

## Synthesis and characterization of Cu(I) and Cu(II) complexes containing ketimate ligands

Shih-Hsien Hsu<sup>a</sup>, Chen-Yi Li<sup>a</sup>, Yi-Wen Chiu<sup>a</sup>, Mei-Chun Chiu<sup>a</sup>, Yu-Ling Lien<sup>a</sup>,  
Pei-Cheng Kuo<sup>a</sup>, Hon Man Lee<sup>a</sup>, Jui-Hsien Huang<sup>a,\*</sup>, Cheu-Pyeng Cheng<sup>b</sup>

<sup>a</sup> Department of Chemistry, National Changhua University of Education, Changhua 50058, Taiwan

<sup>b</sup> Department of Chemistry, National Ting-Hua University, Hsinchu, Taiwan

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### Abstract

A series of Cu(I) and Cu(II) complexes containing substituted ketimate ligands was synthesized. Reaction of CuCl<sub>2</sub> with 2 equiv. of Li[OC(Me)CHC(Me)N(Ar)] in toluene generated dark green solid of Cu[OC(Me)CHC(Me)N(Ar)]<sub>2</sub> (**1**). Similarly, Cu(I) complex, {Cu[OC(Me)CHC(Me)N(Ar)]Li[OC(Me)CHC(Me)N(Ar)]}<sub>2</sub> (**2**) was synthesized by reacting 2 equiv. of Li[OC(Me)CHC(Me)N(Ar)] with CuCl in toluene at room temperature for 12 h. While the reaction of CuCl with Li[OC(Me)CHC(Me)N(Ar)] in the presence of triphenylphosphine in THF solution at room temperature, a three-coordinated Cu[OC(Me)CHC(Me)N(Ar)](PPh<sub>3</sub>) (**3**) can be isolated in high yield. Replacing the PPh<sub>3</sub> of **3** with *N*-heterocarbene (NHC) generates Cu[OC(Me)CHC(Me)N(Ar)](NHC) (**4**) in low yield. Complexes **2**, **3**, and **4** were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies and all molecules were structurally characterized by X-ray diffractometry. Two coordination modes of ketimate ligands were found in the molecular structure of **2**, one of which is copper-coordinated terminal ketimates and the other is lithium–copper-coordinated bridging ketimates.

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**Keywords:** Copper; NHC carbene; Ketimate

### 1. Introduction

The coordination chemistry of using β-diketimate derivatives [1] bearing bulky substituents has been studied with wide variety of metals due to easy accessibility of ligands synthesis, inexpensive of the starting material, and controllable of steric and electronic effects. The bulky β-diketimate ligands indeed work effectively in preventing the decomposition of metal complexes by protecting the metal centers using their bulky substituents [2]. We conceived that the bulky substituents of β-diketimate might prevent the reactions of metal complexes with other mole-

cules making these kinetically more stable. Therefore, we adopted the strategy to use bidentate ligands with bulky substituents on one side to protect the metal centers keeping open ends on the other side to increase the activity of the metal complexes. We have demonstrated the use of substituted ketimates [3] as ancillary ligands to form compounds of group 13 [4] and early transition metals [5]. We now have extended the metals from main group and early transition metals to the late transition metals. Herein we report the syntheses of a series of Cu(I) and Cu(II) complexes containing ketimate ligands, [OC(Me)CHC(Me)NH(Ar)] where Ar = 2,6-diisopropylphenyl and measurements of their structures and magnetic properties. The reactivities of β-diketimate copper complexes have also been studied extensively in the literature [6,7]. Therefore, we also tried some reactions of the synthesized Cu

\* Corresponding author. Tel.: +886 4 7232105; fax: +886 4 7211190.  
E-mail address: [juihuang@cc.ncue.edu.tw](mailto:juihuang@cc.ncue.edu.tw) (J.-H. Huang).

complexes with other coordinating ligands and oxygen molecule.

## 2. Results and discussion

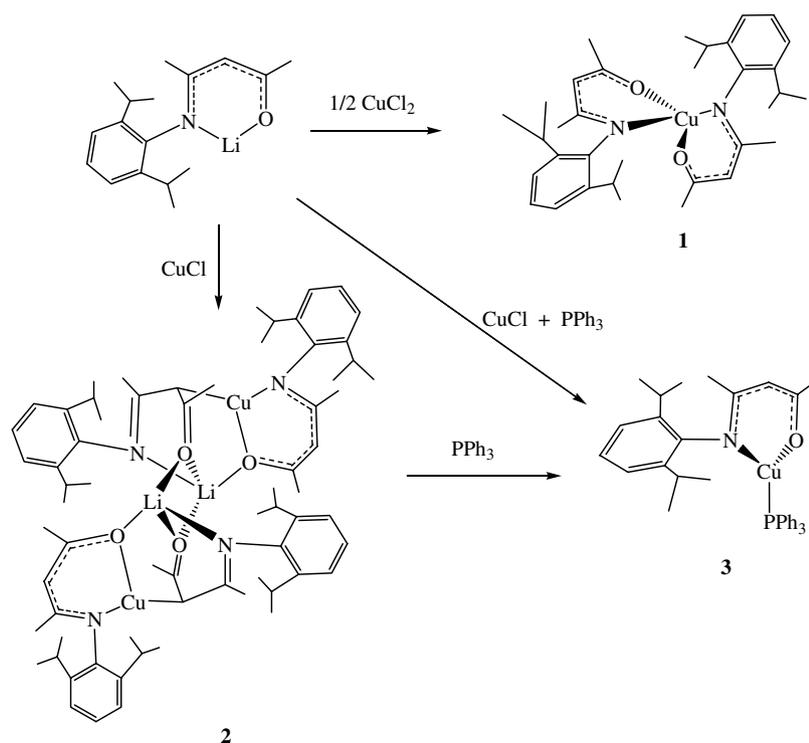
### 2.1. Synthesis and characterization of complexes **1**, **2**, **3**, and **4**

Reaction of  $\text{CuCl}_2$  with 2 equiv. of  $\text{Li}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})]$  [4b] in toluene generated dark green solid of  $\text{Cu}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})]_2$  (**1**) in 63% yield (Scheme 1). Attempts to obtain mono-ketiminate copper complex by reacting  $\text{CuCl}_2$  with 1 equiv. of  $\text{Li}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})]$ , however, leading to the formation of complex **1** only. No NMR signals were observed for the paramagnetic Cu(II) complex. However, we did observe EPR resonances for **1** and the data will be discussed in next section.

