, indicating that π-back bonding interaction exist between copper(I) centers and isocyanide moieties. DFT based frontier molecular orbital analysis demonstrated that the enhanced π-back bonding is a consequence of the π-accepting abilities of the 1,4-diisocyanobenzene and 2,4,6-triisocyanomesitylene ligands.

1. Introduction

The β-diketiminates with differing electronic and steric properties have been utilized as spectator chelating ligands [1–3] in a variety of alkaline earth, main group, lanthanide, actinide and transition metal complexes [4,5]. Moreover, many studies have been conducted to elucidate the effects of functional groups on the β-diketiminate ligands [6–15], but only few have focused on unsymmetrical β-diketiminates [16–20]. β-Diketiminato copper(I) complexes containing CO, isocyanides (CNRs), and phosphine ligands have been widely studied [6–8,10–12,15,18,21,22], and nearly a dozen of investigations have concentrated on complexes where the metal is coordinated with mono-isocyanides [6,7,10–12,15,18].

An understanding of the electron-donating characteristics of copper(I) complexes has come from studies of the CO binding ability in terms of the formation of copper(I)–CO adducts [18,21,22]. However, the reversible nature of CO binding usually causes isolation of copper(I)–CO adducts to be difficult and this issue limits structural characterization of the complexes. In contrast, β-diketiminato copper(I) isocyanide complexes are much more thermodynamically stable and, as a result, they serve as better systems to probe the combined electronic and structural features of Cu(I) complexes. Most of β-diketiminato copper(I)–CO adducts display CO stretching frequencies (ν_{CO}) that are lower (red shifted) than that of uncoordinated CO (2143 cm^{-1}), indicating that the CO ligand participates in a strong π-accepter interaction with the copper(I) center. In contrast, isocyanides are stronger σ-donors and weaker π-accepters than CO [6,7,10–12,15,18]. Therefore, the β-diketiminato copper(I)-isocyanide adducts usually show blue shift on the CNRs stretching frequencies, indicating isocyanide ligand predominantly as σ donors and π acceptor interactions are minor [6,7,10,12,18].

In a previous investigation, we found that the mono-isocyanide (2,6-xylylisocyanide) induces de-coordination of the chelating pyridyl arm of the unsymmetrical *N*-aryl-*N'*-alkylpyridyl β-diketiminato ligand in the copper(I) complexes Cu**L1** (**1**) and Cu**L2** (**2**) (Scheme 1) while the Cu(I) center remains three coordinated [18]. However, no reports exist describing β-diketiminato copper (I) complexes that contain poly-isocyanides as bridging ligands. In the study described below, we prepared β-diketiminato copper (I) complexes that contain 1,4-diisocyanobenzene and new 2,4,6-triisocyanomesitylene as bridging ligands, and assessed their structural and electronic properties by using NMR and FT-IR spectroscopy as well as X-ray crystallography. Importantly, an analysis the CN vibrational frequencies in the isocyanide ligands in these

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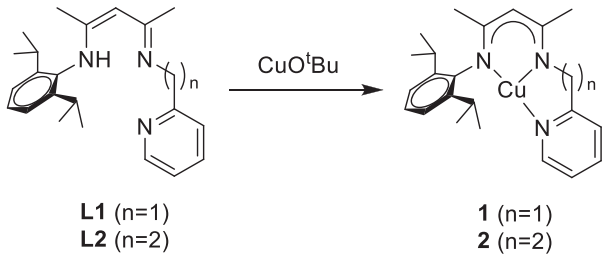


Scheme 1. Synthesis of copper(I) complexes Cu**L1** (**1**) and Cu**L2** (**2**).

complexes has contributed to an understanding of bonding interactions occurring between metal fragment and new isocyanide ligands.

2. Results and discussion

2.1. Synthesis of new 2,4,6-triisocyanomesitylene

Isocyanides are typically synthesized by using dehydration reactions of *N*-substituted formamides or by the carbylamine reaction of amines with chloroform under basic conditions [23–25]. We have employed the earlier procedure used to produce 1,4-diisocyanobenzene [24] to prepare the previously unknown 2,4,6-triisocyanoomesitylene starting with 2,4,6-triaminomesitylene, generated by a modification of the route used by Havlík et al. [26]. Specifically, 2,4,6-trinitromesitylene was produced by nitration of mesitylene using fuming nitric acid and sulfuric acid (Scheme 2) and then reduced employing $SnCl_2$ and conc. hydrochloric acid to give 2,4,6-triaminomesitylene. The 2,4,6-triaminomesitylene was transformed to 2,4,6-triformamidomesitylene by reaction with formic acid in refluxing toluene for 4 h. Finally, dehydration of the 2,4,6-triformamidomesitylene was carried out by treatment with $POCl_3$ and triethylamine. Column chromatographic purification gave 2,4,6-triisocyanomesitylene as a disagreeable smelling, air stable, non-hygroscopic and highly organic soluble white solid in 25% yield.

