# **Inorganic Chemistry**

# Ligand Noninnocence in $\beta$ -Diketiminate and $\beta$ -Diketimine Copper **Complexes**

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Cite This: Inorg. Chem. 2024, 63, 15705-15715



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ABSTRACT: Metal-ligand cooperative systems have a long precedent in catalysis, with the classification depending on the site of substrate bond cleavage and formation and on redox state changes. Recently, our group reported the participation of a  $\beta$ diketiminate ligand in chemical bonding to heterocumulenes such as CO<sub>2</sub> and CS<sub>2</sub> by tricopper complexes, leading to cooperative catalysis. Herein, we report the reactivity of these copper clusters,  $[Cu_3EL]^-$  (E = S, Se; L = tris( $\beta$ -diketiminate) cyclophane ligand), toward other electrophiles, viz. alkyl halides and Brønsted acids. We identified a family of ligand-functionalized complexes, Cu<sub>3</sub>EL (R) (R = primary alkyls), and a series of disubstituted products, Cu<sub>3</sub>EL (R)<sub>2</sub>, through single-crystal X-ray diffraction, mass spectrometry, and infrared and UV-visible spectroscopy. As part



of mechanistic studies on these alkylation reactions, we evaluated the acid-base reactivity of these complexes and the influence of the backbone substitution on the reduction potential. Implications of these findings for ligand noninnocence and the relevance of the metal core as a cofactor for the ligand's reactivity are discussed.

# INTRODUCTION

Chemical catalysis by metal complexes often relies on the cooperation of the ligand, either to aid in substrate bond activation or provide redox equivalents necessary for the process (chemical vs redox noninnocence). In contrast to the widespread applications of redox-active ligands,<sup>1</sup> reports of productive catalysis by chemically noninnocent ligands are mostly limited to the support of protons or hydrogen atoms.<sup>2-5</sup> In particular, examples in which non-H groups are involved are rare for any ligand.<sup>6-</sup>

In this context, our group showed that tricopper chalcogenide clusters supported by a tris  $\beta$ - diketiminate (BDI) ligand ( $Cu_3EL$ , E = S, Se, 1 and 2, respectively, Figure 1) perform catalytic C–C bond formation from  $CO_2$  to afford oxalate in the presence of a chemical reductant.<sup>10</sup> Notably, we recently demonstrated that this reaction likely proceeds by nucleophilic attack of the ligand on the electrophilic C atom of  $CO_2$ , by analogy to the reaction with  $CS_2$ .<sup>11</sup> The resultant C-C bond between the substrate and the  $\gamma$ -C of the BDI ligand backbone is labile, based on reaction with  $\text{CS}_2$  and DFT studies (Figure 1). Although labile C-C bonds are known in the context of ligand noninnocence (Figure 2), prior examples arise from radicaloid character on the ligand C atom rather than nucleophilic behavior.<sup>12–15</sup>

Despite precedent for the nucleophilicity of BDI ligands,<sup>16,17</sup> and particularly regarding the activation of small molecules (Figure 3), $^{18-25}$  this nucleophilic behavior is generally regarded an undesired and irreversible modification and has



Figure 1. Structures of 1 and 2 and proposed intermediates, 3<sup>-</sup> and 4<sup>-</sup>, in the reductive homocoupling of  $\overline{\text{CS}}_2$  and  $\overline{\text{CO}}_2$  by 1<sup>-</sup>.

led to ligand designs that sterically protect the  $\gamma$ -position.<sup>26</sup> Our recent work, however, evidence that this nucleophilic

Received: April 19, 2024 Revised: July 19, 2024 Accepted: July 22, 2024 Published: August 2, 2024



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Figure 2. Reversible C-C bonds formed by metal radicaloids.



Figure 3. Selected examples of small molecule activation on BDI metal complexes exhibiting ligand noninnocence, with the corresponding small molecules highlighted in red.

behavior can be productive (Figure 1).<sup>11</sup> To further explore this reactivity, we therefore sought to study the behavior of the  $\beta$ -diketimines that result from nucleophilic attack at the  $\gamma$ -C and the new possible avenues for reactivity emerging from the noninnocence of this tris BDI cyclophane ligand.

Herein, we investigate the reaction of  $[Cu_3SL]^-$ ,  $1^-$  and  $[Cu_3SeL]^-$ ,  $2^-$  with electrophiles other than heterocumulenes and report on both the role of the ligand and the metal core in reactivity.