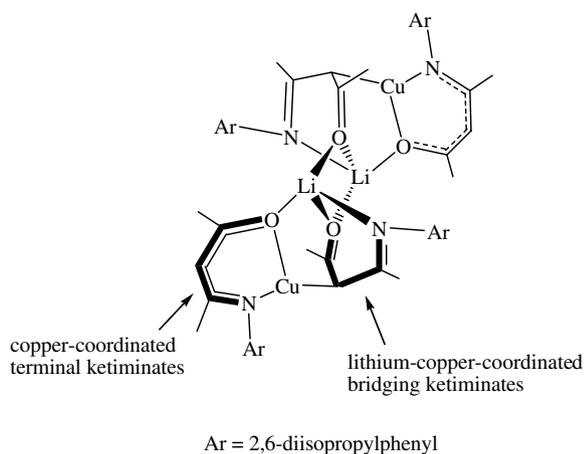
The Cu(I) complex,  $\{\text{Cu}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})]-\text{Li}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})]\}_2$  (**2**) was synthesized by reacting 2:1 ratio of  $\text{Li}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})]$  and  $\text{CuCl}$  in toluene at room temperature for 12 h. While the reaction was performed at 1:1 ratio of  $\text{Li}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})]$  and  $\text{CuCl}$ , **2** was the only product isolated; however, the yield is much lower than that of using 2:1 ratio. Complex **2** was characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. However, the NMR spectral data are very complicated due to the unsymmetrical structure of **2**.  $^{13}\text{C}$  DEPT and  $^1\text{H}$ -coupled spectra as well as 2-D  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectra obtained from a 600 MHz NMR spectrometer were utilized to illustrate the molecular structure of complex **2**.

Noticeably, there are two coordination modes of ketiminate ligands presented in the molecular structure of complex **2**, one of which is copper-coordinated terminal ketiminates and the other is lithium–copper-coordinated bridging ketiminates (Scheme 2). Therefore, the methine protons for the backbone of the terminal and bridging ketiminates were observed at  $\delta$  4.90 and 4.47, respectively. Again, the terminal ketiminate methine carbon is likely to be  $\text{sp}^2$  hybridized with the chemical shift at  $\delta$  96.4 and  $J_{\text{CH}}$  coupling constant at 154 Hz while the bridging ketiminate methine carbon is more like a  $\text{sp}^3$  hybridized with the chemical shift at  $\delta$  69.3 where the value of  $J_{\text{CH}}$  coupling constant is 146 Hz [8]. While the reaction of  $\text{CuCl}$  and  $\text{Li}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})]$  in 1:1 ratio with the presence of triphenylphosphine in THF solution at room temperature, a three-coordinated  $\text{Cu}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})]-(\text{PPh}_3)$  (**3**) can be isolated in high yield. Compound **3** can also be obtained by reacting **2** with  $\text{PPh}_3$  in solution; however, the isolation yield is low. Again, the copper atom of complex **3** exists a  $d^{10}$  electronic configuration and therefore the complex is NMR active and EPR silent. Indeed, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3** show a distinct methine resonance for the backbone of the substituted ketiminate ligand at  $\delta$  5.30 and 96.7, respectively. The methine and methyl protons of the isopropyl groups appear as a septet ( $\delta$  3.39) and two doublets ( $\delta$  0.81 and 1.14).

Replacing phosphine ligand by NHC carbene in organometallic complexes have been seen very often in the literature due to the probability of finding more active catalysts [9]. Therefore we also tried the reactions of compound **3**



Scheme 1.

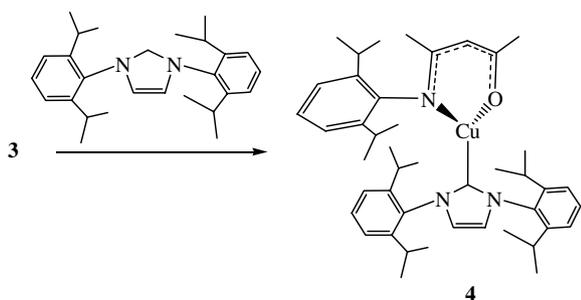


Scheme 2.

with NHC ligands. Reaction of **3** with NHC (*N,N'*-bis(2,6-diphenyl)imidazol-2-ylidene) in THF results the  $\text{PPh}_3$  replaced by NHC to yield  $\text{Cu}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})]\text{-(NHC)}$  (**4**) (Scheme 3). The low reaction yield may result from the lost of the recrystallization and isolation.  $^1\text{H}$  NMR spectrum of **4** shows that the methine proton of ketiminate backbone and the  $\text{CH}=\text{CH}$  protons of the NHC ring appeared at  $\delta$  5.00 and 6.40, respectively. The  $^{13}\text{C}$  NMR spectrum for the  $\text{CH}=\text{CH}$  carbons of the NHC ring exhibits a single resonance at  $\delta$  122.6 with a very large coupling constant ( $J_{\text{CH}} = 194$  Hz). Similarly the coordination NHC carbene is evidenced by higher field shift of NCN carbon from  $\delta$  211.0–188.3.

