

# A Dinuclear Copper(I) Complex Containing a Bridging Chiral Tridentate Carbene Ligand

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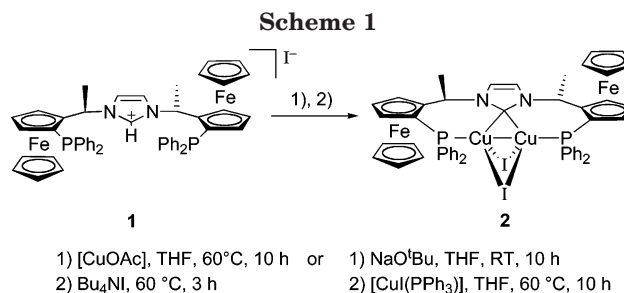
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**Summary:** The deprotonation of the imidazolium salt (PCPH)I (**1**) followed by a reaction with [CuI(PPH<sub>3</sub>)] results in the formation of the dinuclear complex [Cu<sub>2</sub>I<sub>2</sub>(PCP)] (**2**) in 92% yield. The crystal and molecular structural analysis of **2** shows the carbene donor in an extremely rare bridging mode between the two metal centers.

In the past few years N-heterocyclic carbenes (NHC) have become a well-established area of research in organometallic chemistry.<sup>1,2</sup> A large variety of metal complexes containing carbene ligands have been reported, many of which were successfully used in catalytic applications.<sup>3–6</sup> A common feature in essentially all such complexes is the nonbridging coordination mode of the NHC ligand.

Recently, we reported a tridentate PCP ligand based on a ferrocene scaffold.<sup>7</sup> This ligand is analogous to the C<sub>1</sub>-symmetric triphosphine Pigiphos with respect to its coordination geometry.<sup>8</sup> However, the replacement of the central P–Cy fragment with an NHC unit results in a C<sub>2</sub>-symmetric molecule. The palladium and ruthenium complexes of the tridentate NHC ligand show the same 1:1 coordination mode for palladium and ruthenium. Here we report the reaction of the ligand derived from **1** with copper(I), affording a dinuclear species in which the carbene carbon assumes the extremely rare bridging mode between the two metal centers.

We previously described the synthesis of the imidazolium salt (PCPH)I (**1**), the actual ligand precursor, starting from (*R*)-*N,N*-dimethyl-1-ferrocenylethylamine, as well as complexation methods for Pd and Ru.<sup>7</sup> The preparation of the dinuclear copper complex [Cu<sub>2</sub>I<sub>2</sub>(PCP)] (**2**) was achieved via prior deprotonation with NaO<sup>t</sup>Bu of **1** in THF and reaction with 2 equiv of [CuI(PPH<sub>3</sub>)]<sup>9</sup> at 60 °C, giving **2** in 92% yield.<sup>10</sup> An alternative method involves the use of [CuOAc], which already contains the base for the deprotonation of the imidazo-



lium salt. This protocol, however, results in the same copper complex **2** in only 54% yield (Scheme 1). The pure and air-stable complex was obtained in both cases after filtration over alox (CH<sub>2</sub>Cl<sub>2</sub> + 0.5% MeOH) as a crystalline material.

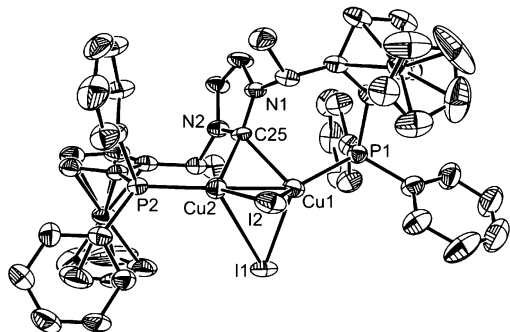
The incorporation of two copper centers in one complex was also observed when using a ratio of copper precursor and ligand precursor of 1:1 and was confirmed by elemental analysis. The HiResMALDI spectrum shows a signal at *m/z* 1113 indicating the formation of the [Cu<sub>2</sub>I<sub>2</sub>(PCP)] cation, confirming the presence of two copper centers. NMR spectroscopic analysis confirms the C<sub>2</sub>-symmetric geometry of complex **2** in solution. The <sup>13</sup>C NMR spectrum shows the signal of the carbene carbon at δ 165.2 ppm as a triplet with a coupling constant *J*<sub>CP</sub> of 30.3 Hz. This is comparable to the values of δ 163.2<sup>11</sup> and 162–165 ppm<sup>12</sup> and is slightly smaller

