

Synthesis and structures of cyclopentadienyl *N*-heterocyclic carbene copper(I) complexes

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Abstract

A series of cyclopentadienyl *N*-heterocyclic carbene copper complexes CpCu(NHC) were synthesized and structurally characterized. The effect of the substituents at the nitrogen atom of the NHC ligands on the structures and thermally stability was discussed. © 2006 Elsevier B.V. All rights reserved.

Keywords: Cyclopentadienyl; Copper; *N*-heterocyclic carbene; Crystal structure

1. Introduction

N-Heterocyclic carbenes (NHCs) are widely used as ligands in inorganic and organometallic chemistry since Arduengo and coworkers isolated the first stable *N*-heterocyclic carbene in 1991 [1]. Some *N*-heterocyclic carbene copper(I) complexes were synthesized and characterized [2]. Several of them have been demonstrated to be efficient catalysts for some organic reaction, such as allylic substitution reaction (with Grignard reagents) [3], conjugate addition [4], and conjugate reduction [5]. The cyclopentadienyl (Cp) ligand is well-known for its utility as a “stabilizing ligand”, as it has yielded many very thermally stable compounds [6]. However, only a few of η^5 -cyclopentadienyl copper complexes has been structurally characterized [7,8], and some of them were used as precursors in deposition of copper film [9]. As alternatives to traditional phosphine ligands, NHCs are stronger σ -donors and weaker π -acceptors. So NHC as ligand instead of phosphine in such class of complexes maybe change the stability and properties of this class of complexes. Here we report the synthesis and structural characterization of a series of

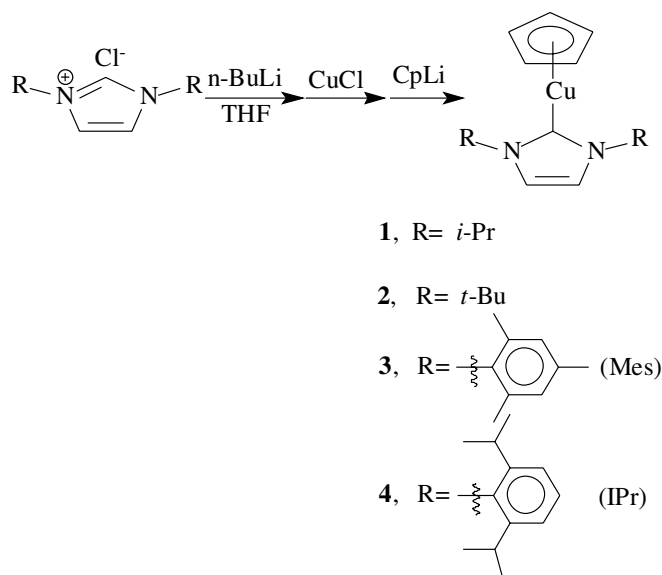
cyclopentadienyl *N*-heterocyclic carbene copper(I) complexes. This is the first report of η^5 -cyclopentadienyl copper complexes with NHC ligands.

2. Results and discussion

The *N*-heterocyclic carbenes were prepared by deprotonation of 1,3-disubstituted imidazolium chloride with *n*-BuLi in THF [10], and the reaction mixture was used for further reaction without separation. Reactions of the *N*-heterocyclic carbenes with CuCl and CpLi gave the corresponding cyclopentadienyl *N*-heterocyclic carbene copper(I) complexes CpCu(NHC) in very high yield (90–95%) (Scheme 1).