## RESULTS AND DISCUSSION

Reactions between  $1^-$  and  $2^-$  with several substrates were assayed to evaluate whether the reactivity is radical or nucleophilic nature. Treatment of a turquoise solution of 1- $(\lambda_{max} = 696 \text{ nm})$  with 1 equiv of BnX (X = Cl, Br) afforded a blue mixture with two absorption maxima, 608 and 735 nm. For both  $1^-$  and  $2^-$ , two species are observed by ESI-MS with molecular weights implying incorporation of one and two benzyl fragments (5-Bn and 6-Bn starting from 1<sup>-</sup> and 7-Bn and 8-Bn from 2<sup>-</sup>, Figures S1 and S2). Single crystals grown from the crude reaction from  $1^-$  were analyzed by singlecrystal X-ray diffraction (XRD) and can be modeled as cocrystals of two species: the mono- and dibenzylated complexes. The major product, Cu<sub>3</sub>SL (Bn) (5-Bn), corresponds to 85% of the electron density in the diffraction pattern and consists of a complex with an intact  $[Cu_3S]^{2+}$  core, a single neutral diketimine arm in which a benzyl group is bound to the  $\gamma$ -C of the diketimine, and two unmodified BDI arms (Figure 4a). The remaining 15% of the electron density



**Figure 4.** Single-crystal structure of  $Cu_3SL$  (Bn), **5-Bn** (a) and  $Cu_3SL$  (Bn)<sub>2</sub>, **6-Bn** (b) at 50% thermal ellipsoid. Solvent molecules and hydrogen atoms omitted for Clarity. Cu, S, N, and C atoms depicted as bronze, yellow, blue, and gray ellipsoids, respectively.

in the diffraction pattern is modeled as  $Cu_3SL$  (Bn)<sub>2</sub> (6-Bn), an analogue of Cu<sub>3</sub>SL (Bn) where the  $\gamma$ -H in a  $\beta$ -diketiminate arm has been substituted by a benzyl group (Figure 4b). An alternative model in which the excess electron density is attributed to positional disorder instead of a second benzyl fragment affords a slightly smaller goodness-of-fit (1.070 vs 1.071 for the cocrystal model); the cocrystallized 5-Bn/6-Bn model, however, is consistent with ESI-MS(+) data collected on a solution of a crystalline sample. We also note that the parent ion observed for 6-Bn is the K<sup>+</sup> adduct rather than the cation  $[6-Bn+H]^+$ , implying that 6-Bn is a neutral species as noted in the crystallographic model. The benzylated ligand arm in 5-Bn features significantly shorter C-N and longer C-C bond lengths when compared to the unsubstituted arms as well as longer Cu-N bond lengths for the substituted arm as compared to the unaffected BDI arms. The Cu-N distances in the benzylated arm are intermediate of those reported for Cu(I) and Cu(II) diimines (2.0331-2.1235 Å and 1.9387-2.006 Å for Cu(I) and Cu(II), respectively, Table 1).<sup>27–30</sup> The

Table 1. Crystallographic parameters of 5-Bn for the two fully occupied ligand arms and for  $9^{-CF3}Bn^-$ 

	$_{(Å)}^{\beta-C-N}$	β-C-γ-C (Å)	Cu–N (Å)	∠γ-C (deg)
5-Bn: Bn arm	1.277 (3)	1.522 (3)	2.016(2)	109.6
5-Bn: H arm	1.326 (3)	1.412 (4)	1.954(2)	120.0
9- <sup>CF3</sup> Bn <sup>-</sup> : <sup>CF3</sup> Bn arm	1.330 (3)	1.430 (3)	1.948 (2)	119.9
9- <sup>CF3</sup> Bn <sup>-</sup> : H arm	1.328 (3)	1.408 (3)	1.958 (2)	120.0

angles about the  $\gamma$ -carbon also decrease from the unmodified to benzylated arms (*viz.* 120.0° to 109.6°), along with the  $\gamma$ -C now significantly out-of-plane with respect to the remaining chelate atoms (0.395 Å from said C to the NC-NC plane). Taken together then, XRD data support a neutral diketimine ligand upon benzylation.