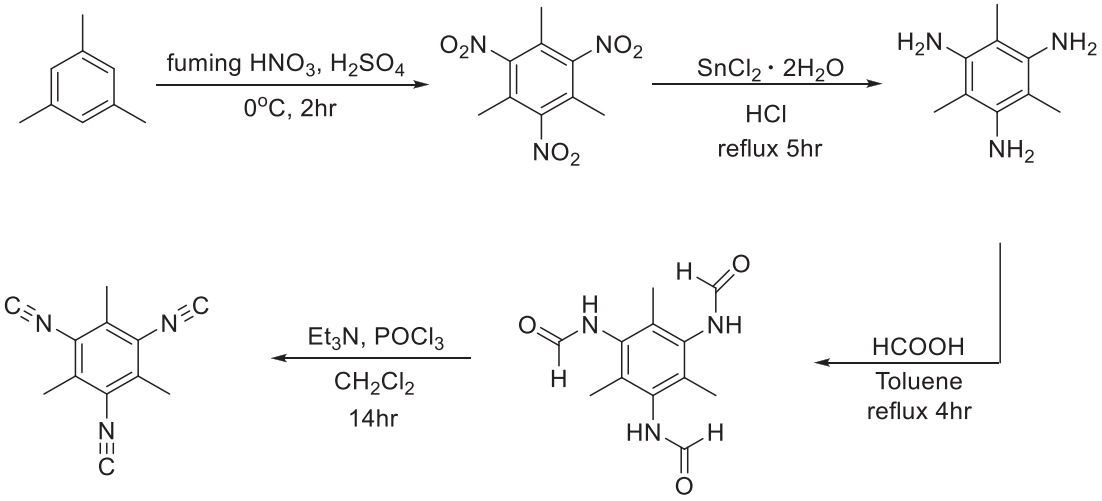
2.2. Synthesis and characterizations of copper(I) isocyanide complexes

The respective di- (**3** and **4**) and tri- (**5** and **6**) nuclear copper complexes were prepared starting with the previously synthesized *N*-aryl-*N*′-alkylpyridyl β-diketiminato copper(I) complexes **1** and **2** [18]. For this purpose, toluene solutions of **1** or **2** containing stoichiometric amounts of either 1,4-diisocyanobenzene or 2,4,6-triisocyanomesitylene were stirred under a N_2 atmosphere at room temperature (Scheme 3). The progress of each reaction was monitored using FT-IR spectroscopy and by following a color change of the solution from clear red–orange to a yellow-orange suspension. The pure orange, air-sensitive copper complexes, obtained by using filtration, were characterized by using ^{1}H NMR, ^{13}C NMR and FT-IR spectroscopy, and elemental analysis.

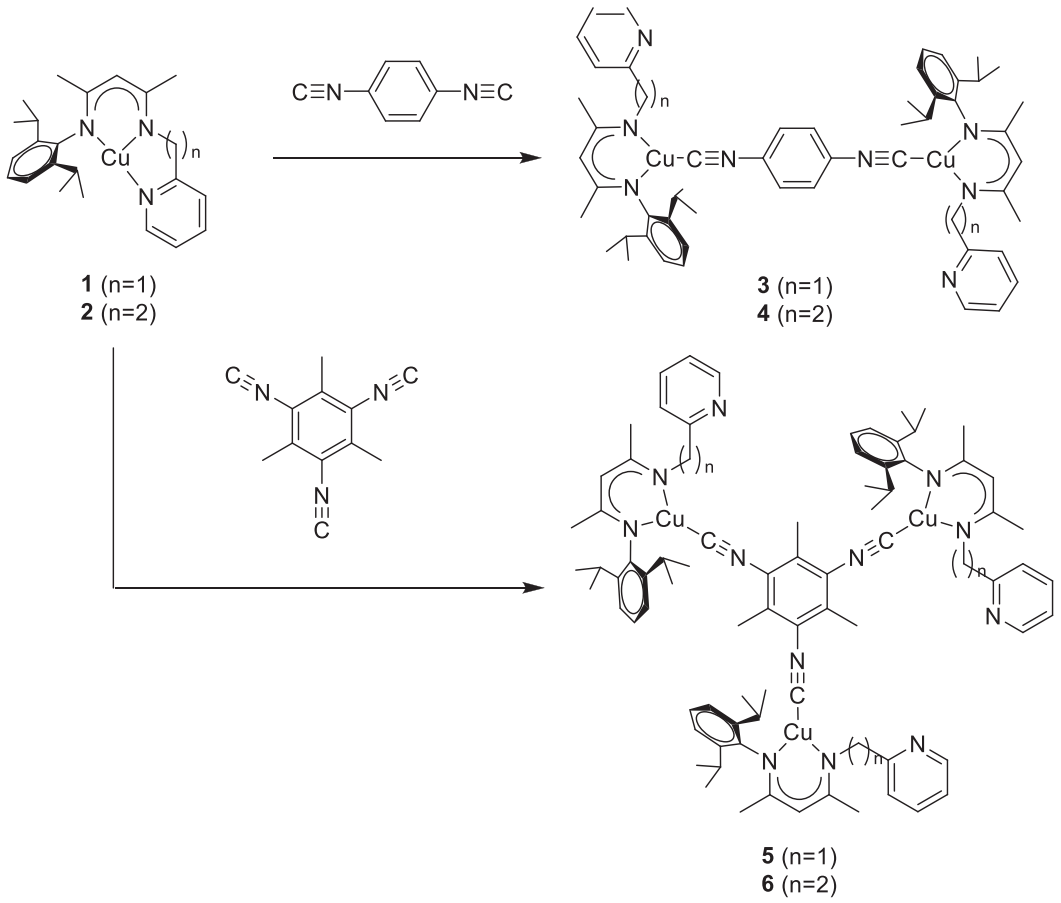
As expected, the ^{1}H NMR spectrum of 2,4,6-triisocyanomesitylene in $CDCl_3$ (Figs. S1-S2) contains a methyl singlet at 2.57 ppm, and its ^{13}C NMR spectrum of contains a peak at 171.68 ppm, assigned to the isocyanide carbon, at 133.61 and 125.98 ppm for the arene ring carbons, and at 16.43 ppm for the methyl groups. The NMR spectra of *N*-aryl-*N*′-alkylpyridyl β-diketiminato copper(I) complexes **1** and **2** have been described in previous studies[18]. The ^{1}H NMR and ^{13}C NMR spectra of complexes **3**–**6** (Figs. S3-S10) contain signals associated with both β-diketiminate and isocyanide ligands. Moreover, in a manner that is consistent with previous findings[18], the ^{1}H NMR signals for H-6 of the pyridine ring in the uncoordinated pyridyl arm of complexes **3**–**6** (8.47, 8.47, 8.57 and 8.53 ppm, respectively) are shifted downfield with respect to the analogous proton resonances in the corresponding copper(I) complexes **1**–**2** (7.86 and 7.95 ppm, respectively[18].