## 2.2. EPR study of **1**

At 25 °C, the EPR spectrum of **1** in toluene can be interpreted by the presence of an unpaired electron ( $g_{\text{iso}} = 2.1059$ ) interacting with a copper nucleus ( $A_{\text{Cu}} = 73.82$  G) and 2 equiv. nucleus ( $A_{\text{N}} = 11.60$  G). When the solution is immersed in a liquid nitrogen, the EPR spectrum was anisotropic with the following parameters:  $g_x = 2.2117$ ,  $g_y = 2.0349$ ,  $g_z = 2.0096$ ;  $A_{\text{Cu}x} = 173.4$  G,  $A_{\text{Cu}y} = 24$  G,  $A_{\text{Cu}z} = 20$  G;  $A_{\text{N}x} = 10.4$  G,  $A_{\text{N}y} = 12$  G,  $A_{\text{N}z} = 10$  G. Both the solution and solid EPR parameters are consistent with the assignment of the structure of **1**.



Scheme 3.

## 2.3. Reactivity study of complexes **2**, **3**, and **4**

The reactions of Cu(I) complexes **2**, **3**, and **4** with oxygen molecules are monitored with  $^1\text{H}$  NMR spectra in  $\text{C}_6\text{D}_6$  in J-Young NMR tubes. Detail procedures can be seen in Section 3. The results show that complex **2** reacted fast with oxygen molecules and color changed from yellow to deep brown. The sharp resonances of **2** also became very broad and only a few resonances at ca.  $\delta$  2.0 were observed. Similarly, complex **3** can also react with oxygen atoms fast and color changed from yellow to deep brown too. Only triphenylphosphine oxide resonances were observed. A bulk reaction of **3** with  $\text{O}_2$  in  $\text{CH}_2\text{Cl}_2$  in a Schlenk flask results the isolation of black crystal of **1**, which has been confirmed by X-ray crystallography or NMR spectroscopy. A large quantity of triphenylphosphine oxide was also observed in the residual of the solution. No terminal (Cu–O) or bridging (Cu–O–Cu) oxo compound was observed or isolated. However, while complex **4** reacted with oxygen molecules, the reaction remained unchanged after one day. Apparently the NHC ligands binded to Cu(I) atom strongly preventing the oxidization of Cu(I) to Cu(II) by oxygen. Attempting to isolate the products of complexes **2** and **3** with oxygen molecules is still in processing.

## 2.4. Molecular structures of **1**, **2**, **3**, and **4**

Crystal structures of complexes **1**, **2**, **3**, and **4** were studied and the summaries of data collections and selected bond lengths and angles were shown in Tables 1 and 2, respectively. The dark green black cubic crystals of **1** were obtained from a saturated toluene solution of the complex. The crystal structure of **1** is shown in Fig. 1. Complex **1** represents a distorted square planar geometry, in which two ketiminate bidentate ligands are held in trans positions where the  $\text{O}(1)\text{--Cu--O}(1\text{A})$  and  $\text{N}(1)\text{--Cu--N}(1\text{A})$  angles are  $153.42(7)^\circ$  and  $153.74(7)^\circ$ , respectively. The dihedral angle of the two copper–ketiminate chelate rings is  $41.5^\circ$ . The trans arrangement around the Cu center avoids steric repulsions of the bulky 2,6-diisopropylphenyl groups. The structure is similar to the reported copper ketiminate complex [10].

Crystals of **2** were obtained from a concentrated toluene solution at  $-20$  °C. There are two independent molecules of **2** and two toluene molecules in form the asymmetrical unit. One of the methyl groups of toluene molecules is disordered and was splitted by a 50/50 ratio. The geometries and bond parameters of the two molecules are very similar; therefore, only one of the structures is described here (Fig. 2). The molecular structure of **2** contains two three-coordinate terminal ketiminate–copper fragments and two four-coordinate bridging ketiminate–lithium fragments. The two four-coordinate bridging ketiminate–lithium fragments form a  $\text{Li}_2\text{O}_2$  square planar core in which the lithium atoms were bound to the oxygen atoms of the terminal ketiminate–copper fragments and the methine

Table 1  
The summary of crystallographic data for complexes 1–4

	1	2	3	4
Formula	C <sub>34</sub> H <sub>48</sub> CuN <sub>2</sub> O <sub>2</sub>	C <sub>78.5</sub> H <sub>106.5</sub> Cu <sub>2</sub> Li <sub>2</sub> N <sub>4</sub> O <sub>4</sub>	C <sub>35</sub> H <sub>39</sub> CuNOP	C <sub>44</sub> H <sub>60</sub> CuN <sub>3</sub> O
Fw	580.28	1131.14	584.18	710.49
Temperature (K)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	C2/c	P $\bar{1}$	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n
a (Å)	24.0933(13)	8.8465(3)	17.2066(19)	11.1842(3)
b (Å)	11.5163(6)	19.1370(8)	11.3098(14)	15.9524(5)
c (Å)	12.1798(7)	22.7828(9)	16.434(2)	23.3328(6)
$\alpha$ (°)		93.298(2)		
$\beta$ (°)	109.5180(2)	96.876(2)	100.819(4)	96.5240(10)
$\gamma$ (°)		98.984(2)		
Volume (Å <sup>3</sup> )/Z	3185.3(3)/4	3770.9(3)/2	3141.2(6)/4	4136.0(2)/4
Density (calc.) (Mg/m <sup>3</sup> )	1.210	1.155	1.235	1.141
Absorption coefficient (mm <sup>-1</sup> )	0.716	0.612	0.773	0.562
F(000)	1244	1403	1232	1528
Crystal size (mm)	0.42 × 0.25 × 0.17	0.25 × 0.09 × 0.08	0.43 × 0.36 × 0.26	0.46 × 0.28 × 0.25
$\theta$ Range (°)	1.79–28.97	0.90–29.06	2.17–29.13	1.55–29.98
Number of reflections collected	23808	57726	27777	46742
Number of independent reflections	4232 ( $R_{\text{int}} = 0.0471$ )	20066 ( $R_{\text{int}} = 0.1058$ )	8333 ( $R_{\text{int}} = 0.0403$ )	10845 ( $R_{\text{int}} = 0.0254$ )
Maximum and minimum transmission	0.8879 and 0.7529	0.9527 and 0.8620	0.8243 and 0.7323	0.8722 and 0.7820
Number of data/restraints/parameters	4232/0/183	20066/0/846	8333/0/358	10,845/0/456
Goodness-of-fit on $F^2$	1.053	0.963	1.076	1.059
Final R indices [ $I > 2\sigma(I)$ ], $R_1^a$ , $wR_2^b$	0.0341, 0.0821	0.0616, 0.1342	0.0379, 0.1011	0.0464, 0.1219
R indices (all data), $R_1^a$ , $wR_2^b$	0.0442, 0.0857	0.1561, 0.1707	0.0564, 0.1078	0.0691, 0.1320
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.429 and -0.320	0.836 and -0.439	0.504 and -0.636	1.706 and -0.973