These complexes are very air-sensitive in solution, but in solid state, they do not decompose for several days and can be kept for months in an Argon atmosphere. The decomposition temperatures of complexes 1–4 decrease in the order 1 > 3 > 4 > 2, indicating that the thermally stability decreases in the same order. Previous experimental and computational results demonstrate that the electronic differences between these alkyl- and aryl-substituted carbenes are relatively small and the steric hindrance increases in the order I^tPr < IMes < IPr < I^tBu [11]. So it can be concluded that the steric hindrance of the carbene ligand plays an important role on the thermally stability. The ¹H NMR

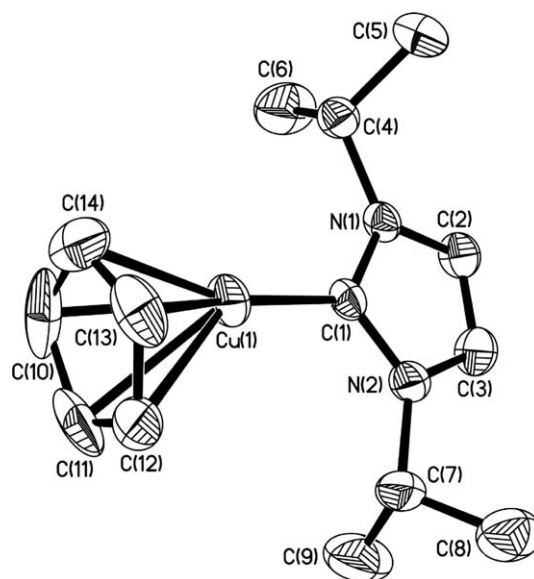
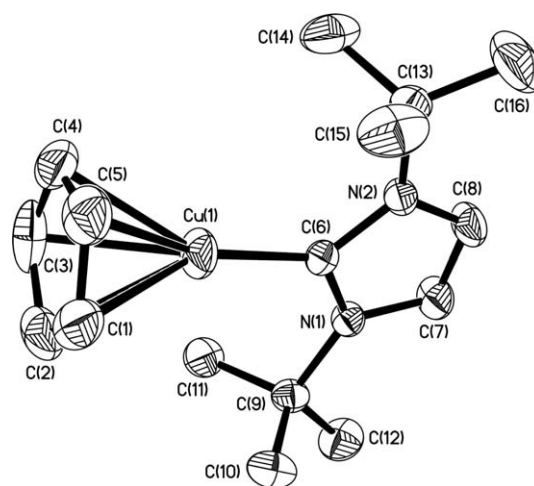
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Scheme 1.

spectra of **1–4** show a singlet for Cp protons at 6.54, 6.56, 5.90, and 5.78 ppm, respectively, suggesting an η^5 -coordination of the cyclopentadienyl to copper. The lower chemical shifts of complexes **3** and **4** can be attributed to the shielding effect of the aromatic substituents at the nitrogen atom of the NHC ligands. The signals of the two imidazole protons appear as a singlet at 6.10, 6.29, 6.01, and 6.31 ppm for complexes **1–4**, respectively. Similar to the imidazolium chloride [12b], the methyl protons of isopropyl groups of complex **4** show two doublets. It can be attributed to the large steric effects of two IPr groups, which increased the intramolecular interaction and limited the free rotation of isopropyl groups. The ^{13}C NMR spectra of **1–4** also show a singlet for Cp carbons at 110.1, 110.1, 95.0, and 95.0 ppm, respectively, further supporting the η^5 -coordination mode of cyclopentadienyl. The ^{13}C NMR spectrum of **3** shows the characteristic low-field resonance for the carbeneic carbon at 179.1 ppm. However, there are no the carbeneic carbon signal in the ^{13}C NMR spectra of complexes **1**, **2**, and **4**. Similar results were also reported in literature [13].

The crystal structures of complexes **1–4** were determined by X-ray diffraction analysis (Figs. 1–4). The four complexes have similar structures. Each copper of the complexes is bonded to the Cp ring in an η^5 -coordination mode, just as the known cyclopentadienyl phosphine copper complexes [7a,7b,7e,7i]. The Cu–Cen (centroid of Cp ring) distances increase with the increasing of the steric bulk of the substituents at the nitrogen atom of the NHC ligands, and are comparable or slightly longer than that of the cyclopentadienyl phosphine copper complexes (Table 1) [7a,7b]. It is worth to note that the average C–C bond lengths of the Cp ring in complexes **1–4** (1.304–1.375 Å) are evidently shorter than that of the cyclopentadienyl phosphine copper complexes (1.381–1.399 Å). The Cu–C_{carbene} distances in complexes **1–4** range