2.3. X-ray crystallographic results

X-ray quality single crystals of 2,4,6-triisocyanomesitylene and Cu(I) complexes **3**–**6** were obtained from concentrated hexane solutions at −20 ℃. Representations of the molecular structures of 2,4,6-triisocyanomesitylene and complexes **3**–**6** are shown in Figs. 1-3 and supporting information (Figs. S11-S13), and selected bond distances and angles are listed in Table 1. In its molecular structure, the three isocyanide groups of the 2,4,6-triisocyanomesitylene ligand are oriented in a 120° manner with each C—N—R angle lying in the range of 178-179°. In addition, the CN bond distances in fall in the range of 1.157–1.161 Å, which is expected for isocyanide CN triple bonds[27–30]. Furthermore, analysis of the structures of complexes **3**–**6** shows that the de-coordinated pyridine moiety is replaced by an isocyanide ligand and that all related bond distances and angles are similar to those reported for other β-diketiminato copper isocyanide complexes[6,10–12,18]. The



Scheme 2. Synthesis of triisocyanomesitylene.



Scheme 3. Synthesis of *N*-aryl-*N'*-alkylpyridyl β-diketiminato copper(I) complexes **3**–**6** containing isocyanide bridging ligands.

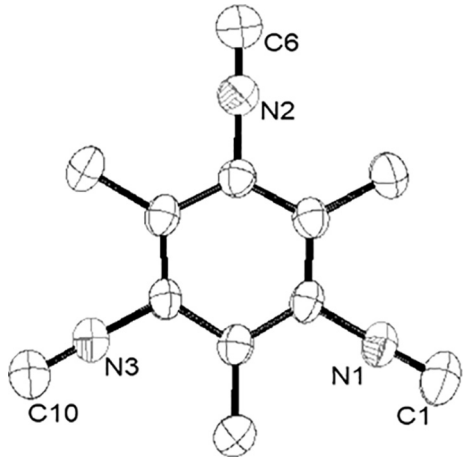


Fig. 1. ORTEP representation of the crystal structure of 2,4,6-triisocyanomesitylene. (50% ellipsoid; all H atoms are omitted for clarity).

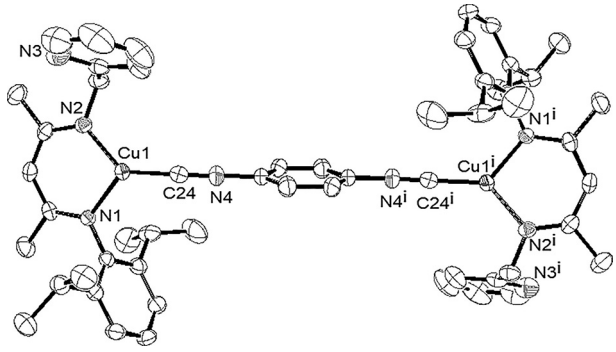


Fig. 2. ORTEP representation of the crystal structure of **3**. (50% ellipsoid; all H atoms are omitted for clarity).

copper(I) centers in the complexes all display three coordination geometries arising from bonding with two N donors from β-diketiminate backbone and one C donor from isocyanide ligand. The CN triple bond distances in **3**–**6** are in the 1.146–1.175 Å range, which are similar to those of related complexes [6,10–12,18]. In **3**–**6**, the CN bonds are slightly longer and the C—N—R bond angles are slightly distorted away from 180° than the those of the free 2,4,6-triisocyanomesitylene ligand as a consequence of π-back bonding interactions with the copper(I) center (see below).