The crystal structure of **6-Bn** will be treated as showing connectivity-only, given the 15% occupancy obtained from the model. Comparable thermal ellipsoids at a given probability level in the structures of **5-Bn** and **6-Bn**, however, suggest similar bond metrics with analogous  $[Cu_3S]^{2+}$  clusters.

**5-Bn** can be synthesized using BnCl or BnBr as the benzyl source, with the reaction proceeding qualitatively faster in the bromide case, consistent with a nucleophilic attack by  $1^-$  on the alkyl halide and precedent from others.<sup>31</sup> Most reports of  $\gamma$ -C functionalization in BDI ligands in transition metal or main group complexes result from unsaturated substrates adding across the metal center and ligand backbone.<sup>18,20–25,32</sup>

Treatment of  $1^-$  and  $2^-$  with other alkyl halides, RX, also afforded blue reaction products with UV–visible spectra comparable to those of **5-Bn** (Figure S9) and our previously reported CS<sub>2</sub> adduct,  $3^-$ , which implies comparable electronic structures for the alkylated species and heterocumulene adduct. For example, derivative  $5^{-CF3}Bn$  exhibits two absorption maxima in the visible range, at 580 and 756 nm (Figure S10), which is similar to the maxima at 608 and 735 nm for  $3^-$ .<sup>11</sup> Molecular weights of these products were confirmed by ESI-MS and agree with formation of the expected analogues, **5-R**, arising from nucleophilic attack by the  $\gamma$ -C onto the electrophilic alkyl carbon (Figures 5, S1–S7). Notably, formation of **5-Me** from the MeI or MeOTf and **5-**CH<sub>2</sub><sup>Cy</sup>Pr from <sup>Cy</sup>PrCH<sub>2</sub>Cl or <sup>Cy</sup>PrCH<sub>2</sub>OTf, support a concerted nucleophilic mechanism (S<sub>N</sub>2). The intact cyclo-



Figure 5. Reaction scheme for synthesis of compounds 5-R and 6-R, and 7-R and 8-R (top). Chemical structures of the 5-R complexes reported with the alkyl fragments highlighted in red (bottom).



Figure 6. Proposed pathways to proceed from 5-R to 6-R and (6-R)'.

propyl group was confirmed by <sup>1</sup>H NMR spectroscopy after deprotonation and oxidation of  $5-CH_2^{Cy}Pr$  to a diamagnetic species (*vide infra*). We conclude then that the observed reactivity here and previously with CS<sub>2</sub> lack radical character and arise from two-electron processes.

Crude reaction mixtures from the syntheses of **5-R** and **7-R** were analyzed by ESI-MS, and the corresponding disubstituted products, **6-R** and **8-R** (i.e.,  $Cu_3SeL(R)_2$ ), were observed in all cases, with the exception of **6-Me** and **6-CH<sub>2</sub><sup>Cy</sup>Pr** (Figures S1–S7). Absence of electron density for a counteranion in the

XRD of the **5-Bn** and **6-Bn** cocrystal implies that **6-R** is a neutral species, conceding that corresponding partial occupancy of that counteranion may be limiting. To support that hypothesis, we envisioned several routes from **5-R** to **6-R** (Figure 6), with a similar analysis is expected for 7-**R** and **8-R**. Nucleophilic attack by **5-R** on RX can generate a cationic species, and subsequent deprotonation or reduction by  $1^-$ , afford the disubstituted neutral species (pathways A and B, Figure 6). Conversely, deprotonation or reduction of **5-R** followed by nucleophilic attack (pathways C and D, Figure 6)

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Figure 7. Synthesis of (a) 5-H from  $1^-$ , (b)  $(1-D_3)^-$  from  $1^-$ , and (c) 9-R from 5-R.