Fig. 1. ORTEP diagram of **1**. Thermal ellipsoids are shown at the 30% level.Fig. 2. ORTEP diagram of **2**. Thermal ellipsoids are shown at the 30% level.

between 1.831 and 1.886 Å, which compare well to those found in other reported monomeric Cu–NHC complexes [2c,2h,2i]. The carbene carbon, copper atom, and the center of the Cp ring are nearly linear in complexes **2**, **3** and one of the three independent molecules of **4** (Cen–Cu–C_{carbene} angle: 172–177°), but with a distortion in complex **1** and two of the three independent molecules of **4** (Cen–Cu–C_{carbene} angle: 165.3°, 166.1°, and 168.5°). The Cp ring planes are nearly perpendicular to the NHC planes with angles range between 82.0° and 89.8° in complexes **1–4**.

In conclusion, the new cyclopentadienyl *N*-heterocyclic carbene copper complexes **1–4** have been synthesized and characterized. The effect of the substituents at the nitrogen atom of the NHC ligands on the structures and thermally stability was also discussed.

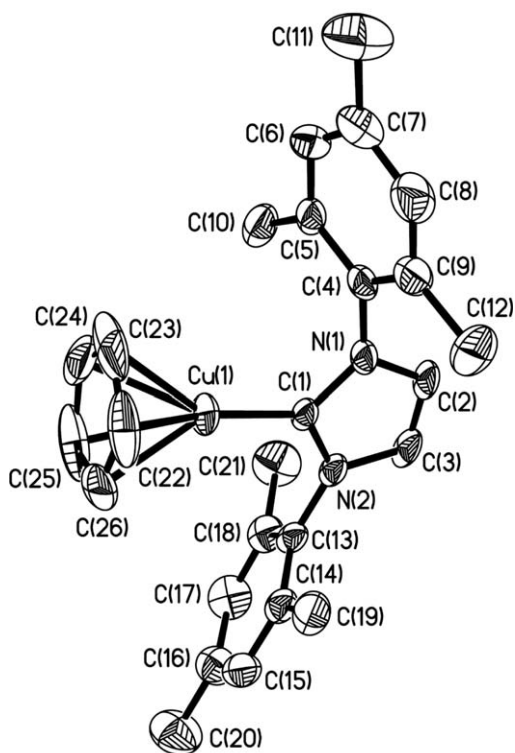


Fig. 3. ORTEP diagram of **3** (One of the two independent molecules). Thermal ellipsoids are shown at the 30% level.

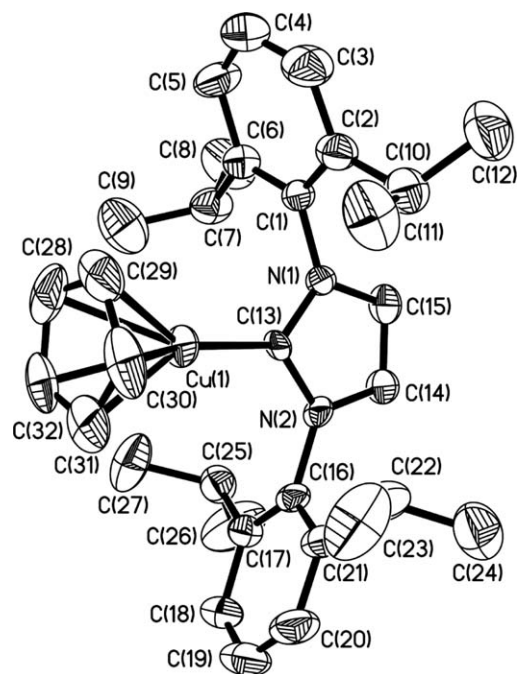


Fig. 4. ORTEP diagram of **4** (One of the three independent molecules). Thermal ellipsoids are shown at the 30% level.

