

# Notes

## Synthesis and Structural Characterization of an Air-stable $\{[\text{HC}(\text{pyrazolyl})_3]\text{Cu}(\text{PPh}_3)\}\text{PF}_6$

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The tris(pyrazolyl)methane ligands,  $\text{HCpz}_3$ ,<sup>1</sup> have received less attention than the isoelectronic tris(pyrazolyl)borate, with which many transition metal complexes are synthesized and their structural features and reactivity in the biomimetic area and catalytic systems have been intensively studied.<sup>2,3</sup> Copper(I) plays an important role in biological systems<sup>4</sup> and it is a powerful catalyst in many organic syntheses.<sup>5</sup> Triaryl- and trialkylphosphine copper(I) derivatives have attracted attention in view of their potential applications in micro-electronic technology.<sup>6</sup>

Although the analogous tris(pyrazolyl)methane copper(I) derivatives were first reported in 1996 by Reger,<sup>7</sup> their chemistry still remains unexplored compared to  $\text{HBpz}_3$ . Even though tris(pyrazolyl)methane ligand is structurally similar to tris(pyrazolyl)borate, it differs in being neutral rather than anionic, which is likely to make a significant difference to its coordination behavior and chemistry.<sup>8</sup>

In this paper we describe the synthesis and the crystal structure of the novel phosphino-copper(I) complex with neutral tris(pyrazolyl)methane ligand. The structural feature of this complex are discussed compared to the congeners, such as  $(\text{HBpz}_3)\text{Cu}(\text{PPh}_3)$  and  $[(\text{HCpz}_3)\text{Cu}(\text{CO})]\text{X}$ .

### Experimental Section

All procedures for syntheses and handling during this experiment were carried out under an atmosphere of  $\text{N}_2$ , using standard Schlenk techniques. All solvents were dried, degassed and distilled before use. Elemental analyses were performed at Korea Basic Science Institute Daegu Branch. IR spectra were recorded with Nicolet Impact 410 FT-IR instrument,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra on a Bruker 500 MHz.

**Collection of X-ray Data.** All data were collected on a Bruker Smart Diffractometer equipped with a graphite monochromated  $\text{Mo K}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation source and a CCD detector at 173(2) K. The 45 frames of two

dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The first 50 frames were retaken after complete data collection. The crystal showed no significant decay and no correction was applied for absorption or decay. The frame data were processed to give structure factors, using the program SAINT.<sup>9</sup> The structure was solved by direct methods and refined by full matrix least squares method on  $F^2$  for all data, using SHELXTL software.<sup>10</sup> The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined with a riding model with  $U_{\text{iso}}$  constrained to be 1.2 times  $U_{\text{eq}}$  of the parent atom. Cell data for  $\text{C}_{28}\text{H}_{25}\text{N}_6\text{P}_2\text{CuF}_6$ :  $M = 685.02$ , monoclinic,  $P2_1/c$ ,  $a = 12.3216(6)$ ,  $b = 15.9573(8)$ ,  $c = 16.0864(8)$ ,  $\beta = 109.2600(10)$ ,  $V = 2985.8(3) \text{ \AA}^3$ ,  $Z = 4$ , 18909 reflections measured, 6969 independent [ $R_{\text{int}} = 0.0973$ ]. The final  $R_1$  and  $\omega R_2$  factors 0.0594 and 0.1190 were for [ $I > 2(I)$ ] and 388 parameters; goodness-of-fit = 1.023, largest diff. peak and hole = 0.738 and  $-0.649 \text{ e}\text{\AA}^{-3}$ .

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-234259). The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/perl/catreq.cgi> (12 Union Road, Cambridge CB2 1EZ, UK; fax: +444-1224-336033; e-mail: deposit@ccdc.cam.ac.uk).

