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## Isolable Copper(I) $\eta^2$ -Cyclopropene Complexes

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**ABSTRACT:** Treatment of bis(pyrazolyl)borate ligand supported  $[(CF_3)_2Bp]Cu(NCMe)$  with 1,2,3-trisubstituted cyclopropenes produced thermally stable copper(I)  $\eta^2$ -cyclopropene complexes amenable to detailed solution and solid-state analysis. The  $[(CF_3)_2Bp]Cu(NCMe)$  also catalyzed [2 + 1]-cycloaddition chemistry of terminal and internal alkynes with ethyl diazoacetate affording cyclopropenes, including those used as ligands in this work. The tris(pyrazolyl)borate  $[(CF_3)_2Tp]Cu(NCMe)$  is a competent catalyst for this process as well. The treatment of  $[(CF_3)_2Tp]Cu$  with ethyl 2,3-diethylcycloprop-2-enecarboxylate substrate gave an O-bonded rather than a  $\eta^2$ -cyclopropene copper complex.

C yclopropenes are highly strained, small carbocyclic alkenes with a long history.<sup>1</sup> They have been investigated extensively during past decades and found to be impactful in multiple fields ranging from organic synthesis,<sup>2–5</sup> materials chemistry,<sup>4,6,7</sup> horticulture,<sup>8,9</sup> biochemistry, and natural product chemistry to the bioorthogonal labeling reactions.<sup>10,11</sup> For example, cyclopropenes are energy packed organic synthones (with strain energy of over 200 kJ mol<sup>-1</sup>)<sup>12</sup> that undergo reactions such as addition, substitution, isomerization, and metatheses often not seen in the related nonstrained olefins.<sup>2–4</sup> 1-Methyl cyclopropene is an economically important ethylene antagonist utilized widely to prolong the shelf life of fruits, vegetables, and cut flowers.<sup>8,9</sup> Cyclopropenes are popular minitags in chemical biology to label biomolecules in live cells.<sup>10,13,14</sup>

In comparison to the diverse uses of cyclopropenes, synthetic routes to cyclopropenes are relatively limited. The metal-catalyzed  $\begin{bmatrix} 2 + 1 \end{bmatrix}$  cycloaddition of diazoalkanes with alkyne substrates is perhaps the most promising and leading route. Catalysts based on metals such as rhodium,<sup>15-1</sup> copper,<sup>18-23</sup> silver,<sup>23,24</sup> cobalt,<sup>25</sup> and a few others<sup>26-28</sup> are useful for this purpose with even heme proteins and metal foils entering the fray in the search for better catalysts.<sup>23,29</sup> Metals also play a key role in cyclopropene utilizations as a synthone in organic chemistry, which either proceed with the preservation or opening of the three-membered carbocyclic ring.<sup>3,5,30</sup> Although the commonly invoked intermediates in quite a few of these metal-mediated processes are metalcyclopropene complexes,<sup>2,3</sup> many of them are too reactive for direct investigations, and therefore reliable structural or spectroscopic information have been extremely limited.<sup>3,5,30</sup> Most notably, despite the multiple roles copper plays in cyclopropene chemistry from the synthesis, 5,18-23,31 ring opening chemistry, 3,32-35 and carbometalations, 30,36 to being the target of ethylene antagonists (because of the ethylene binding copper-cofactor in plants),<sup>8,37,38</sup> there are no structurally authenticated  $\eta^2$ -cyclopropene complexes of copper to date.<sup>39</sup> Herein we report the isolation and complete

characterization of three copper(I)  $\eta^2$ -cyclopropene complexes, as well as a useful copper-mediated route to cyclopropenes.