2.4. FT-IR investigations of copper(I) isocyanide adducts

FT-IR is a superior method for characterizing the nature of electronic interactions occurring between metals and CNR ligands. Typically in higher-valent metal or Group 11 triad metal (formal + 1 oxidation state) complexes, the stretching frequencies of the CN triple bond in metal bonded CNRs are higher than that of the free ligand (blue shift), indicating that the ligands interact with the metal ion predominantly as σ donors and that their π acceptor interactions are minor [11,15,31–40]. However, some examples of isocyanide complexes (especial on the electron rich low-valent metal center) do exist in which C—N stretching frequencies are red shifted, indicating significant π-interactions occur in these

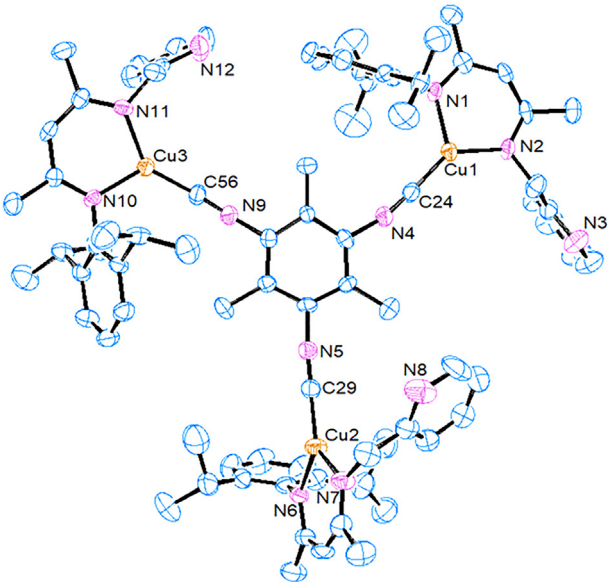


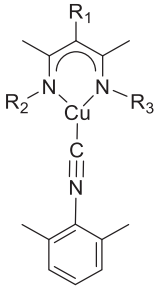
Fig. 3. ORTEP representation of the crystal structure of **5**. (50% ellipsoid; all H atoms are omitted for clarity).

systems between the metal and isocyanide ligand [41–46]. It is clear that a systematic study analysing factors for β-diketiminato copper(I) complexes that govern the degree of π-interactions by using CNR stretching frequencies is required in order to gain understanding of the electronic features of bonding between β-diketiminato copper(I) moieties and CNRs [6,7,10–12,15,18].

In order to explore relationships that exist between the structures and the isocyanide ligand electronic interactions with β-diketiminato copper(I) fragment, we compared differences of CN stretching frequencies ($\Delta\nu_{CNR}$) between complexes and the corresponding free ligand of the previously prepared β-diketiminato copper(I) isocyanide adducts **A**-**H** with those of the new isocyanide copper(I) complexes **3**–**6** (Table 2). The data show that differences in the $\Delta\nu_{CNR}$ values of complexes **A**, **B** and **D**, which contain the same 2,6-xylyl isocyanide ligand, are a consequence of the nature of functional groups present on the *N*-aryl substituents. Specifically, the mesityl, dimethylphenyl, and diisopropylphenyl groups in these substances increasingly enhance σ donation from the isocyanide ligand to the copper(I) core. The stretching frequency of complex **C**, which possess Cl groups on β-diketiminate backbone, occurs at a higher wavenumber (larger blue shift) than that of **B**, where as those of complexes **G** and **H**, containing *N*, *N*′-isopropyl and *N*, *N*′-benzyl groups have negative $\Delta\nu_{CNR}$ values (red shifted). The red shift of the CN stretching frequency in these cases indicates that stronger π-back bonding interactions take place between the isocyanide ligand and copper center as a result of the stronger electron donating ability of *N*, *N*′-alkyl substituents in comparison to *N*, *N*′-aryl substituents on the β-diketiminate backbone. The positive $\Delta\nu_{CNR}$ values displayed by complexes **E** and **F** suggest that the electron donation abilities of the unsymmetrical β-diketiminate ligands are similar to those of the *N*, *N*′-aryl substituted analogs.

Inspection of the CN stretching regions of the FT-IR spectra of complexes **3**–**6** displayed in Figs. 4 and 5 shows that the stretching

Table 2
C—N Vibrational Frequency Data for Selected β-Diketiminato Copper(I) – CNR Complexes



compound	ν_{CNR}, cm^{-1}	$\Delta\nu_{CNR}$[a], cm^{-1}	ref
2,6-xylyl isocyanide	2119	–	[18]
1,4-diisocyanobenzene	2121	–	[24]
2,4,6-triisocyanomesitylene	2115	–	this work
3	2111	−10	this work
4	2109	−12	this work
5	2101	−14	this work
6	2100	−15	this work
A	2121	+2	[10]
B	2123	+4	[12]
C	2128	+9	[7]
D	2126	+7	[6]
E	2122	+3	[18]
F	2122	+3	[18]
G	2114	−5	[15]
H	2114	−5	[11]

[a] $\Delta\nu_{CNR}$ = the difference of wavenumber between complexes and the corresponding free ligand.

Table 1
Selected Bond Lengths and Angles for β-Diketiminato Copper(I) – CNR Complexes.