or reduction of the alkyl halide followed by radical coupling to 5-R (pathway E, Figure 6) are also plausible. Since the rate of nucleophilic attack by an anionic species should exceed that of a neutral one for comparable species, pathways A and B are unlikely, as reaction of  $1^-$  with an alkyl halide should proceed faster than that of 5-R. All pathways involving reductions (B, D and E) would afford a bis( $\beta$ -diketimine) and a formal [Cu<sub>3</sub>S]<sup>+</sup> core, (6-R)'. Since the extent of protonation of the  $\gamma$ -C in the second alkylated arm cannot be unambiguously determined by XRD or ESI-MS, we cannot directly disregard pathways B, D and E. However, we do not observe larger thermal ellipsoids for the benzylated BDI arms or the cluster-bond lengths in the cluster and the second benzylated arm for (6-R)' are expected to differ from those in 5-R—hinting that (6-R)' is not the minor species observed by XRD. Attempts to reduce 5-Bn and 5-<sup>CF3</sup>Bn, both chemically and electrochemically, have been unsuccessful; thus, reduction of 5-R by  $1^-$  is unlikely (pathway D). Finally, the  $E_{1/2}$  of BnCl is substantially more negative that of 1 (-2.18 V and -1.48 V vs Fc/Fc<sup>+</sup>, respectively),<sup>33-35</sup> providing further evidence against pathway E. Protonation at the BDI  $\gamma$ -C has been widely reported for other transition metal complexes in support of  $1^-$  acting as a base.<sup>36-40</sup> Collectively, the data support pathway C in which deprotonation of the  $\gamma$ -CH in the diketimine arm of 5-R by unreacted  $1^-$  yields a monoanionic complex ([9-R]<sup>-</sup>, vide infra) and 5-H. The resultant  $[9-R]^-$  is then competent to attack another equivalent of RX, yielding 6-R (pathway C, Figure 6).

In contrast with the lability of the  $C-CS_2$  bond observed in  $3^-$  (Figure S18),<sup>11</sup> formation of 5-R from  $1^-$  is irreversible as one might expect. In the latter case, precipitation of corresponding alkali metal halide salt, MX, favors product

formation. Additionally, the leaving group generated from C–C bond homolysis from  $3^-$ ,  $CS_2$ , is more stable and volatile as compared to that generated from 5-R.

Resonances and molecular ion peaks consistent with 1 are observed by <sup>1</sup>H NMR spectroscopy and ESI-MS(+) data collected on crude reaction mixtures of 1<sup>-</sup> and BnCl. Column chromatographic purification of the crude reaction mixture allows separation of three species; unit cell analysis by XRD of single crystals grown from the first fraction agree with those reported for 1. We infer that formation of 1 arises from decomposition of 5-H, which we then evaluated by monitoring the reaction of  $1^-$  with various proton sources. Treatment of 1<sup>-</sup> with excess of Brønsted acids, such as Et<sub>3</sub>NHCl, regenerates 1 based on <sup>1</sup>H NMR spectra (Figure S12). The basicity of 1<sup>-</sup> was estimated by reacting with excess of various weak acids, viz. 2,6-lutidinium triflate, triethylammonium hydrochloride, the conjugate acid of Proton Sponge, phenol, and water. Immediate reaction was observed in all cases except water, which was unreactive even in >10-fold excess for prolonged periods of time (>24 h). Reaction with a stoichiometric amount of the weaker acids noted above afforded a blue species with a UV-vis spectrum reminiscent to those of 5-R (Figures S9–S11) and a paramagnetically broadened <sup>1</sup>H NMR spectrum, rather than regeneration of 1. By analogy then, and consistent with literature precedent,  $^{36-40}$  protonation occurs at a similar site as alkylation, generating 5-H (Figure 7a). Relatedly, Phillips and co-workers reported an Os BDI complex that bifunctionally and irreversibly activates H<sub>2</sub> across the metal and  $\gamma$ -C of BDI under mild conditions (Figure 3).<sup>19</sup> Further downstream reactivity of 5-H to release  $H_2$  through oxidation of the  $[Cu_3S]^{2+}$  core provides a possible route to regenerate 1; however, efforts to identify the predicted  $H_2$ 

product in the reaction mixture have thus far been unsuccessful.

To confirm that the BDI  $\gamma$ -C acts as a basic site, an isotope labeling experiment was performed using Et<sub>3</sub>NDCl. Serial treatment of 1<sup>-</sup> with 1 equiv of Et<sub>3</sub>NDCl, followed by 1 equiv of alkali metal bis(trimethylsilylamide) (13 iterations) was performed (Figure 7b). After this process, addition of 1 equiv of AgBr yields a diamagnetic product readily identifiable by <sup>1</sup>H NMR spectroscopy. Resonances for this product were consistent with 1, except for a decrease of 50% in the <sup>1</sup>H NMR signal corresponding to the  $\gamma$ -proton, as expected for deuteration of the  $\gamma$ -position (Figures S13 and S14). The signal observed in the <sup>2</sup>H NMR spectrum at 4.69 ppm agrees with protonation occurring at the  $\gamma$ -position (Figure S15). Thus, NMR data point to the formation of (1–0.5D<sub>3</sub>), with 50% D enrichment.