Treatment of  $[(CF_3)_2Bp]Cu(NCMe)$  (1)<sup>40</sup> with cyclopropene Cyp-2 in dichloromethane at room temperature led to the displacement of acetonitrile ligand from copper and the formation of copper  $\eta^2$ -cyclopropene complex [(CF<sub>3</sub>)<sub>2</sub>Bp]Cu-(Cyp-2) in 82% isolated yield (Scheme 1 and Supporting Information). It is a colorless, thermally stable solid that can be handled in air for short periods without decomposition. The room-temperature  ${}^{13}C{}^{1}H$  NMR spectrum of  $[(CF_3)_2Bp]$ -Cu(Cyp-2) in CDCl<sub>3</sub> shows a peak at  $\delta$  91.1 ppm corresponding to the carbons of the copper bound olefinic moiety of cyclopropene ligand, which is an upfield shift ( $\Delta\delta$  of 15.4 ppm;  $\Delta \delta = \delta$  free ligand  $-\delta$  metal complex) compared with the corresponding resonance of the free ligand Cyp-2 ( $\delta$ 106.5 ppm, Table S1). The early transition metal  $\eta^2$ cyclopropene complexes such as Cp\*Mo(CO)<sub>2</sub>(2,3-Ph<sub>2</sub>-2cyclopropene-1-carboxylate),<sup>41</sup> [Me<sub>2</sub>Tp]Nb(cyclo-C<sub>3</sub>H<sub>4</sub>)- $(NC_5H_5)(MeCCMe)^{42}$  and  $W(3,3-Ph_2-cyclopropene)$ - $Cl_2(NPh)[P(OMe)_3]_2^{43}$  with stronger metal-cyclopropene bonds display their metal-bound cyclopropene carbon chemical shifts at significantly greater upfield regions:  $\delta$ 71.91, 58.64 ppm;  $\delta$  74.5, 68.4 ppm; and  $\delta$  64.8 ppm, respectively. The carbonyl carbon signal of [(CF<sub>3</sub>)<sub>2</sub>Bp]Cu-(Cyp-2) also shows a small but noticeable 4 ppm shift relative to that of the free ligand Cyp-2.

We have also synthesized two other copper(I) cyclopropene complexes using a similar route (Scheme 1). The  $[(CF_3)_2Bp]$ -Cu(Cyp-3) and  $[(CF_3)_2Bp]$ Cu(Cyp-4) has been obtained in 94% and 80% yields from a reaction between 1 and the corresponding Cyp-3 and Cyp-4 in dichloromethane. Compounds  $[(CF_3)_2Bp]$ Cu(Cyp-3) and  $[(CF_3)_2Bp]$ Cu(Cyp-4)

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Scheme 1. Synthesis of Copper(I) Cyclopropene Complexes



Figure 1. Molecular structures of  $[(CF_3)_2Bp]Cu(Cyp-2)$ ,  $[(CF_3)_2Bp]Cu(Cyp-3)$ , and  $[(CF_3)_2Bp]Cu(Cyp-4)$ , from left to right.

also show notable upfield shifts of the olefinic carbon resonances ( $\Delta\delta$  of 21.4 and 30.2 ppm, respectively, Table S1) relative to those of the free ligands Cyp-3 and Cyp-4, indicating the presence of copper-olefin interactions in solution.

Copper(I) cyclopropene complexes  $[(CF_2)_2Bp]Cu(Cyp-2)$ ,  $[(CF_3)_2Bp]Cu(Cyp-3)$ , and  $[(CF_3)_2Bp]Cu(Cyp-4)$  have been characterized by X-ray crystallography (Figure 1). Selected bond distances and angles are summarized in Table 1. Molecular structures show that the cyclopropene ligands are bonded to copper atoms in  $\eta^2$ -fashion. Interestingly, the carbonyl group of the CO2Et moiety also coordinates to copper, albeit weakly as evident from the relatively long Cu-O bond distances (2.2625(10)-2.2983(7) Å) compared with typical Cu–O(ester) separations of ~2.00 Å (Table S2)<sup>39</sup> as well as 1.954 Å of [(CF<sub>3</sub>)<sub>2</sub>Tp]Cu(Cyp-2) noted below, and nearly trigonal planar copper sites with the sum of angles (excluding oxygen) at copper of ~354-356° compared to 360° and 328° for ideal trigonal planar and tetrahedron arrangements, respectively. The copper-bound C=C distances (1.3481(12), 1.3583(18), and 1.3659(11) Å) display a

significant lengthening relative to typical C==C distances of free cyclopropenes (e.g., 1.296 Å for parent cyclopropene<sup>44</sup> and 1.2968(12) Å for Cyp-3 (see Supporting Information for the crystal structure)). The olefinic carbon centers of copper coordinated cyclopropene ligands in  $[(CF_3)_2Bp]Cu(Cyp-2)$ ,  $[(CF_3)_2Bp]Cu(Cyp-3)$ , and  $[(CF_3)_2Bp]Cu(Cyp-4)$  show clear pyramidalizations with the sum of the angles of 340–343° at olefinic carbons (not involving copper).