	C≡N (Å)	Cu–C (Å)	Cu–N (Å)	C≡N–C (°)	N–Cu–N(°)	ref
2,4,6-triisocyanomesitylene	1.157(4) 1.157(4) 1.161(4)	–	–	178.0(3) 178.8(3) 178.7(3)	–	This work
3	1.163(3)	1.804(3)	1.9298(19)[a], 1.924(2)[b]	174.5(3)	99.41(8)	This work
4	1.150(11), 1.146 (10)	1.829(10)1.822 (10)	1.940(7)[a], 1.920(7)[b],1.942(7)[a], 1.894(8)[b]	177.7(10)177.8 (10)	100.4(3)99.3(3)	This work
5	1.156(6), 1.175(6), 1.152(6)	1.804(6)1.775(6) 1.800(5)	1.927(4)[a], 1.909(4)[b],1.918(4)[a], 1.931 (4)[b],1.939(4)[a], 1.918(4)[b]	167.7(5)175.9(5) 176.4(5)	99.40(17)98.92 (17)99.03(17)	This work
6	1.159(12), 1.159 (14) 1.174(14)	1.802(11)1.798 (13)1.808(15)	1.934(9)[a], 1.930(8)[b],1.967(11)[a], 1.903 (11)[b],1.956(8)[a], 1.921(9)[b]	175.7(12)172.8 (13)171.9(11)	101.7(4)99.6(5) 100.1(4)	This work
A	1.159(2)	1.814(2)	1.945(1)[a], 1.926(2)[a]	177.01(16)	97.85(6)	[10]
B	1.157(3)	1.822(2)	1.933(2)[a], 1.946(2)[a]	173.8(2)	98.08(6)	[12]
D	1.158(3)	1.817(2)	1.928(2)[a], 1.962(2)[a]	171.4(2)	98.20(7)	[6]
E	1.159(4)	1.808(4)	1.937(3)[a], 1.921(3)[b]	176.6(3)	98.55(11)	[18]
H	1.159(2)	1.816(2)	1.941(1)[b], 1.941(1)[b]	172.49(16)	98.4(1)	[11]

[a] Cu – N[amide(aryl)]. [b]Cu – N[amide(alkyl)].

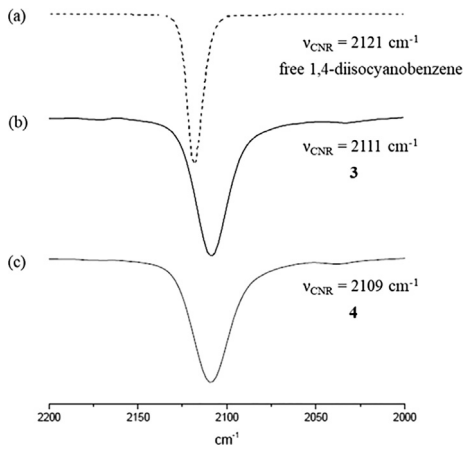


Fig. 4. CNR regions of FT-IR spectra of toluene solutions of (a) 1,4-diisocyanobenzene, (b) **3**, and (c) **4**.

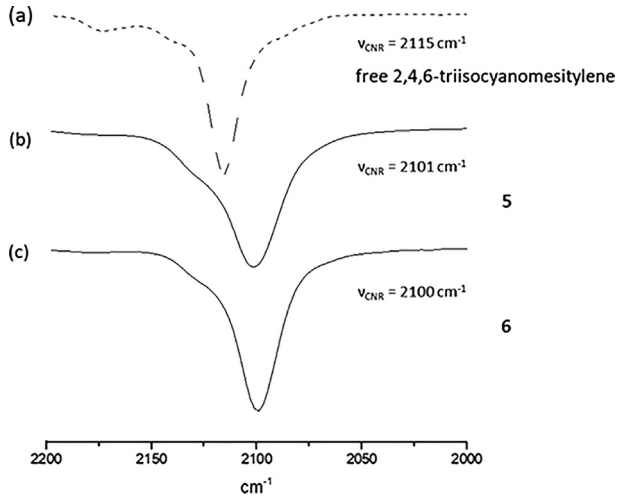


Fig. 5. CNR regions of FT-IR spectra of toluene solutions of (a) 2,4,6-triisocyanomesitylene, (b) **5**, and (c) **6**.

frequencies (ν_{CNR}) of free 1,4-diisocyanobenzene and 1,3,5-triisocyanomestylene ligands are 2121 and 2115 cm^{-1}, respectively. The ν_{CNR} values of the Cu(I) complexes **3** (2111 cm^{-1}), **4** (2109 cm^{-1}), **5** (2101 cm^{-1}), and **6** (2100 cm^{-1}) are red-shifted relative to the corresponding free isocyanide ligands (significant negative $\Delta\nu_{CNR}$), indicating that the isocyanide ligands in all complexes participate in strong π-back bonding. Significantly, the respective ν_{CNR} values of **5** and **6** of 2101 and 2100 cm^{-1} are the lowest observed thus far for copper(I) isocyanide complexes. It is interesting to speculate that the abnormally strong back bonding taking place between Cu(I) and the isocyanide groups in these complexes is a result of the stronger π-accepting abilities of 1,4-diisocyanobenzene and 2,4,6-triisocyanomesitylene.

2.5. Computational results

DFT calculations were carried out to gain insight into the π-accepting ability of arylisocyanide ligands. The energies and population analysis of LUMOs of arylisocyanide ligands, obtained using wave function analysis performed at B3LYP/Def2-TZVP level and X-ray structural data for the isocyanide ligands are given in Fig. 6. Results of the current DFT calculations show that the LUMO populations on carbon sites of isocyanide ligands are relatively small (<20%), leading to a relatively weaker π-acceptor ability. As a consequence, in most 2,6-xylyl isocyanide complexes with Cu (I), the inductive effect of the positively charged metal dominates over π-back donation by the isocyanide ligand,[44] resulting in blue shifts of ν_{CNR} (**A**-**F** in Table 1). However, the presence of a second and third CN group on the aryl ring significantly lowers the LUMO energy and, therefore, enhances the π -accepting capability of ligand (-2.326 eV for 1,4-diisocyanobenzene and −2.149, −2.131 eV for 1,3,5-triisocyanomesitylene vs. −1.240 eV for 2,6-xylyl isocyanide). Thus, π-back donation by the 1,4-diisocyanobenzene and 2,4,6-triisocyanomesitylene ligands overwhelms the Cu(I) inductive effect in the newly prepared complexes **3**–**6**.