Armed with both redox and  $pK_b$  data for 1<sup>-</sup>, the bond dissociation free energy (BDFE) of the  $\gamma$ -C–H bond in **5-H** can be estimated using a square scheme (Figures 8 and



**Figure 8.** Square scheme for the reduction- H atom transferprotonation processes from 1 and 1<sup>-</sup>. Only the relevant half of the square scheme is shown.  $E_{1/2} = -1.44$  V vs Fc/Fc<sup>+</sup> = -0.82 V vs SHE;<sup>35</sup> -209 kJ/mol <  $\Delta G_{H+}$  < -156 kJ/mol in MeCN, thus 78 kJ/ mol < BDFE < 130 kJ/mol.

S19).<sup>35,41–43</sup> In this manner, the BDFE in MeCN was estimated to be between 78 and 130 kJ/mol. For reference, the BDFE of TEMPO–H is 278 kJ/mol,<sup>44</sup> consistent with TEMPOH being incompetent for conversion of 1 to 5-H. Peters and co-workers reported a BDFE of 163 kJ/mol for the N–H in their cobaltocene dimethylaniline complex,<sup>45</sup> whereas the O–H BDFE of SmI<sub>2</sub>(H<sub>2</sub>O) in THF is calculated to be 157 kJ/mol.<sup>46</sup> Recently, Boyd et al. reported two Sm(II) complexes with BDFE values of 114 and <101 kJ/mol and Sinhababu et al. reported a BDFE value for an O–H bond as low as 4.18 kJ/mol, generated by coordination-induced bond weakening.<sup>47,48</sup> Expectedly given the weak X–H bond as compared to the bond in H<sub>2</sub>, **5-H** decomposes over ~24 h to regenerate 1, which is analogous to the solution instability reported for the SmI<sub>2</sub> complexes from Boyd et al.

We then exploited the acid—base chemistry of the  $\gamma$ -C of the diimine arm to examine the reactivity of **5-R**. Treatment of **5**-<sup>CF3</sup>**Bn** with an alkali metal bis(trimethylsilylamide) affords the anionic species,  $[9^{-CF3}Bn]^-$ , in which one alkylated and two unsubstituted  $\beta$ -diketiminate ligands are present, as seen from the X-ray structure (Figures 7c and 9). The identity of the anion was further confirmed by ESI-MS(–) (Figure S8). Previously, the groups of Busch and later Goedken had reported a similar deprotonation of the  $\gamma$ -C of an Fe  $\beta$ -diketimine, leading to the intramolecular nucleophilic attack of an acetonitrile ligand bound to the Fe center.<sup>49–51</sup>



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**Figure 9.** Single crystal XRD structure of  $[K(18\text{-crown-6})THF] \cdot [9^{-CF3}Bn]$  at 50% thermal ellipsoid. Guest solvent molecules and hydrogen atoms have been omitted for clarity. Cu, S, N and C, F, O and K atoms are depicted as bronze, yellow, blue, gray, green, red, and pink ellipsoids, respectively.

Selected bond lengths and angles for 9-<sup>CF3</sup>Bn<sup>-</sup> are reported in Table 1. The alkylated  $\gamma$ -carbon is trigonal planar based on the sum of the angles about this atom  $(359.6^{\circ})$ . Further comparison of this structure with that of 5-Bn reveals that the average Cu-N bond lengths shorten in the alkylated arm after deprotonation. In contrast, the Cu-N distances for the unmodified BDI arms are indistinguishable throughout the series 1<sup>-</sup> (1.957(6) Å), 5-Bn and [9-<sup>CF3</sup>Bn]<sup>-</sup>. Oxidation of [9-<sup>CF3</sup>Bn]<sup>-</sup> with 1 equiv of AgBr afforded a green diamagnetic product with solution  $C_{2\nu}$  symmetry based on the number of <sup>1</sup>H and <sup>19</sup>F-NMR resonances, consistent with the expected product, 9-<sup>CF3</sup>Bn (Figure 7c). A similar procedure was repeated on 5-CH2<sup>Cy</sup>Pr and the <sup>1</sup>H NMR spectrum of the crude product mixture lacks vinylic protons expected for ringopened products, featuring instead upfield resonances for the intact cyclopropyl ring (Figure S16). These findings exclude radical steps in the formation of 5-R.