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$^b wR_2 = \frac{[\sum (\omega(F_o^2 - F_c^2))^2]}{[\sum (\omega(F_o^2))]^{1/2}}$$

carbons of the bridging ketimate–lithium fragments were connected to the copper atoms (Fig. 3). The lithium atoms can be described as trigonal pyramidal while the geometry about copper atoms were shown as T shaped geometries where the C(20)–Cu(1)–N(1) is 158.43(13)°. A more careful examination of the bond distances of the ketimate backbones of complex 2, we have found that the bridging ketimate backbones tend to exist with a C=O (ca. 1.268 Å), a C=N (ca. 1.302 Å) bond, and a sp<sup>3</sup> hybrid methine carbon atom. While examination of the terminal ketimate NCCCO backbones showed that the C–O and C–N bond lengths (ca. 1.286 Å and ca. 1.316 Å, respectively) are longer than the bridging ketimates indicating bond order less than double bonds. In searching the molecular structures of organo-cuprate complexes, there are numerous “Li<sub>x</sub>Cu<sub>y</sub>” aggregates structurally characterized [11]. However, there is only one “Li<sub>2</sub>Cu<sub>2</sub>”, Li<sub>2</sub>Cu<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub>, aggregate found in the literature [12]. Comparing the structures of 1 with Li<sub>2</sub>Cu<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub>, the “Li<sub>2</sub>Cu<sub>2</sub>” array in 1 is more like a dimeric of “LiCu” unit with very long Cu···Cu distance of 7.78 Å where the “Li<sub>2</sub>Cu<sub>2</sub>” array in Li<sub>2</sub>Cu<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub> forms a pseudo square planar with short of Cu···Cu distance of 2.984(1) Å.

The molecular structures of 3 and 4 (Figs. 4 and 5) are both exhibiting three-coordinated geometries and will be discussed together. Both of the structures of complexes 3 and 4 are trigonal planar, with the ketimate N,O atoms and triphenylphosphine P atom or NHC carbon atom taking the trigonal positions. The sums of the bond angles

N(1)–Cu(1)–P(1), N(1)–Cu(1)–O(1), and O(1)–Cu(1)–P(1) for complex 3 and N(1)–Cu(1)–P(1), N(1)–Cu(1)–O(1), and O(1)–Cu(1)–P(1) for complex 4 are both very close to perfect 360°. However, complex 3 is more like Y-shape geometry and complex 4 can be describes as T-shape geometry. Three-coordinated trigonal planar complexes of transition metals with partially filled d shell electrons form T-shape and Y-shape geometries due to the electronic effect or the differential charge donation from the ligands to the metals [13]. Complexes 3 and 4 have the same bidentate ketimate ligands, filled d shell electrons, and similar auxiliary ligands (PPh<sub>3</sub> and NHC), therefore, the geometries differences between complexes 3 and 4 are attributed as the steric effect of the bulkiness of PPh<sub>3</sub> and NHC. The ketimates bind to copper atoms with similar angles (96.48(6)° and 93.16(7)° for 3 and 4, respectively) and their phenyl rings are perpendicular to the Cu–ketimate formed six-membered rings. The bond length of Cu(1)–P(1) for complex 3 (2.1384(5) Å) is in the average for majority complexes of Cu(I)–triphenylphosphine bond lengths [14]. Again, the bond length of Cu(I) to the carbon atom of NHC for complex 4 (1.8946(19) Å) is similar to those of majority complexes of Cu(I)–NHC [15].

In conclusion, we have synthesized a series of Cu(I) and Cu(II) complexes by using lithium salt of bulky ketimate ligand, Li[OC(Me)CHC(Me)N(Ar)]. Complexes 1–4 are fully characterized by spectroscopic techniques and X-ray structure determination. The weaker Cu(I)–P bonding in complex 3 can be replaced by Cu(I)–NHC bonding as