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(10) Experimental procedure for the preparation of (*SP-4*)-[*μ-1,3-Bis*[(*R*)-1-(*S*)-2-diphenylphosphino-*p*-ferrocenyl]ethyl]imidazole-2-*μ*-ylidene]bis(*μ*-iodo)dicopper(I), [Cu<sub>2</sub>I<sub>2</sub>(PCP)] (**2**). All operations have been carried out using standard Schlenk techniques under argon. A solution of **1** (200 mg, 0.202 mmol) and NaO<sup>t</sup>Bu (20 mg, 0.202 mmol) in THF (6 mL) was stirred overnight, affording a suspension. A THF (6 mL) solution of [CuI(PPH<sub>3</sub>)] (182.9 mg, 0.404 mmol) was added, and the mixture was heated at 60 °C for 5 h. After the mixture was cooled to room temperature, the product was precipitated by the addition of hexane. After filtration and washing three times with hexane the crude product was chromatographed (alox, CH<sub>2</sub>Cl<sub>2</sub> + 0.5% MeOH). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 0.98 (d, 6 H, *J*<sub>CHMe</sub> = 7.2 Hz, CHMe), 4.00 (s, 10 H, Cp'), 4.15 (m, 2 H, *J*<sub>CHCH</sub> = 1.2 Hz, Cp), 4.45 (t, 2 H, *J*<sub>CHCH</sub> = 2.6 Hz, Cp), 4.61 (m, 2 H, *J*<sub>CHCH</sub> = 0.9 Hz, Cp), 6.54 (s, 2 H, HC=CH Im), 6.82 (m, 4 H, PPh<sub>2</sub>), 7.14 (m, 6 H, PPh<sub>2</sub>), 7.21 (q, 2 H, *J*<sub>CHCH</sub> = 7.2 Hz, CHMe), 7.59 (m, 6 H, PPh<sub>2</sub>), 8.02 (m, 4 H, PPh<sub>2</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 17.51 (CH<sub>3</sub>, CHMe), 53.79 (CH, CHMe), 69.32 (d, *J*<sub>CP</sub> = 6.3 Hz, CH, Cp), 70.40 (d, *J*<sub>CP</sub> = 3.9 Hz, CH, Cp), 70.57 (CH, Cp'), 71.94 (d, *J*<sub>CP</sub> = 33.6 Hz, C, Cp), 73.08 (CH, Cp), 93.01 (d, *J*<sub>CP</sub> = 19.4 Hz, C, Cp), 117.12 (CH, HC=CH Im), 127.68 (d, *J*<sub>CP</sub> = 8.4 Hz, CH, PPh<sub>2</sub>), 128.05 (CH, PPh<sub>2</sub>), 128.56 (d, *J*<sub>CP</sub> = 10.9 Hz, CH, PPh<sub>2</sub>), 130.90 (CH, PPh<sub>2</sub>), 131.45 (d, *J*<sub>CP</sub> = 12.6 Hz, CH, PPh<sub>2</sub>), 133.52 (d, *J*<sub>CP</sub> = 36.2 Hz, C, PPh<sub>2</sub>), 135.51 (d, *J*<sub>CP</sub> = 18.0 Hz, CH, PPh<sub>2</sub>), 136.72 (d, *J*<sub>CP</sub> = 34.9 Hz, C, PPh<sub>2</sub>), 165.21 (t, *J*<sub>CP</sub> = 30.3 Hz, C–Pd, Im). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ –16.91 (br, line width 103 Hz, PPh<sub>2</sub>). MS (HiRes-MALDI): *m/z* 1113 [Cu<sub>2</sub>I(PCP)]<sup>+</sup>, 923 [Cu(PCP)]<sup>+</sup>. Anal. Calcd for C<sub>51</sub>H<sub>46</sub>Cu<sub>2</sub>Fe<sub>2</sub>I<sub>2</sub>N<sub>2</sub>P<sub>2</sub>: C, 49.34; H, 3.73; N, 2.26. Found: C, 49.06; H, 3.56; N, 2.20.