$[(\text{HCpz}_3)\text{Cu}(\text{NCMe})]\text{PF}_6$  was prepared by the reaction of  $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$ <sup>11</sup> with  $\text{HCpz}_3$ , a previously reported procedure.<sup>12</sup>

$[(\text{HCpz}_3)\text{Cu}(\text{PPh}_3)]\text{PF}_6$ . To a solution of  $[(\text{HCpz}_3)\text{Cu}(\text{NCMe})]\text{PF}_6$  (0.6 g, 1.6 mmol) in 50 mL of  $\text{CH}_2\text{Cl}_2$ ,  $\text{PPh}_3$  (0.45 g, 3.6 mmol) was added, and the reaction solution was stirred at room temperature for 1 h. After removal of solvent in vacuo, the residue was extracted with  $\text{CHCl}_3$  (10  $\times$  10 mL), then the combined extracts were mixed with a small amount of ether and stored at  $-25 \text{ }^\circ\text{C}$  to give white crystals. Anal. Calc.  $\text{CuC}_{28}\text{H}_{25}\text{N}_6\text{P}_2\text{F}_6$ : C, 49.09; H, 3.68; N, 12.27%. Found: C, 49.20; H, 4.060; N, 11.91%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ;  $\delta$ ): 9.14 (s; 1; HC); 8.306 (d;  $J_{\text{HH}} = 2.5 \text{ Hz}$ ; 3; 3H pz); 7.321 (d;  $J_{\text{HH}} = 1.6 \text{ Hz}$ ; 3; 5H pz); 6.314 (t;  $J_{\text{HH}} = 1.6 \text{ Hz}$ ,  $J_{\text{HH}} = 2.5 \text{ Hz}$ ; 3; 4H pz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ;  $\delta$ ): 142 (s; 3C pz); 129 (s; 5C

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pz); 107 (s; 4C pz); 75 (s; HCpz<sub>3</sub>), <sup>31</sup>P NMR (CDCl<sub>3</sub>; δ): 9.0404 (PPh<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): 3129, 3052 (H-C, m), 1516, 1480, 1439, 1403, 1291, 1239 (aromatic C-H), 845, 794, 768, 748 (PF<sub>6</sub>, s).

**HCpz<sub>3</sub>** <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>; δ): 8.73 (s; 1; HC); 7.66 (d; *J*<sub>HH</sub> = 2.3 Hz; 3; 3H pz); 7.51 (d; *J*<sub>HH</sub> = 1.1 Hz; 3; 5H pz); 6.23 (b; 3; 4H pz). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>; δ): 140 (s; 3C pz); 129 (s; 5C pz); 107 (s; 4C pz); 65 (s; HCpz<sub>3</sub>).

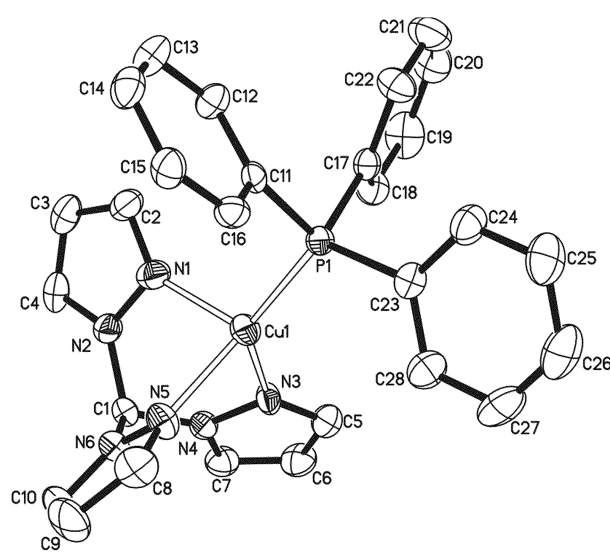
## Results and Discussion

[(HCpz<sub>3</sub>)Cu(PPh<sub>3</sub>)]PF<sub>6</sub> was prepared in 60% yield by the reaction of [(HCpz<sub>3</sub>)Cu(NCMe)]PF<sub>6</sub> with PPh<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>. The complex is very stable in air and soluble in the most organic solvents.