Table 2  
Selected bond lengths (Å) and angles (°) for complexes 1–4

<i>Complex 1</i>			
Cu(1)–O(1A)	1.8931(11)	Cu(1)–O(1)	1.8931(11)
Cu(1)–N(1A)	1.9742(12)	Cu(1)–N(1)	1.9743(12)
O(1)–C(2)	1.2861(19)	N(1)–C(4)	1.3213(19)
C(2)–C(3)	1.378(2)	C(4)–C(3A)	1.411(2)
C(3)–C(4A)	1.411(2)		
O(1A)–Cu(1)–O(1)	153.42(7)	O(1A)–Cu(1)–N(1A)	92.25(5)
O(1)–Cu(1)–N(1A)	93.74(5)	O(1A)–Cu(1)–N(1)	93.74(5)
O(1)–Cu(1)–N(1)	92.24(5)	N(1A)–Cu(1)–N(1)	153.74(7)
<i>Complex 2</i>			
Cu(1)–N(1)	1.915(3)	Cu(1)–C(20)	2.027(3)
Cu(1)–O(1)	2.105(2)	Li(1A)–O(1)	1.921(6)
Li(1A)–N(2)	2.029(6)	Li(1A)–O(2)	1.964(6)
Li(1A)–O(2A)	1.883(6)	Li(1)–O(2A)	1.964(6)
N(1)–C(4)	1.316(4)	C(3)–C(4)	1.418(5)
C(2)–C(3)	1.391(5)	O(1)–C(2)	1.280(4)
Cu(1A)–N(1A)	1.915(3)	Cu(1A)–C(20A)	2.027(3)
N(2)–C(21)	1.302(4)	C(20)–C(21)	1.467(4)
C(19)–C(20)	1.420(5)	O(2)–C(19)	1.268(4)
Cu(1A)–O(1A)	2.105(2)	Li(1)–O(1A)	1.921(6)
Li(1)–N(2A)	2.029(6)	Li(1)–O(2)	1.883(6)
N(1A)–C(4A)	1.316(4)	C(3A)–C(4A)	1.418(5)
N(2A)–C(21A)	1.302(4)	C(20A)–C(21A)	1.467(4)
C(19A)–C(20A)	1.420(5)	O(2A)–C(19A)	1.268(4)
C(2A)–C(3A)	1.391(5)	O(1A)–C(2A)	1.280(4)
Cu(2)–N(3)	1.915(3)	Cu(2)–C(54)	2.035(3)
Cu(2)–O(3)	2.110(2)	Li(2A)–O(3)	1.909(6)
Li(2A)–N(4)	2.029(7)	Li(2A)–O(4)	1.958(6)
Li(2A)–O(4A)	1.867(6)	Li(2)–O(4)	1.867(6)
N(3)–C(38)	1.310(4)	C(37)–C(38)	1.423(5)
C(36)–C(37)	1.384(4)	O(3)–C(36)	1.283(4)
N(4A)–C(55A)	1.291(4)	C(54A)–C(55A)	1.456(4)
C(53A)–C(54A)	1.430(5)	O(4A)–C(53A)	1.261(4)
Cu(2A)–N(3A)	1.915(3)	Cu(2A)–C(54A)	2.035(3)
Cu(2A)–O(3A)	2.110(2)	Li(2)–O(3A)	1.909(6)
Li(2)–N(4A)	2.029(7)	Li(2)–O(4A)	1.958(6)
N(3A)–C(38A)	1.310(4)	C(37A)–C(38A)	1.423(5)
C(36A)–C(37A)	1.384(4)	O(3A)–C(36A)	1.283(4)
N(1)–Cu(1)–O(1)	96.16(10)	C(20)–Cu(1)–O(1)	104.55(11)
N(1)–Cu(1)–C(20)	158.43(13)	N(2)–Li(1A)–O(2A)	126.5(3)
O(2)–Li(1A)–O(2A)	92.1(3)	N(2)–Li(1A)–O(2)	91.4(3)
O(1)–Li(1A)–O(2)	104.3(3)	N(2)–Li(1A)–O(1)	102.6(3)
N(1A)–Cu(1A)–O(1A)	96.16(10)	C(20A)–Cu(1A)–O(1A)	104.55(11)
N(1A)–Cu(1A)–C(20A)	158.43(13)	N(2A)–Li(1)–O(2)	126.5(3)
O(2A)–Li(1)–O(2)	92.1(3)	N(2A)–Li(1)–O(2A)	91.4(3)
O(1A)–Li(1)–O(2A)	104.3(3)	N(2A)–Li(1)–O(1A)	102.6(3)
O(2)–Li(1)–O(1A)	127.8(3)	O(2A)–Li(1A)–O(1)	127.8(3)
N(3)–Cu(2)–O(3)	95.69(10)	C(54)–Cu(2)–O(3)	104.62(11)
N(3)–Cu(2)–C(54)	158.70(12)	N(4)–Li(2A)–O(4)	91.8(3)
O(4)–Li(2A)–O(4A)	92.8(2)	N(4)–Li(2A)–O(4A)	127.2(3)
<i>Complex 3</i>			
Cu(1)–N(1)	1.9341(14)	Cu(1)–O(1)	1.9653(12)
Cu(1)–P(1)	2.1384(5)		
N(1)–Cu(1)–O(1)	96.48(6)	N(1)–Cu(1)–P(1)	143.19(5)
O(1)–Cu(1)–P(1)	120.33(4)		
<i>Complex 4</i>			
Cu(1)–C(18)	1.8946(19)	Cu(1)–N(1)	1.9296(16)
Cu(1)–O(1)	2.0799(15)		
N(1)–Cu(1)–O(1)	93.16(7)	N(1)–Cu(1)–C(18)	161.96(7)
O(1)–Cu(1)–C(18)	104.85(7)		

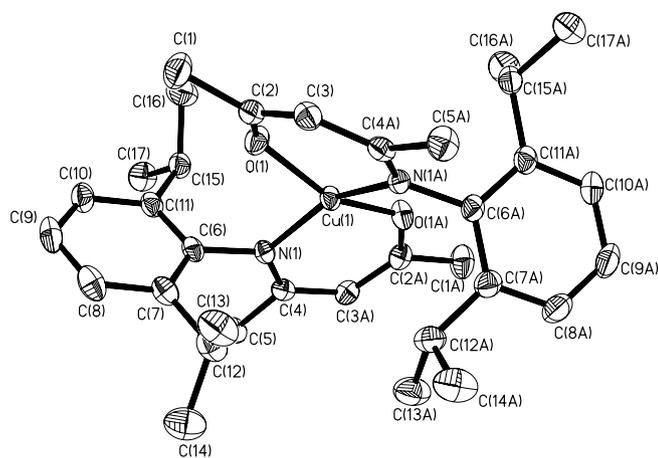


Fig. 1. The molecular diagram for complex 1. The thermal ellipsoids were drawn at 50% probability and all hydrogen atoms were omitted for clarity.