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**Figure 1.** ORTEP representation of **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are at the 30% probability level.

than the value of  $\delta$  175.3 ppm<sup>13</sup> reported for polynuclear structures with silver as bridged metal centers. The <sup>31</sup>P NMR spectrum shows a broad signal at  $\delta$  -16.91 ppm with a line width of 103 Hz at room temperature. This value lies between the ones measured for the noncoordinated ligand precursor ( $\delta$  -24.81 ppm) and the corresponding palladium complexes [PdCl(PCP)]PF<sub>6</sub> ( $\delta$  -2.16 ppm) and [PdI(PCP)]OAc ( $\delta$  -1.89 ppm).<sup>7</sup> Cooling down to -80 °C did not show any splitting, only slight narrowing of the signal to a line width of 24 Hz. Also, in the <sup>1</sup>H NMR spectrum no significant change was observed upon cooling. We reason that the broad signal in the <sup>31</sup>P NMR spectra may arise from a relatively weak Cu-P bond, leading to a dynamic behavior.

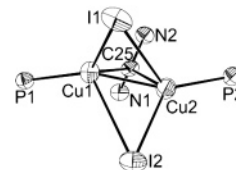
Crystals of **2**, suitable for X-ray analysis, were obtained from a dichloromethane solution overlaid with hexane. They contain cocrystallized solvent and belong to space group *P*2<sub>1</sub>.<sup>14</sup> The slow evaporation of a concentrated dichloromethane solution, i.e., without the addition of an apolar solvent, leads to a different crystal modification which does not contain solvent. This second modification belongs to space group *P*4<sub>1</sub>2<sub>1</sub>2 and is characterized by a crystallographic *C*<sub>2</sub> axis coinciding with the molecular symmetry axis. Although this is not the case for the first structure, i.e., the molecules display only approximate *C*<sub>2</sub> symmetry, we shall limit our discussion to this one case. The molecular structure is shown in Figure 1, crystallographic parameters are given in Table 1, and selected bond lengths and angles are provided in Table 2.

The ligand atoms P(1/2), I(1), I(2), and C(25) around each of the copper centers adopt a distorted-tetrahedral arrangement with C(25), I(1), and I(2) acting as bridging ligands. The copper atoms are separated by 2.3561(13) Å. This separation is shorter than the distances found

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(14) X-ray structural measurements were carried out on a Bruker CCD diffractometer (Bruker SMART PLATFORM, with CCD detector, graphite monochromator, Mo K $\alpha$  radiation). The program SMART served for data collection. Integration was performed with SAINT. The structure solution (direct methods) and refinement on *F*<sup>2</sup> were accomplished with SHELXTL 97. Model plots were made with ORTEP32. All non-hydrogen atoms were refined freely with anisotropic displacement parameters. One of the CH<sub>2</sub>Cl<sub>2</sub> molecules is disordered over two sites, with Cl(1) and C(52) in common. The C-Cl bond lengths were restrained to standard values. The hydrogen atoms were refined at calculated positions riding on their carrier atoms. Weights were optimized in the final refinement cycles. Crystallographic data are given in Table 1.