The <sup>1</sup>H NMR spectrum of the complex shows that upon complexation the resonances for *H*-Cpz<sub>3</sub> and H(3) of pyrazol rings slightly shift downfield, whereas signals for H(5) and H(4) of pyrazol rings shift upfield. In the <sup>13</sup>C NMR H-C resonance absorption undergoes 10 ppm downfield shift, others remain unchanged. Compared to the NMR resonance peaks of [(HCpz<sub>3</sub>)Cu(NCMe)]PF<sub>6</sub>,<sup>12</sup> interestingly the coordination of PPh<sub>3</sub> mostly influences the farthest proton and carbon atom of HCpz<sub>3</sub> ligand; the signals shift 0.44 ppm and 10 ppm downfield, respectively.

The <sup>31</sup>P NMR spectrum of the complex shows a broad resonance signal on 9.040 ppm. The signal appears more downfield than that observed for the free PPh<sub>3</sub> (-7 ppm). For Δδ<sup>31</sup>P = δ<sup>31</sup>P<sub>complex</sub> - δ<sup>31</sup>P<sub>ligand</sub>, the difference in shift between the free PPh<sub>3</sub> and this complex is 16 ppm, whereas the difference in shift between free PPh<sub>3</sub> and the (HBpz<sub>3</sub>)-Cu(PPh<sub>3</sub>)<sup>13</sup> is only 0.78 ppm. This can be attributed to the decreased electron density of the neutral tris(pyrazolyl)-methane.

The ORTEP drawing of the complex [(HCpz<sub>3</sub>)Cu(PPh<sub>3</sub>)]<sup>+</sup> and selected bond distances and angles are shown in Figure 1. The copper(I) center is four coordinate with strongly distorted tetrahedral geometry, owing to the structural rigidity of tris(pyrazolyl)methane ligand: in the coordination sphere the N-Cu-P angles (average 126.3 (1)°) are larger than the N-Cu-N angles (average 87.6 (1)°). This distortion is more extreme than in the case of (HBpz<sub>3</sub>)Cu(PPh<sub>3</sub>)<sup>14</sup>; in the latter N-Cu-P and N-Cu-N are 125(1)° and 90.4(2)°, respectively. A comparison of the selected structural data of the analogous complexes is given in Table 1. The Cu-N bond lengths of [(HCpz<sub>3</sub>)Cu(PPh<sub>3</sub>)]<sup>+</sup> vary from 2.057(4) Å to 2.158 (1) Å (average 2.094 Å), this value is 0.014 Å greater than that observed in {[HC(3-Bu<sup>t</sup>pz)<sub>3</sub>]Cu(CO)}<sup>+</sup>. The



**Figure 1.** ORTEP plot for [(HCpz<sub>3</sub>)Cu(PPh<sub>3</sub>)]<sup>+</sup>; selected bond lengths (Å) and angles (°): Cu(1)-N(1) 2.130 (4), Cu(1)-N(3) 2.096 (4), Cu(1)-N(5) 2.057 (4), Cu(1)-P(1) 2.158 (1), N(5)-Cu(1)-N(3) 86.9 (1), N(5)-Cu(1)-N(1) 89.6(1), N(3)-Cu(1)-N(1) 86.4 (1), N(5)-Cu(1)-P(1) 131.9 (1), N(3)-Cu(1)-P(1) 133.6 (1), N(1)-Cu(1)-P(1) 113.5 (1), C(23)-P(1)-Cu(1) 118.2 (2), C(11)-P(1)-Cu(1) 111.3 (1), C(17)-P(1)-Cu(1) 112.1 (1), C(23)-P(1)-C(11) 103.5 (2), C(23)-P(1)-C(17) 105.3 (2), C(11)-P(1)-C(17) 105.5 (2).