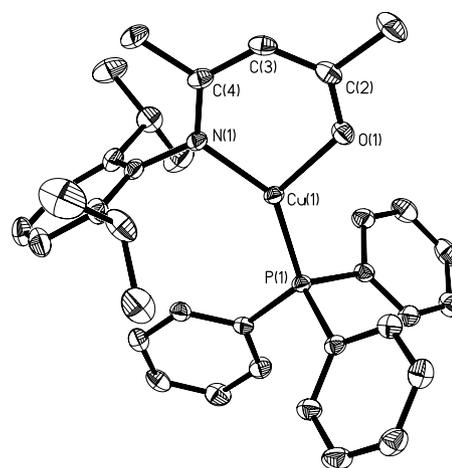


Fig. 4. The molecular structure of complex 3. The thermal ellipsoids were drawn at 30% probability. The toluene molecules and all hydrogen atom were omitted for clarity.

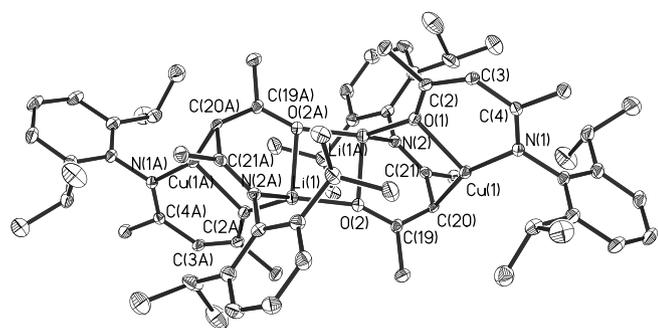


Fig. 2. The molecular structure of complex 2. The thermal ellipsoids were drawn at 30% probability. The toluene molecules and all hydrogen atom were omitted for clarity.

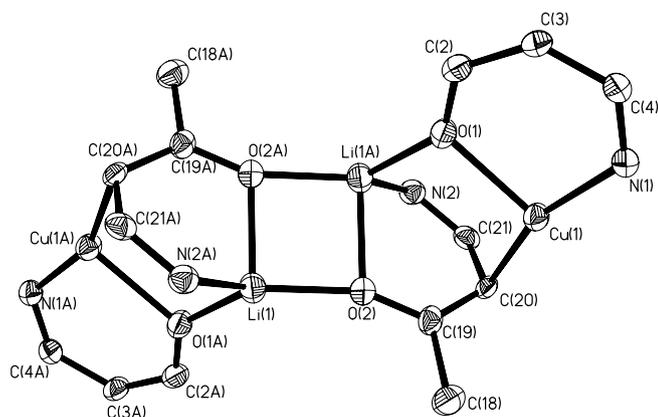


Fig. 3. The core structure of complex 2 including four ketimate backbones, two lithium atoms, and two copper atoms. All the other atoms were omitted for clarity.

showed in Scheme 3. Further studies on the chemistry of complexes 1 and 2 including oxidation of Cu(I) and de-clusterification of Cu(II) complexes and the isolation of reaction products of complexes 2–4 with oxygen atoms are in progress.

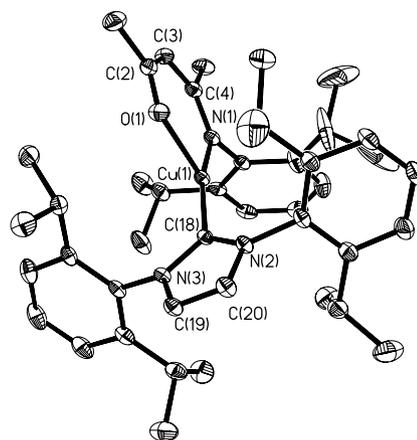


Fig. 5. The molecular structure of complex 4. The thermal ellipsoids were drawn at 30% probability. The toluene molecules and all hydrogen atom were omitted for clarity.

### 3. Experimental

#### 3.1. General procedure

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques or in a glove box. Toluene, heptane, diethyl ether, and tetrahydrofuran were dried by refluxing over sodium benzophenone ketyl.  $\text{CH}_2\text{Cl}_2$  was dried over  $\text{P}_2\text{O}_5$ . NHC (*N,N'*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) was synthesis by follow the published procedure [16]. All solvents were distilled and stored in solvent reservoirs which contained 4 Å molecular sieves and were purged with nitrogen.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance 300 spectrometer. Chemical shifts for  $^1\text{H}$  and  $^{13}\text{C}$  spectra were recorded in ppm relative to the residual protons and  $^{13}\text{C}$  of  $\text{C}_6\text{D}_6$  ( $\delta$  7.16, 128.0). Elemental analyses were performed on a Heraeus CHN–OS Rapid Elemental Analyzer at the Instrument Center, NCHU.

### 3.2. Synthesis of $\text{Cu}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})]_2$ (**1**)

A 50 mL Schleck flask was charged with  $\text{CuCl}_2$  (0.50 g, 3.72 mmol) and  $\text{Li}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})]$  (1.97 g, 7.43 mmol) and cooled to 0 °C. To the flask 30 mL of toluene was added and the solution was stirred at room temperature for 12 h. The solution was filtered through Celite and the filtrate was concentrated to small volume, stored at –20 °C to generate 1.33 g (68% yield) of dark green black crystals. Anal. Calc. for  $\text{C}_{34}\text{H}_{48}\text{N}_2\text{O}_2\text{Cu}$ : C, 70.37; H, 8.34; N, 4.83. Found: C, 69.89; H, 8.85; N, 4.87%.