There are no copper cyclopropene  $\eta^2$ -complexes for comparisons. However, a search of CSD<sup>39</sup> revealed that structural data are available for a few transition metal  $\eta^2$ -cyclopropenes complexes (See also Table S3),<sup>41-43,45-55</sup> and they all show much longer cyclopropene C=C bond distances (with an average of 1.448 Å for 14 molecules spanning 1.50(1) Å for a Pt(0) complex (PPh<sub>3</sub>)<sub>2</sub>Pt(1,2-Me<sub>2</sub>-cyclopropene)<sup>45</sup> to 1.407 Å for a Mo(II)<sup>41</sup> adduct, Cp\*Mo(CO)<sub>2</sub>(2,3-Ph<sub>2</sub>-2-cyclopropene-1-carboxylate)) relative to the corresponding bond distance in [(CF<sub>3</sub>)<sub>2</sub>Bp]Cu(Cyp-2), [(CF<sub>3</sub>)<sub>2</sub>Bp]Cu(Cyp-3), and [(CF<sub>3</sub>)<sub>2</sub>Bp]Cu(Cyp-4) of 1.3481(12), 1.3583(18), and 1.3659(11) Å, respectively. This indicates that compared to these early transition metal complexes, the  $\sigma/\pi$ -interaction

Table 1. Selected Bond Distances (A) and	Angles (deg) of Copper(I) C	Complexes [(CF <sub>3</sub> ) <sub>2</sub> Bp]Cu(Cyp-2	2), [(CF <sub>3</sub> ) <sub>2</sub> Bp]Cu(Cyp-
3), [(CF <sub>3</sub> ) <sub>2</sub> Bp]Cu(Cyp-4) and [(CF <sub>3</sub> ) <sub>2</sub> Tp]	Cu(Cyp-2) <sup><i>a</i></sup>		

Parameter	$[(CF_3)_2Bp]Cu(Cyp-2)$	$[(CF_3)_2Bp]Cu(Cyp-3)$	[(CF <sub>3</sub> ) <sub>2</sub> Bp]Cu(Cyp-4)	$[(CF_3)_2Tp]Cu(Cyp-2)^a$
C=C	1.3481(12)	1.3583(18)	1.3659(11)	1.269(4)
				1.286(4)
Cu-C	2.0303(9)	2.0266(13)	2.0306(8)	
	2.0185(8)	2.0187(13)	2.0311(8)	
Cu–O	2.2983(7)	2.2625(10)	2.2818(6)	1.956(4)
				1.951(2)
Cu–N	2.0036(7)	1.9964(11)	2.0263(7)	2.074(2)
				2.050(2)
				2.108(2)
	2.0051(7)	1.9917(11)	2.0056(7)	2.054(2)
				2.047(2)
				2.116(2)
C-C(H)-C (interior cyclopropene)	52.66(5)	53.12(8)	52.97(5)	49.35(19)
				49.92(18)
Cu-C=C-R (dihedral)	123.63	121.07	123,22	
	123.20	121.73	122.63	
$\Sigma$ angles at Cu omitting O	354.55	356.19	354.48	271.99
				271.81
$\Sigma$ angles at C(=C) (not involving Cu)	342.79	340.33	339.91	360.00
				359.98
	342.49	342.99	340.94	359.91
				360.00

<sup>a</sup>Data for second molecules in the asymmetric unit *in italics* 

between  $d^{10}$ -copper(I) and cyclopropenes in  $[(CF_3)_2Bp]Cu$ -(Cyp-2), [(CF<sub>3</sub>)<sub>2</sub>Bp]Cu(Cyp-3), and [(CF<sub>3</sub>)<sub>2</sub>Bp]Cu(Cyp-4) are weaker. The cyclopropene interior C-C(H)-C bond angle involving the bridge-head carbon is an another indicator of relatively weaker interaction (and greater ring-strain) in the copper complexes which is at  $\sim 53^{\circ}$ , while the corresponding angle is much larger in the early transition metal complexes noted above (range from 55 to 59° with an average of 57°), approaching the typical cyclopropane ring angle of  $60^{\circ}$  from the starting 50.4° of free cyclopropene.44 These observations are not surprising since unlike early transition metals ions, copper(I) is not a metal known for strong  $\pi$ -backbonding. The highly fluorinated supporting ligand on copper makes the  $\pi$ -backbonding even weaker in these complexes (although it can enhance the Lewis acidity at Cu and perhaps also the olefin  $\rightarrow$  Cu electrostatic interactions). The <sup>13</sup>C NMR chemical shifts described above are also consistent with bond distance and angle changes. We have also collected Raman and IR data of the  $[(CF_3)_2Bp]Cu(Cyp-2)$ ,  $[(CF_3)_2Bp]Cu(Cyp-3)$ , and [(CF<sub>3</sub>)<sub>2</sub>Bp]Cu(Cyp-4) complexes (see ESI), but unfortunately, the assignment of cyclopropene C=C stretch was obscured by the presence of aromatic C=C and C=N stretching signals in the same region.