**Figure 2.** Coordination sphere around the copper centers in **2**.

**Table 1. Crystallographic Data of [Cu<sub>2</sub>I<sub>2</sub>(PCP)] (**2**)**

color, shape	orange prism
empirical formula	C <sub>51</sub> H <sub>46</sub> Cu <sub>2</sub> Fe <sub>2</sub> I <sub>2</sub> N <sub>2</sub> P <sub>2</sub> ·2CH <sub>2</sub> Cl <sub>2</sub>
formula wt	1409.25
temp (K)	293(2)
wavelength (Å)	0.710 73
cryst syst	monoclinic
space group	<i>P</i> 2 <sub>1</sub>
unit cell dimens	
<i>a</i> (Å)	9.033(3)
<i>b</i> (Å)	24.752(8)
<i>c</i> (Å)	13.027(4)
$\alpha$ (deg)	90
$\beta$ (deg)	104.991(6)
$\gamma$ (deg)	90
<i>V</i> (Å <sup>3</sup> )	2813.6(16)
<i>Z</i>	2
calcd density (g cm <sup>-3</sup> )	1.663
abs coeff (mm <sup>-1</sup> )	2.631
cryst size (mm)	1.20 × 0.60 × 0.28
no. of rflns: collected, unique	21 989, 9561
<i>R</i> <sub>int</sub>	0.0289
refinement method	full-matrix least squares on <i>F</i> <sup>2</sup>
no. of data, restraints, params	9561, 6, 617
GOF	1.016
<i>R</i> , <i>R</i> <sub>w</sub>	0.0395, 0.1012
abs structure param	0.065(17)
min/max resd (e Å <sup>-3</sup> )	1.068, -0.492

**Table 2. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of **2****

Cu(1)-Cu(2)	2.3561(13)	I(1)-Cu(1)	3.1096(11)
Cu(1)-C(25)	2.113(5)	I(1)-Cu(2)	2.5588(10)
Cu(2)-C(25)	2.174(5)	I(2)-Cu(1)	2.5908(11)
Cu(1)-P(1)	2.2059(17)	I(2)-Cu(2)	3.0949(12)
Cu(2)-P(2)	2.1814(18)		
Cu(1)-C(25)-Cu(2)	66.66(14)	P(1)-Cu(1)-Cu(2)	153.95(6)
C(25)-Cu(1)-P(1)	105.84(16)	P(2)-Cu(2)-Cu(1)	152.53(6)
C(25)-Cu(2)-P(2)	102.21(15)	N(1)-C(25)-N(2)	104.0(4)
P(1)-Cu(1)-Cu(2)-P(2)			96.42(18)
P(1)-Cu(1)-C(25)-N(1)			-37.5(4)
P(2)-Cu(2)-C(25)-N(1)			91.5(5)
P(2)-Cu(2)-C(25)-N(2)			-39.5(4)
P(1)-Cu(1)-C(25)-N(2)			99.0(5)

for other carbon-bridged copper clusters with distances in the range from 2.376 Å in the aryl-bridged complex [CuC<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6]<sub>3</sub><sup>15</sup> and 2.389 Å in the acetylide-bridged complex [Cy<sub>3</sub>PCu( $\mu$ -C $\equiv$ C<sup>t</sup>Bu)<sub>2</sub>Cu(PPh<sub>3</sub>)<sub>2</sub>]<sup>16</sup> up to 3.175 Å in the acetylide-bridged complex [Cu<sub>3</sub>(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>( $\mu$ <sub>3</sub>-C $\equiv$ C<sup>t</sup>Bu)](PF<sub>6</sub>)<sub>2</sub>,<sup>17</sup> with most distances lying between 2.4 and 2.6 Å (acetylide and aryl bridged; vide infra).

Concerning the central part of the structure as depicted in Figure 2, a zigzag arrangement results for the atoms P(1)-Cu(1)-Cu(2)-P(2). This is confirmed by the corresponding torsion angle of 96.42(18)° and the

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angles P(1)–Cu(1)–Cu(2) = 153.95(6)° and P(2)–Cu(2)–Cu(1) = 152.53(6)°, which are smaller than 180°. The significantly different Cu–I distances (short distance around 2.6 Å and long distance ca. 3.1 Å, respectively) are indicative of a distortion around the copper centers, as pointed out by Eisenstein and Caulton<sup>18</sup> in their analysis of halide-bridged dinuclear Cu(I) complexes. In fact, a better orbital overlap between the iodide bridges and the Cu–P fragments is attained if one of the Cu–I bonds becomes shorter and the other longer.

The angle of 101.8° between the least-squares plane of the carbene heterocycle and the least-squares plane containing Cu(1), Cu(2), and C(25) shows a tilting of the imidazole plane away from a 90° angle. This indicates that the geometry around the carbene carbon atom is distorted tetrahedral. A similar tilting of the heterocycle ring with respect to the main metal coordination plane has been observed for the previously reported mononuclear square-planar complexes containing this ligand.