shortening in the latter can be attributed more to the CO ligand pulling more electron density *via* back bonding than to the PPh<sub>3</sub> ligand to the copper, causing the nitrogen donor atoms of the tridentate ligand to bond to copper more strongly. As expected, the Cu-N distance of {[HC(3-Bu<sup>t</sup>pz)<sub>3</sub>]Cu(NCMe)}<sup>+</sup><sup>7</sup> is longer than that of [(HCpz<sub>3</sub>)-Cu(PPh<sub>3</sub>)]<sup>+</sup>, showing the decreasing π-acceptor ability in the order of CO > PR<sub>3</sub> > RCN. On the other hand, the average Cu-N bond length in [(HCpz<sub>3</sub>)Cu(PPh<sub>3</sub>)]<sup>+</sup> is 0.018 Å longer than that in the (HBpz<sub>3</sub>)Cu(PPh<sub>3</sub>), the anionic HBpz<sub>3</sub> makes a stronger Cu-N bond than neutral HCpz<sub>3</sub>. The C-P-C angles (average 104.7(1)) are larger than the value 103.7(2) found in (HBpz<sub>3</sub>)Cu(PPh<sub>3</sub>) and the Cu-P-C angles (average 113.9(1)) are consequently smaller than that 114.8(1) of (HBpz<sub>3</sub>)Cu(PPh<sub>3</sub>). The Cu-P bond distance 2.158(1) Å is comparable with the values 2.153(2) Å reported for analogous (HBpz<sub>3</sub>)Cu(PPh<sub>3</sub>), indicating there is no electronic effect on Cu-P distance caused by the neutral HCpz<sub>3</sub> ligand contrast to anionic HBpz<sub>3</sub> congener.

In summary, [(HCpz<sub>3</sub>)Cu(PPh<sub>3</sub>)]PF<sub>6</sub> has been synthesized and structurally characterized, revealing a distorted tetrahedral geometry. This complex is the first copper(I) complex

**Table 1.** Selected structural data for copper(I) complexes

Complexes	Cu-N, Å	Cu-P, Å	N-Cu-N, °	N-Cu-P or N-Cu-C, °	Ref.
[(HCpz <sub>3</sub> )Cu(PPh <sub>3</sub> )]PF <sub>6</sub>	2.094 (4)	2.158 (1)	87.6 (1)	126.3 (1)	This study
(HBpz <sub>3</sub> )Cu(PPh <sub>3</sub> )	2.076 (6)	2.153 (2)	90.4 (2)	125 (1)	14
{[HC(3-Bu <sup>t</sup> pz) <sub>3</sub> ]Cu(CO)}PF <sub>6</sub>	2.080 (5)		89.0 (2)	126 (3)	7
{[HC(3-Bu <sup>t</sup> pz) <sub>3</sub> ]Cu(NCMe)}PF <sub>6</sub>	2.107 (9)		89.2 (4)	125.7 (4)	7

where neutral tris(pyrazoly)methane ligand and  $\text{PPh}_3$  ligand coexist. Compared to copper complexes of the analogous anionic  $\text{HBpz}_3$  ligand, x-ray structure shows a 0.018 Å lengthening of the Cu-N bond distance as expected owing to the reduced electron density of neutral  $\text{HCpz}_3$ . However, in both complexes the Cu-P bond distances are almost same.

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  12. This can be isolated as a white solid. Moderate air-stable in solid.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ;  $\delta$ ): 8.70 (s; 1; HC); 8.05 (s; 3; 3H pz); 7.626 (s; 3; 5H pz); 6.298 (s; 3; 4H pz).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ;  $\delta$ ): 142.3 (3C pz); 132.2 (5C pz); 107.2 (4C pz); 65 (HCpz<sub>3</sub>)
  13.  $^{31}\text{P}$  of  $(\text{HBpz}_3)\text{Cu}(\text{PPh}_3)$ : -6.12 ppm.
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