Considering the importance of new metal-mediated synthetic routes to cyclopropenes, we tested the prowess of 1 in cyclopropenation chemistry using internal alkynes and ethyl diazoacetate (EDA) as the carbene source (Scheme 2). The Cyp-2, Cyp-3, and Cyp-4 used in the copper coordinating chemistry (Scheme 1) were of particular interest. At room temperature, the reaction involving 3 mol % of catalyst 1 (based on EDA) and 1:3 molar ratio of EDA to 3-hexyne produced Cyp-2 in 61% isolated and 71% NMR yield, while the remaining EDA ended up as diethyl fumarate and maleate (Table S4). Quite interestingly, the copper cyclopropene complex  $[(CF_3)_2Bp]Cu(Cyp-2)$  can also function as a catalyst

Scheme 2. [(CF<sub>3</sub>)<sub>2</sub>Bp]Cu(NCMe)-Catalyzed Cyclopropenation of Alkynes with Ethyl Diazoacetate



remarkably well affording Cyp-2 in over 90% yield. It suggests that  $[(CF_3)_2Bp]Cu(Cyp-2)$  could play a direct role in cyclopropenation catalytic cycle or as a resting state. These cyclopropene product yields are respectable compared with the yields observed with other copper catalyzed cyclopropenations (see Table S5). Diarylated and disilyl substituted Cyp-3 and Cyp-4, as well as several other cyclopropenes with an alkyl-aryl substituent combination or with longer alkyl substituents (e.g., Cyp-6) can also be obtained using 1 as the catalyst and the appropriate alkyne substrate. The isolated yield of cyclopropene Cyp-4, however, was poor but still better than the 18% yield of the CuBr-mediated route to the closely related Cyp-4 analogue.<sup>57</sup>

We then tested the cyclopropenation of terminal alkynes, 1hexyne and 1-octyne, using the same process utilized with internal alkynes to obtain Cyp-7 and Cyp-8. Although the isolated product yields were disappointing initially, analyses of crude reaction mixtures revealed high product yields. It became clear that the issue was the copper-mediated decomposition of terminal cyclopropene products during the concentration and workup of the reaction mixture rather than with the cyclopropenation step. In fact, a reaction of  $[(CF_3)_2Bp]Cu(NCMe)$  with independently prepared Cyp-7 and Cyp-8 in CH<sub>2</sub>Cl<sub>2</sub> indicated the decomposition of these cyclopropenes to yet unidentified products, even above -50 °C. Copper-mediated cyclopropene ring-opening as well as carbometalation chemistry is well-known, and the products depend on the nature of the copper source.<sup>30,32-36</sup> Thus, on the basis of these observations, we improved the procedure by using a slightly larger ratio of alkyne:EDA followed by treatment with H<sub>2</sub>S to deactivate the catalyst before the workup of the reaction mixture, which led to Cyp-7 and Cyp-8 in 56% and 37% isolated yields, respectively.

Challenges with the cyclopropenation process of terminal alkynes using  $[(CF_3)_2Bp]Cu(NCMe)$  prompted us to test the more sterically demanding tris(pyrazolyl)borate catalyst  $[(CF_3)_2Tp]Cu(NCMe)$ .<sup>58</sup> Gratifyingly, it produced Cyp-8 in excellent, 93% yield. It could be that the resulting Cyp-8 is less prone to decomposition by  $[(CF_3)_2Tp]Cu(NCMe)$  due to the steric crowding at the copper. Interestingly, the cyclopropenation of the internal alkyne, 3-hexyne by  $[(CF_3)_2Tp]-Cu(NCMe)$  was somewhat less effective relative  $[(CF_3)_2Bp]-Cu(NCMe)$  under the same conditions (NMR yields of Cyp-2: 61% and 71% respectively for the two catalysts), perhaps because of the steric effects. Nevertheless, the differential reactivity is a useful observation and provides opportunities for further catalyst optimizations.