### 3.3. Synthesis of $\{\text{Cu}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})]\text{Li}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})]\}_2$ (**2**)

A 100 mL Schleck flask was charged with  $\text{CuCl}$  (0.25 g, 2.45 mmol) and  $\text{Li}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})]$  (1.30 g, 4.90 mmol) and cooled to 0 °C. To the flask 80 mL of toluene was added and the solution was stirred at room temperature for 12 h. The solution was filtered through Celite and the filtrate was concentrated to small volume, stored at –20 °C to generate 0.76 g (53% yield) of dark pale yellow crystals.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.17 (d, 6H,  $\text{CHMe}_2$ ), 1.26 (d, 6H,  $\text{CHMe}_2$ ), 1.28 (d, 6H,  $\text{CHMe}_2$ ), 1.30 (d, 6H,  $\text{CHMe}_2$ ), 1.35 (d, 6H,  $\text{CHMe}_2$ ), 1.36 (d, 6H,  $\text{CHMe}_2$ ), 1.37 (d, 6H,  $\text{CHMe}_2$ ), 1.39 (d, 6H,  $\text{CHMe}_2$ ), 1.48 (s, 6H,  $\text{CMe}$ ), 1.52 (s, 6H,  $\text{CMe}$ ), 1.64 (s, 6H,  $\text{CMe}$ ), 1.85 (s, 6H,  $\text{CMe}$ ), 3.18 (m, 2H,  $\text{CHMe}_2$ ), 3.28 (m, 4H,  $\text{CHMe}_2$ ), 3.44 (m, 2H,  $\text{CHMe}_2$ ), 4.47 (s, 2H,  $\text{MeCCHCMe}$ ), 4.90 (s, 2H,  $\text{MeCCHCMe}$ ), 7.10–7.26 (m, 12H, phenyl CH).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ): 22.2 (q,  $J_{\text{CH}} = 126$  Hz,  $\text{CMe}$ ), 23.0 (q,  $J_{\text{CH}} = 128$  Hz,  $\text{CMe}$ ), 23.4 (q,  $J_{\text{CH}} = 125$  Hz,  $\text{CHMe}_2$ ), 23.6 (q,  $J_{\text{CH}} = 125$  Hz,  $\text{CHMe}_2$ ), 23.7 (q,  $J_{\text{CH}} = 125$  Hz,  $\text{CHMe}_2$ ), 23.8 (q,  $J_{\text{CH}} = 130$  Hz,  $\text{CHMe}_2$ ), 24.4 (q,  $J_{\text{CH}} = 130$  Hz,  $\text{CHMe}_2$ ), 24.5 (q,  $J_{\text{CH}} = 130$  Hz,  $\text{CHMe}_2$ ), 24.7 (q,  $J_{\text{CH}} = 128$  Hz,  $\text{CHMe}_2$ ), 25.7 (q,  $J_{\text{CH}} = 126$  Hz,  $\text{CHMe}_2$ ), 27.8 (d,  $J_{\text{CH}} = 128$  Hz,  $\text{CHMe}_2$ ), 28.1 (d,  $J_{\text{CH}} = 126$  Hz,  $\text{CHMe}_2$ ), 28.3 (d,  $J_{\text{CH}} = 129$  Hz,  $\text{CHMe}_2$ ), 28.4 (d,  $J_{\text{CH}} = 125$  Hz,  $\text{CHMe}_2$ ), 28.5 (q,  $J_{\text{CH}} = 125$  Hz,  $\text{CMe}$ ), 29.8 (q,  $J_{\text{CH}} = 126$  Hz,  $\text{CMe}$ ), 69.3 (d,  $J_{\text{CH}} = 146$  Hz,  $\text{MeCCHCMe}$ ), 96.4 (d,  $J_{\text{CH}} = 154$  Hz,  $\text{MeCCHCMe}$ ), 123.1 (d,  $J_{\text{CH}} = 155$  Hz, phenyl-CH), 123.2 (d,  $J_{\text{CH}} = 155$  Hz, phenyl-CH), 123.6 (d,  $J_{\text{CH}} = 155$  Hz, phenyl-CH), 123.7 (d,  $J_{\text{CH}} = 155$  Hz, phenyl-CH), 124.4 (d,  $J_{\text{CH}} = 155$  Hz, phenyl-CH), 124.8 (d,  $J_{\text{CH}} = 155$  Hz, phenyl-CH), 128.3 (s, phenyl  $C_{\text{ipso}}$ ), 128.8 (s, phenyl  $C_{\text{ipso}}$ ), 139.4 (s, phenyl  $C_{\text{ipso}}$ ), 140.0 (s, phenyl  $C_{\text{ipso}}$ ), 146.3 (s, phenyl  $C_{\text{ipso}}$ ), 147.3 (s, phenyl  $C_{\text{ipso}}$ ), 168.9 (s, CN), 169.1 (s, CN), 181.6 (s, CO), 189.1 (s, CO). Anal. Calc. for  $\text{C}_{68}\text{H}_{96}\text{N}_4\text{O}_4\text{Cu}_2\text{Li}_2$ : C, 69.54; H, 8.24; N, 4.77. Found: C, 69.00; H, 8.70; N, 4.72%.

### 3.4. Synthesis of $\text{Cu}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})](\text{PPh}_3)$ (**3**)

A 100 mL Schleck flask charged with  $\text{CuCl}$  (1.10 g, 11.02 mmol),  $\text{Li}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})]$  (2.90 g, 11.02