3. Experimental details

3.1. General procedures and starting materials

Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive compounds. All solvents were distilled from appropriate drying agents under argon before use. NMR spectra were recorded on a VARIAN AS-400 instrument. Elemental analyses were performed on a Perkin–Elmer 240C ana-

lyzer. The 1,3-disubstituted imidazolium chlorides were prepared according to literature methods [12].

3.2. General procedures for preparation of complexes **1–4**

A solution of *n*-BuLi (1.9 M, 2.0 mmol) in hexane was added dropwise into the suspension of 1,3-disubstituted imidazolium chloride (2.0 mmol) in THF (30 mL) at 0 °C, then the reaction mixture was allowed slowly warm to room temperature. CuCl (0.2 g, 2.0 mmol) was added while being stirred. Then a fresh solution of CpLi (2.0 mmol) in THF (20 mL) was added by cannula. The reaction mixture was stirred at room temperature overnight. After removal of

Table 1
Selected bond lengths (Å) and angles (°) for copper complexes

Complexes	C(Cp)–C (Cp) (ave)	Cu–Cen ^a	Cu–E ^b	Cen–Cu–E	∠Cp–NHC	Reference
1	1.364	1.926	1.878(3)	165.3	82.0	This work
2	1.375	1.966	1.886(3)	176.9	88.2	This work
3^c	1.341	1.922	1.864(4)	171.8	89.8	This work
	1.304	1.896	1.865(4)	177.0	89.1	
4^d	1.359	1.909	1.861(5)	176.2	86.3	This work
	1.365	1.924	1.831(6)	166.1	83.9	
	1.374	1.922	1.878(7)	168.5	86.6	
CpCu(PPh ₃)	1.399	1.864	2.135(1)	175.2		[7a]
CpCu(PEt ₃)	1.381	1.90	2.136(9)	179.9		[7b]
(C ₅ H ₄ Me)Cu(PPh ₃)	1.402	1.865	2.131(1)	173.1		[7e]
(C ₅ Ph ₅)Cu(PPh ₃)	1.430	1.876	2.216(3)	179.1		[7i]

^a Cen: centroid of the Cp ring.

^b E: C for NHC and P for phosphine.

^c Two independent molecules in an unit.

^d Three independent molecules in an unit.

Table 2
Crystal data and summary of X-ray data collection for complexes 1–4

	1	2	3	4·THF
Formula	C ₁₄ H ₂₁ CuN ₂	C ₁₆ H ₂₅ CuN ₂	C ₂₆ H ₂₉ CuN ₂	C ₁₀₀ H ₁₃₁ Cu ₃ N ₆ O
Fw	280.87	308.92	433.05	1623.73
<i>T</i> (K)	294(2)	293(2)	294(2)	293(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	6.090(2)	15.354(19)	11.970(3)	49.298(14)
<i>b</i> (Å)	9.391(3)	9.564(11)	12.457(4)	9.357(3)
<i>c</i> (Å)	13.860(5)	11.462(13)	17.192(4)	49.393(14)
α (°)	100.795(6)	90	105.221(5)	90
β (°)	100.407(6)	102.26(2)	106.677(5)	118.897(5)
γ (°)	101.394(6)	90	91.678(5)	90
<i>V</i> (Å ³)	743.6(5)	1645(3)	2354.4(11)	19946(10)
<i>Z</i>	2	4	4	8
<i>D</i> _{calc} (g cm ⁻³)	1.254	1.247	1.222	1.081
μ (mm ⁻¹)	1.451	1.318	0.941	0.679
<i>F</i> (000)	296	656	912	6944
Cryst size (mm)	0.38 × 0.28 × 0.24	0.38 × 0.28 × 0.16	0.26 × 0.22 × 0.16	0.30 × 0.24 × 0.16
θ Range (°)	2.27–25.01	1.36–25.01	1.71–26.50	0.94–25.01
Number of reflections collected	3728	8294	13,326	50,925
Number of independent reflections/ <i>R</i> _{int}	2593/0.0171	2908/0.0293	9496/0.0375	17570/0.0740
Number of parameters	158	179	535	1050
Goodness-of-fit on <i>F</i> ²	1.038	1.079	1.028	1.053
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0378, 0.0903	0.0370, 0.0959	0.0569, 0.1092	0.0822, 0.2235
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0588, 0.1016	0.0630, 0.1146	0.1813, 0.1404	0.1710, 0.2776

solvents in vacuo, the residue was extracted with benzene and filtered through Celite. The benzene was removed in vacuum and a yellow solid was obtained in high yield.