3. Conclusion

In the effort described above, the new isocyanide ligand, 2,4,6-triisocyanomesitylene, was synthesized and its structural features were characterized by using X-ray diffraction analysis. This ligand and its 1,4-diisocyanobenzene analog, where the respective isocyanides are 120° and 180° disposed, were utilized to prepare *N*-aryl-*N*′-alkylpyridyl β-diketiminato copper(I) dinuclear and trinuclear complexes **3**–**6**. The NMR, FT-IR, and X-ray structures of the complexes indicate that the pyridine ring nitrogen in the pyridyl arm is not coordinated with the copper(I) center and isocyanide binds in its place. A comparison of CN stretching frequencies shows that π-back bonding from the copper(I) center to the isocyanide group in 2,6-xylylisocyanide containing *N*-aryl-*N*′-alkylpyridyl β-diketiminate complexes is enhanced by more strongly electron donating substituents on the β-diketiminate. Moreover, a π-back bonding from Cu(I) to the isocyanide moieties take place in **3**–**6** relative to complexes of 2,6-xylylisocyanide. DFT analysis indicates that 1,4-diisocyanobenzene and 2,4,6-triisocyanomesitylene ligands have enhanced π-accepting abilities relative to that of 2,6-xylylisocyanide as a result of their lower LUMO energies. Furthermore, the results show that 1,4-diisocyanobenzene and 2,4,6-triisocyanomesitylene ligands act as bridging units in metal complexes with unique linear and triangular coordination sites.

4. Experimental section

All manipulations carried out under an atmosphere of purified dinitrogen using standard Schlenk techniques. Chemical reagents were purchased from Aldrich Chemical Co. Ltd., Lancaster Chemicals Ltd. or Fluka Ltd. IR spectra were recorded on a Bruker Optics FTIR Alpha OPUS. ^{1}H NMR and ^{13}C NMR spectra were acquired on JEOL-400 NMR. Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer. Cu**L1** and Cu**L2** were synthesized by using a previously reported method [18]. 1,4-Diisocyanobenzene was synthesized by using a previously reported method[24]. 2,4,6-Triaminomesitylene was synthesized using a slight modification of a previously reported method[26].

4.1. Preparation of 2,4,6-Triisocyanomesitylene

Mesitylene (10 mL, 71.6 mmol) was slowly added to a mixture of 42 mL sulfuric acid and 21 mL fuming nitric acid at 0 ℃. The mixture was stirred at 0 ℃ for 2 h and poured onto ice. Precipitated solid was separated by filtration, and washed with water and methanol. A solution of the solid in ethanol was stirred at reflux overnight, and filtered to give a solid that was dried in vacuum, giving 10.4 g (57%) of 2,4,6-trinitromesitylene as a white solid. 2,4,6-Trinitromesitylene (3.0 g, 11.8 mmol) was stirred with $SnCl_2{\cdot}2H_2O$ (31.8 g, 140.9 mmol) in concentrated HCl (300 mL) at 110 ℃ for 5 h. The solution was carefully made basic at 0 ℃ by addition of concentrated aq·NH_3 and extracted with dichloromethane. The extracts were dried over by $MgSO_4$ and concentrated

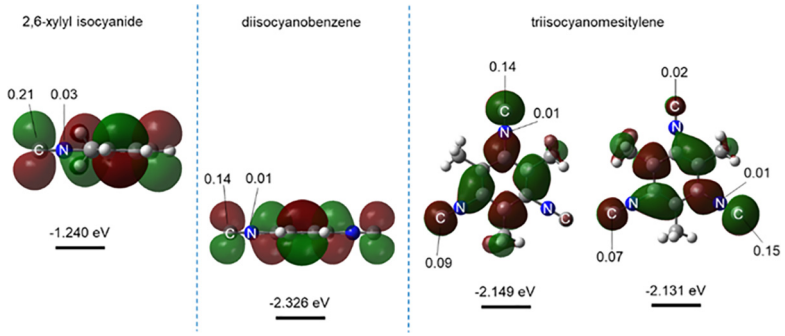


Fig. 6. Calculated LUMO energies and populations of isocyanide ligands.