In the literature, several X-ray structures of copper clusters with a carbon bridging mostly two or three copper atoms have been reported. Next to carbonyl- and cyanide-bridged structures the most often encountered bridging units in Cu clusters are aryl and acetylide, bridging two or, for acetylide, two or three copper centers.<sup>19</sup> To the best of our knowledge a carbene bridging two copper atoms is unprecedented. It is, however, closely related to the systems described by Garrison<sup>11,12</sup> and Catalano,<sup>13</sup> where an NHC unit is bridging two silver centers. In these clusters the NHC unit adopts, similarly to our structure, a perpendicular orientation with respect to the Ag–C–Ag plane, indicating a similar binding mode. Finally, there are examples of dinuclear Cu complexes containing monodentate<sup>20</sup> or tridentate<sup>21</sup> NHC ligands. However, none of these derivatives displays the carbene in a bridging position.

There are mainly two possibilities to describe the bond between the bridging carbon and the two copper atoms. The first possibility describes a reduced carbene with

an sp<sup>3</sup> hybridization of the bridging carbon with two copper(II) atoms present. However, in the literature no evidence was found for this situation. The other possibility involves an sp<sup>2</sup>-hybridized carbon and two copper(I) centers. Garrison describes this bonding mode for a similar silver cluster as a  $\sigma$ -bonding interaction with one silver center and an unconventional  $\pi$  interaction between the carbene and a neighboring silver atom.<sup>11,12</sup> Alternatively, one could view this interaction as a three-center–two-electron bond, a situation often discussed also for the aryl-bridged copper clusters.<sup>22</sup> An often-debated question for copper clusters is the presence of a Cu–Cu interaction. Since the Cu–Cu distance for **2** is 2.3561(13) Å, i.e., of the same magnitude as other short distances for clusters in which bonding Cu–Cu interactions have been shown to exist,<sup>22</sup> it seems likely that such an interaction can be assumed here. Further support for this description is provided by calculations on copper(I) clusters with bridging aryl groups, providing clear evidence for the presence of Cu–Cu bonds.<sup>18,23–28</sup>

In summary, we have documented the unexpected formation of a dinuclear copper complex supported by a tridentate NHC ligand. The crystal structure of this new species shows an unusual binding mode with the NHC unit bridging the two copper centers. This particular coordination mode of an NHC has previously been observed only for a few Ag derivatives. We are currently exploring the reactivity of complex **2**, which upon abstraction of iodide leads to a Lewis acidic complex. A possible application might be the Cu-catalyzed conjugate reduction of nitroalkenes<sup>29</sup> and enones,<sup>30</sup> as recently reported by Carreira and Lipshutz, respectively.

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**Supporting Information Available:** Full crystallographic data for the compound **2** as a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(19) Examples of structurally characterized copper complexes containing a carbon atom bridging two or three metal centers are reported in the Cambridge Structural Database with the following CSD codes: (a) for carbonyl, BILVOH, BUKVUY, BZENCV; (b) for cyanide, DIDKEG, DOLXOR, TANBOZ, UBURYOY, WOWYIQ; (c) for aryl, WEQNIP, WEQNOV, BEYROM, BEYRUS, CAKPEJ10, CAKPIN10, CUTCAV, CUTCEZ, FITJUN, FOFHOX, CEBQIN, KACYAO, KISKUS, LADCAU, LICGUZ, MAPCUB, MCUBZA01, NOMSAJ, NOMSEN, NOMSIR, PEJTAZ, RARCOC, RARCU, RARDET, SIDNAU, SIMREL, YALNOO, ELEFIK, ELEFOQ; (d) for acetylide, CUJLUO, GAMNEN, GAMNIR, JEBPAH10, JEFSOC, KUXYOR, NEVWUG, RIXLEP, SACFIL, SITNIS, TIYMAP, WARKEF, XIBYUC, XIFWUE, YIGSEM, ZEPZID, ASEN0B.

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