3.2.1. 1 (*R* = *i*-Pr)

90% yield, m.p. >250 °C (dec.). Anal. Calc. for C₁₄H₂₁CuN₂: C, 59.87%; H, 7.54%; N, 9.97%. Found: C, 59.63%; H, 7.36%; N, 9.82%. ¹H NMR (C₆D₆): 6.54 (s, 5H, C₅H₅), 6.10 (s, 2H, NCH), 4.60 (sept, 2H, *J* = 6.80 Hz, CH(CH₃)₂), 0.91 (d, 12H, *J* = 6.80 Hz, CH(CH₃)₂). ¹³C NMR (C₆D₆): 115.9, 110.1, 52.7, 23.4.

3.2.2. 2 (*R* = *t*-Bu)

90% yield, m.p. 95 °C (dec.). Anal. Calc. for C₁₆H₂₅CuN₂: C, 62.21%; H, 8.16%; N, 9.07%. Found: C, 62.29%; H, 8.01%; N, 9.15%. ¹H NMR (C₆D₆): 6.56 (s, 5H, C₅H₅), 6.29 (s, 2H, NCH), 1.42 (s, 18H, C(CH₃)₃). ¹³C NMR (C₆D₆): 116.2, 110.1, 57.8, 31.8.

3.2.3. 3 (*R* = *Mes*)

95% yield, m.p. 175 °C (dec.). Anal. Calc. for C₂₆H₂₉CuN₂: C, 72.11%; H, 6.75%; N, 6.47%. Found: C, 72.03%; H, 6.51%; N, 6.23%. ¹H NMR (C₆D₆): 6.76 (s, 4H, Ar-*H*), 6.01 (s, 2H, NCH), 5.90 (s, 5H, C₅H₅), 2.11 (s, 6H, *p*-CH₃), 1.96 (s, 12H, *o*-CH₃). ¹³C NMR (C₆D₆): 179.1, 138.5, 136.0, 135.2, 129.3, 121.0, 95.0, 21.2, 18.0.

3.2.4. 4 (*R* = *IPr*)

93% yield, m.p. 120 °C (dec.). Anal. Calc. for C₃₂H₄₁CuN₂: C, 74.31%; H, 7.99%; N, 5.42%. Found: C, 74.21%; H, 7.80%; N, 5.49%. ¹H NMR (C₆D₆): 7.25 (t, 2H,

J = 7.80 Hz, Ar-*H*), 7.10 (d, 4H, *J* = 7.80 Hz, Ar-*H*), 6.31 (s, 2H, NCH), 5.78 (s, 5H, C₅H₅), 2.53 (sept, 4H, *J* = 6.80 Hz, CH(CH₃)₂), 1.39 (d, 12H, *J* = 6.80 Hz, CH(CH₃)₂), 1.05 (d, 12H, *J* = 6.80 Hz, CH(CH₃)₂). ¹³C NMR (C₆D₆): 145.9, 136.5, 130.1, 123.9, 122.1, 95.0, 28.8, 24.4, 24.0.

3.3. Crystallographic studies

Single crystals of complexes 1–4 suitable for X-ray diffraction were obtained from saturated THF solution. Data collection was performed on a BRUKER SMART 1000 diffractometer, using graphite-monochromated Mo K α radiation (ω – 2θ scans, λ = 0.71073 Å). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were done using the SHELXL-97 program system. The crystal data and summary of X-ray data collection are presented in Table 2.

4. Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 605773–605776 for compounds 1–4, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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