in vacuum to give 1.2 g (50%) of 2,4,6-triaminomesitylene as a pale-yellow solid. A solution of 2,4,6-triaminomesitylene (1.2 g, 7 mmol) and formic acid 3 mL in toluene (100 mL) was stirred at refluxed for 4 h, cooled to room temperature, and filtered. The precipitate was washed with ether giving a resulting brown solid containing 2,4,6-triformamidomesitylene. To a solution of 2,4,6-triformamidomesitylene and triethylamine (12 mL) in CH_2Cl_2 (100 mL) was slowly added $POCl_3$ (3 mL) at 0 ℃. The mixture was stirred at 0℃ for 1 h and at room temperature for 14 h, followed by slow addition of 10% $Na_2CO_{3(aq)}$ at 0 ℃. Extraction with dichloromethane gave an the organic layer that was dried over $MgSO_4$ and concentrated in vacuum to give a residue that was subjected to silica gel column chromatography (EA:Hexane = 5:100) to give 2,4,6-triisocyanomesitylene as a white solid. Yield: 512 mg (25%). ^{1}H NMR ($CDCl_3$, 400 Hz, 298 K, δ): 2.56 (s, 9H, Ph(CH_3)). ^{13}C NMR ($CDCl_3$, 400 Hz, 298 K, δ): 171.68(C≡N), 133.61(C_6H_6), 125.98(C_6H_6), 16.43(CH_3). IR(Hexane): ν_{CNR} = 2115 cm^{-1}. Anal. Calcd for $C_{12}H_9N_3$: C, 73.83; H, 4.65; N, 21.52. Found: C, 73.89; H, 4.72; N, 21.34.

Caution: Polynitroaromatic compounds are explosive; proper precautions and protective equipment (shields, glasses) should be used during even small-scale experiments.

4.2. General procedures for Synthesis of Di- and Tri-Isocyanide Cu(I) complexes

Under an inert atmosphere, the appropriate complex (Cu**L1** or Cu**L2)** (0.36 mmol) in toluene (20 mL) was added to a half equivalent amount of 1,4-diisocyanobenzene or a one-third equivalent amount of 2,4,6-triisocyanomesitylene in toluene (10 mL). The resulting solution was stirred for 1 h, while the color changed from clear red–orange solution to a yellow-orange suspension solution. The product was collected by using filtration and dried by vacuum. All complexes were recrystallized from hexane at −20 ℃ to form yellow crystal.

3: Yield: 51.8%. ^{1}H NMR (C_6D_6, 400 Hz, 298 K, δ): 8.47 (d, 2H, *J* = 4 Hz, Py1), 7.44 (d, 2H, *J* = 8 Hz, Py4), 7.00–7.19 (m, 6H, Py + Ph), 6.57 (d, 4H, *J* = 8 Hz, Py2), 5.79 (s, 4H, Ph(C≡N)), 5.34 (s, 4H, CH_2Py), 4.92 (s, 2H, CH(C═N)$_2$), 3.53 (m, 4H, *J* = 8 Hz, PhCH(Me)$_2$), 1.95 (s, 6H, CH_3(C═N)), 1.81 (s, 6H, CH_3(C═N)), 1.33 (d, 12H, *J* = 8 Hz, PhCH(Me)$_2$), 1.28 (d, 12H, *J* = 8 Hz, PhCH(Me)$_2$). ^{13}C NMR (C_6D_6, 100 Hz, 298 K, δ): 166.7 (C═N), 164.90 (Py5), 163.53 (C═N), 152.42 (C≡N), 150.66 (Py1), 149.94 (*ipso* Ph), 141.30 (*ortho* Ph), 136.60 (Py3), 127.09 (*para* Ph), 124.68 (*meta* Ph), 124.02 (Ph(C≡N)), 122.16 (Py4), 121.92 (Py2), 96.28 (CH(C═N)$_2$), 62.59 (CH_2Py), 28.77 (PhCH(Me)$_2$), 25.37 (PhCH(Me)$_2$), 24.03 (CH_3(C═N)), 23.86 (PhCH(Me)$_2$), 22.66 (CH_3(C═N)). IR(-toluene): ν_{CNR} = 2111 cm^{-1}. Anal. Calcd for $C_{54}H_{64}N_8$: C,68.11; H, 6.72; N, 11.77. Found: C, 68.09; H, 6.89; N, 11.68.

4: Yield: 32.6%. ^{1}H NMR (C_6D_6, 400 Hz, 298 K, δ): 8.47 (d, 2H, *J* = 4 Hz, Py1), 7.06–7.20 (m, 6H, Py + Ph), 6.91 (d, 2H, *J* = 8 Hz, Py4), 6.63 (td, 2H, *J* = 8 Hz, Py3), 6.15 (s, 4H, Ph(C≡N)), 4.90 (s, 2H, CH(C═N)$_2$), 4.2 (t, 4H, CH_2CH_2Py), 3.54 (m, 4H, *J* = 8 Hz, PhCH(Me)$_2$), 3.42 (t, 4H, *J* = 8 Hz, CH_2CH_2Py), 2.00 (s, 6H, CH_3(C═N)), 1.82 (s, 6H, CH_3(C═N)), 1.34 (d, 12H, *J* = 8 Hz, PhCH(Me)$_2$), 1.29 (d, 12H, *J* = 8 Hz, PhCH(Me)$_2$). ^{13}C NMR (C_6D_6, 100 Hz, 298 K, δ): 165.70 (C═N), 162.79(C═N), 161.79 (Py5), 153.34 (C≡N), 150.88 (*ipso* Ph), 150.34 (Py1), 141.54 (*ortho* Ph), 136.15 (Py3), 127.47 (Ph(C N)), 124.53 (Py4), 124.06 (*para* Ph), 123.98 (*meta* Ph), 121.62 (Py2), 96.03 (CH(C═N)$_2$), 55.83 (CH_2CH_2-Py), 44.47 (CH_2CH_2Py), 28.70 (PhCH(Me)$_2$), 25.48 (CH_3(C═N)), 24.11 (PhCH(Me)$_2$), 23.85 (CH_3(C═N)), 22.75 (CH_3(C═N)). IR(toluene): ν_{CNR} = 2109 cm^{-1}. Anal. Calcd for $C_{56}H_{68}N_8$: C, 68.61; H, 6.94; N, 11.43. Found: C, 68.49; H, 7.17; N, 11.24.