Next, we investigated the coordination chemistry of  $[(CF_3)_2Tp]Cu$  with cyclopropenes. The in situ generated  $[(CF_3)_2Tp]Cu$  with Cyp-2 afforded a 1:1 cyclopropene complex of copper(I),  $[(CF_3)_2Tp]Cu(Cyp-2)$  in 59% yield (Scheme 1). The <sup>13</sup>C{<sup>1</sup>H} MMR data of  $[(CF_3)_2Tp]Cu(Cyp-2)$  exhibited only a small change in olefinic carbon resonance (1.6 ppm, Table S1), in contrast to  $[(CF_3)_2Bp]Cu(Cyp-2)$ , indicating less involvement of the olefinic moiety in the adduct formation. Indeed, the X-ray crystal structure of  $[(CF_3)_2Tp]$ -Cu(Cyp-2) revealed it to be a solely O-bonded Cyp-2 via the ester group rather than an  $\eta^2$ -cyclopropene complex (Figure 2). A comparison of metrical parameters of  $[(CF_3)_2Tp]Cu(Cyp-2)$  to  $[(CF_3)_2Bp]Cu(Cyp-2)$  summarized in Table 1 nicely illustrates the effect of Cu(I) on the cyclopropene C==C bond, C-C(H)-C angle, as well as the differences between



Figure 2. Molecular structure of tris(pyrazolyl)borate ligand supported  $[(CF_3)_2Tp]Cu(Cyp-2)$ .

weak and strong C=O…Cu bonds involving the ester moiety, in the two systems. The C=O stretch of  $[(CF_3)_2Tp]Cu(Cyp-2)$  in IR displays a 76 cm<sup>-1</sup> reduction from that of the free Cyp-2 due to this latter O…Cu interaction, while the corresponding lowering in  $[(CF_3)_2Bp]Cu(Cyp-2)$  is only 34 cm<sup>-1</sup> (see ESI). The  $[(CF_3)_2Bp]Cu(Cyp-3)$  and  $[(CF_3)_2Bp]-Cu(Cyp-4)$  also show a reduction in C=O stretch by 23 and 28 cm<sup>-1</sup>, respectively, relative to the corresponding value in their free cyclopropenes.

$$[(CF_3)_2Bp]Cu(3-hexyne) + Cyp-2$$
  

$$\Rightarrow [(CF_3)_2Bp]Cu(Cyp-2) + 3-hexyne \qquad K_c = 0.12$$
(1)

$$[(CF_3)_2Bp]Cu(Cyp-2) + 3-hexyne$$
  

$$\Rightarrow [(CF_3)_2Bp]Cu(3-hexyne) + Cyp-2 \qquad K_c = 9.1$$
(2)

$$[(CF_3)_2Bp]Cu(NCMe) + Cyp-2$$
  

$$\Rightarrow [(CF_3)_2Bp]Cu(Cyp-2) + MeCN \qquad K_c = 11.0$$
(3)

Considering that copper-catalyzed cyclopropenation of alkynes producing cyclopropenes likely involve several ligand exchanges, we also assessed the relative binding affinities of MeCN, Cyp-2 and 3-hexyne with  $[(CF_3)_2Bp]Cu$  using isolable compounds. Details of  $[(CF_3)_2Tp]Cu(3-hexyne)$  are given in the Supporting Information. The relative equilibrium concentrations were measured using NMR spectroscopy at various temperatures. The equilibrium constants  $K_c$  for eq 1 and the control experiment noted in eq 2 (to ensure equilibrium was achieved under reverse conditions) are 0.12 and 9.1, respectively, at 243 K, which are consistent for a system in equilibrium for the forward and reverse directions. The data indicate that the alkyne preferentially binds to copper(I) over the cyclopropene, despite the predisposition of strained alkenes for metal ion coordination. Both the precursor alkyne and product cyclopropene also have a greater affinity to  $[(CF_3)_2Bp]Cu$  fragment than acetonitrile. For example,  $K_c$  for eq 3 is 11.0 at 243 K.

In summary, we have isolated for the first time, a group of copper  $\eta^2$ -cyclopropene complexes using a highly fluorinated, bis(pyrazolyl)borate auxiliary ligand, and a Cu–O bonded linkage isomer using a bulkier tris(pyrazolyl)borate ligand support, and characterized them using multiple methods including X-ray crystallography. The cyclopropenes used in this work as well as several others were also obtained in reasonable to excellent yields by the copper catalyzed cyclopropenation process involving the same ligand supports. We are currently probing these interesting complexes more deeply and the chemistry of cyclopropenes with other important metal ions.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02886.

Materials, methods, catalysis, spectroscopic and structural data, comparative literature data, and additional figures (PDF)

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#### Accession Codes

CCDC 2032777–2032781 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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