mmol), and  $\text{PPh}_3$  (2.90 g, 11.02 mmol) was cooled to 0 °C and THF (80 mL) was added. The solution was stirred at room temperature for 12 h. Volatiles were removed under vacuum and the residues were extracted with toluene and filtered through Celite. The filtrate was vacuum dried and solid was washed with heptane to yield 4.89 g of final product (76%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 0.81 (d, 6H,  $\text{CHMe}_2$ ), 1.14 (d, 6H,  $\text{CHMe}_2$ ), 1.70 (s, 3H,  $\text{CMe}$ ), 2.28 (s, 3H,  $\text{CMe}$ ), 3.39 (m, 2H,  $\text{CHMe}_2$ ), 5.30 (s, 1H,  $\text{CMeCHCMe}$ ), 6.95 (m, 10H, phenyl CH), 7.10 (m, 2H, phenyl CH), 7.32 (m, 6H, phenyl CH).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ): 22.9 (q,  $J_{\text{CH}} = 134$  Hz,  $\text{CMe}$ ), 23.5 (q,  $J_{\text{CH}} = 131$  Hz,  $\text{CHMe}_2$ ), 28.2 (d,  $J_{\text{CH}} = 128$  Hz,  $\text{CHMe}_2$ ), 28.8 (q,  $J_{\text{CH}} = 127$  Hz,  $\text{CMe}$ ), 96.7 (d,  $J_{\text{CH}} = 157$  Hz,  $\text{CMeCHCMe}$ ), 123.8 (d,  $J_{\text{CH}} = 154$  Hz, phenyl CH), 124.1 (d,  $J_{\text{CH}} = 158$  Hz, phenyl CH), 128.8 (d,  $J_{\text{CH}} = 159$  Hz, phenyl CH), 128.9 (d,  $J_{\text{CH}} = 159$  Hz, phenyl CH), 129.8 (d,  $J_{\text{CH}} = 159$  Hz, phenyl CH), 133.1 (s, phenyl  $C_{\text{ipso}}$ ), 133.6 (s, phenyl  $C_{\text{ipso}}$ ), 133.9 (d,  $J_{\text{CH}} = 160$  Hz, phenyl CH), 134.2 (d,  $J_{\text{CH}} = 160$  Hz, phenyl CH), 140.3 (s, phenyl  $C_{\text{ipso}}$ ), 148.7 (s, phenyl  $C_{\text{ipso}}$ ), 167.7 (s, CN), 184.3 (s, CO). Anal. Calc. for  $\text{C}_{35}\text{H}_{39}\text{CuNOP}$ : C, 71.96; H, 6.73; N, 2.40. Found: C, 71.55; H, 6.29; N, 2.10%.

### 3.5. Synthesis of $\text{Cu}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})](\text{NHC})$ (**4**)

A 30 mL Schleck flask charged with **3** (0.133 g, 0.22 mmol) and NHC (0.089 g, 0.222 mmol) was cooled to 0 °C and THF (10 mL) was added. The solution was stirred at room temperature for 12 h and solvent was removed under vacuum. The solid was recrystallized from a diethyl ether solution to yield the final product (0.041 g, 27.5%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 0.75 (d, 6H,  $\text{CHMe}_2$ ), 1.05 (d, 12H,  $\text{CHMe}_2$ ), 1.07 (d, 6H,  $\text{CHMe}_2$ ), 1.20 (d, 12H,  $\text{CHMe}_2$ ), 1.50 (s, 3H,  $\text{CMe}$ ), 2.04 (s, 3H,  $\text{CMe}$ ), 2.97 (m, 6H,  $\text{CHMe}_2$ ), 5.00 (s, 1H,  $\text{CMeCHCMe}$ ), 6.40 (s, 2H,  $\text{NCHCHN}$ ), 7.00–7.22 (m, 9H, phenyl CH). 23.3 (q,  $J_{\text{CH}} = 130$  Hz,  $\text{CMe}$  and  $\text{CHMe}_2$ ), 23.82 (q,  $J_{\text{CH}} = 126$  Hz,  $\text{CHMe}_2$ ), 23.87 (q,  $J_{\text{CH}} = 126$  Hz,  $\text{CHMe}_2$ ), 25.2 (q,  $J_{\text{CH}} = 126$  Hz,  $\text{CHMe}_2$ ), 28.1 (d,  $J_{\text{CH}} = 130$  Hz,  $\text{CHMe}_2$ ), 28.6 (d,  $J_{\text{CH}} = 126$  Hz,  $\text{CHMe}_2$ ), 28.8 (q,  $J_{\text{CH}} = 129$  Hz,  $\text{CMe}$ ), 95.2 (d,  $J_{\text{CH}} = 153$  Hz,  $\text{CMeCHCMe}$ ), 122.6 (d,  $J_{\text{CH}} = 194$  Hz,  $\text{NCHCHN}$ ), 123.1 (d,  $J_{\text{CH}} = 150$  Hz, phenyl CH), 123.3 (d,  $J_{\text{CH}} = 158$  Hz, phenyl CH), 124.1 (d,  $J_{\text{CH}} = 158$  Hz, phenyl CH), 128.7 (s, phenyl  $C_{\text{ipso}}$ ), 128.8 (s, phenyl  $C_{\text{ipso}}$ ), 129.7 (d,  $J_{\text{CH}} = 159$  Hz, phenyl CH), 134.0 (d,  $J_{\text{CH}} = 160$  Hz, phenyl CH), 134.3 (d,  $J_{\text{CH}} = 160$  Hz, phenyl CH), 136.9 (s, phenyl  $C_{\text{ipso}}$ ), 139.9 (s, phenyl  $C_{\text{ipso}}$ ), 146.3 (s, phenyl  $C_{\text{ipso}}$ ), 149.3 (s, phenyl  $C_{\text{ipso}}$ ), 166.6 (s, CN), 183.1 (s, CO), 188.3 (s, NCN).

### 3.6. Reactivity studies of complexes **2**, **3**, and **4** with oxygen molecules

Complexes **2–4** were dissolved in  $\text{C}_6\text{D}_6$  in J-Young NMR tubes and then the tubes were immersed in a liquid nitrogen dewar to freeze the solutions. Vacuum was applied

to the NMR tubes to remove the inert gas and then oxygen gas was introduced into the NMR tubes. The pressure of oxygen is no larger than 15 psi.  $^1\text{H}$  NMR spectrometer was used to monitor the reactions.

### 3.7. X-ray structure determination

Crystal data collection, refinement parameter, and bond lengths and angles were listed in Tables 1 and 2, respectively. The crystals were mounted on a goniostat and were collected at 150 K under liquid nitrogen stream. Data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo  $\text{K}\alpha$  radiation. Structural determinations were made using the SHELXTL package of programs. All refinements were carried out by full-matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms are calculated.

### 4. Supplementary material

CCDC 638784, 638785, 638786 and 638787 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. 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.

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