5: Yield: 82.7%. ^{1}H NMR (C_6D_6, 400 Hz, 298 K, δ): 8.57 (d, 3H, *J* = 4.8 Hz, Py1), 7.44(d, 3H, *J* = 4 Hz, Py3), 7.26 (td,3H, *J* = 2,7.6 Hz, Py2), 7.13–7.21 (m, 9H, Ph), 6.73 (dd, 3H, *J* = 5.2,6.8 Hz, Py4), 5.34 (s, 6H, CH_2Py), 4.93 (s, 3H, CH(C═N)$_2$), 3.52 (m, 6H, *J* = 6.8 Hz, PhCH(Me)$_2$), 1.97 (s, 9H, CH_3(C═N)), 1.83 (s, 9H, CH_3(C═N)), 1.32 (m, 18H, PhCH(Me)$_2$), 1.229 (s, 9H, PhCH$_3$(C≡N)).^{13}C NMR (C_6D_6, 100 Hz, 298 K, δ): 165.89, 164.48, 162.94, 150.13 ,149.36 ,140.45, 135.93, 131.29, 125.97, 124.16, 123.42, 121.34, 124.02, 122.16, 121.92, 96.28, 62.59, 28.77, 25.37, 24.03, 23.86, 22.66. IR(toluene): ν_{CNR} = 2101 cm^{-1}. Anal. Calcd for $C_{81}H_{108}Cu_3N_{12}$: C, 67.54; H, 7.56; N, 11.67. Found: C, 67.48; H, 7.67; N, 11.54.

6: Yield: 40.49%. ^{1}H NMR (C_6D_6, 400 Hz, 298 K, δ): 8.53(dq, 3H, *J* = 4.8,0.8 Hz, Py1), 7.11–7.19 (m, 12H, Ph + Py3), 6.96 (td,3H, *J* = 7.6,0.8 Hz, Py4), 6.67 (ddd, 3H, *J* = 7.6,4.8,1.2 Hz, Py2), 4.90 (s, 3H, CH(C═N)$_2$), 4.16 (t, 6H, J = 8, CH_2CH_2Py), 3.50 (m, 12H, PhCH(Me)$_2$ + CH_2CH_2Py), 2.00 (s, 9H, CH_3(C═N)), 1.83 (s, 9H, CH_3(C═N)) , 1.65 (s, 9H, PhCH$_3$(C≡N)), 1.34 (m, 18H, *J* = 6.8 Hz, PhCH(Me)$_2$) , 1.29 (m, 18H, *J* = 7.2 Hz, PhCH(Me)$_2$). ^{13}C NMR (C_6D_6, 400 Hz, 298 K, δ): 165.18, 162.17, 161.09, 154.89(C≡N), 150.39, 149.85, 140.59, 135.79, 132.05, 128.06, 126.31, 124.06, 123.38, 123.17, 121.15, 95.35, 55.04, 44.11, 28.07, 25.04, 23.45, 23.10, 22.31, 15.37. IR(toluene): ν_{CNR} = 2100 cm^{-1}. Anal. Calcd for $C_{84}H_{114}Cu_3N_{12}$: C, 68.05; H, 7.75; N, 11.34. Found: C, 68.19; H, 7.87; N, 11.26.

X-ray Crystal Structure Determination. Single crystals of 2,4,6-triisocyanomesitylene and complexes **3**–**6** suitable for X-ray diffraction analysis were grown from a concentrated hexane solution at −20 ℃. All single-crystal X-ray diffraction data were recorded on a Bruker Nonius Kappa CCD diffractometer using λ (Mo K$_\alpha$) radiation (λ = 0.71073 Å). The data collection was executed using the *SMART* program[47]. Cell refinement and data reduction were made with the *SAINT* program[48]. The structures were determined using the *SHELXTL/PC* program[47] and refined using full-matrix least squares. All non-H atoms were refined anisotropically, whereas H atoms were placed at calculated positions and included

in the final stage of refinement with fixed parameters. A summary of the relevant crystallographic data for 2,4,6-triisocyanomesitylene and complexes **3**–**6** is provided in Table S2. The B-level alert message for 2,4,6-triisocyanomesitylene and complexes **4**–**6** is addressed in supporting information.

4.3. Computational methods

DFT wave function analysis was performed at B3LYP/Def2-TZVP level. Crystal structures of isocyanide ligands were adopted in the analysis.

CRediT authorship contribution statement

Yen-Chung Huang: Investigation, Data curation, Visualization, Writing - original draft. **Hsing-Yin Chen:** Methodology, Resources. **Yu-Lun Chang:** Methodology, Resources. **Punitharaj Vasanthakumar:** Writing - original draft. **Shih-Yun Chen:** Investigation, Data curation. **Chai-Lin Kao:** Project administration, Funding acquisition. **Carol Hsin-Yi Wu:** Funding acquisition. **Sodio C.N. Hsu:** Conceptualization, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

CCDC 2007072, 2007051, 2007064, 2007071, and 2007106 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Additional figures (Figures S1–S13), Table S1 - S2, and crystallographic data in CIF format for the structure determinations have been presented. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2020.114828.

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