The redox behavior of  $[9^{-CF3}Bn]^-$  was studied by cyclic voltammetry (Figure 10). The voltammogram exhibits a single quasi-reversible redox wave for the couple  $9^{-CF3}Bn/[9^{-CF3}Bn]^-$ , with a cathodic peak potential at -1.43 V vs Fc/Fc<sup>+</sup> ( $E_{1/2} = -1.35$  V). This reduction event, albeit shifted by +50 mV (+90 mV for the  $E_{1/2}$ ), is reminiscent of that of 1, assigned as the  $[Cu_3S]^{3+/2+}$  couple.<sup>52</sup> Thus, the electron withdrawing group in the ligand backbone exhibits a small but quantifiable influence on the reduction potential of the cluster.

Intrigued by the nucleophilic reactivity of 1<sup>-</sup>, we envisioned scenarios in which complexes could be covalently linked, providing a route to favor downstream reactions (e.g., CO<sub>2</sub> conversion to oxalate). Reaction between  $1^-$  and 1,2dibromoethane (DBE) produces a blue species within 1 h, ultimately evolving to green after ~24 h. In situ <sup>1</sup>H NMR spectra for this reaction show a progression from a paramagnetic species to a diamagnetic mixture. Dihydrogen, bromoethylene and ethylene were identified in the reaction mixture in a 2:4:1 molar ratio, as calculated by <sup>1</sup>H NMR integration values (Figure S17).<sup>53</sup> The first two products can be attributed to an analogous pathway as for mono- and dialkylation noted above (Figure 11a). Namely, nucleophilic attack from one  $\gamma$ -C in 1<sup>-</sup> onto DBE likely affords the corresponding 5-CH<sub>2</sub>CH<sub>2</sub>Br, responsible for the blue color. Then, an equivalent of 1<sup>-</sup> deprotonates 5-CH<sub>2</sub>CH<sub>2</sub>Br at the C lpha to bromide, releasing bromoethylene and 5-H, which



**Figure 10.** Cyclic voltammogram of  $[K(18-crown-6)] \cdot [9^{-CF3}Bn]$ . Complex concentration: 2.2 mM in THF, with 0.2 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte and a scan rate of 100 mV/s. Arrow represents the direction of the scan. Working electrode: 3 mm glassy C button; auxiliary electrode: Pt coil; reference electrode: Ag/AgNO<sub>3</sub> 10 mM in MeCN.

proceeds to release H<sub>2</sub> as suggested previously. A similar ethylene release has been reported through metal–ligand synergy of Ru, Os, Pt and Al BDI complexes.<sup>20,21,24,25</sup> In conjunction with the reversible addition of carbon disulfide by  $1^{-,11}$  these reports set a precedent for the C–C bond rupture from the  $\gamma$ -C in a BDI ligand (Figure S18). In contrast to the reversible addition of ethylene, however, we predict no direct copper-substrate interactions in the release of bromoethylene from 5-CH<sub>2</sub>CH<sub>2</sub>Br, based on our prior report from reaction of  $1^{-}$  and CS<sub>2</sub>.<sup>11</sup>

Given the lack of reactivity between  $1^-$  and vinyl halides, formation of ethylene cannot arise from reaction with bromoethylene. A competing pathway must account for ethylene formation. In a plausible route,  $1^-$  ( $E_{1/2} = -1.44$  V vs Fc/Fc<sup>+</sup>)<sup>52</sup> acts as an electron donor to reduce DBE. This leads to the formation of neutral 1, bromide and the radical decomposition of bromoethylene, which has been shown to produce ethylene at potentials as high as -1.42 V vs Fc/Fc<sup>+</sup>.<sup>35,54,55</sup> Notably, bromoethylene was not reported as a reaction product from electrochemical decomposition of DBE, pointing to  $1^-$  as responsible for its formation, consistent with our proposed pathway (Figure 11).

The formal charge of the metal core in **5-R** and  $[9-R]^-$  is +2. However, a combination of computational and spectroscopic studies on **1** pointed to significant copper-chalcogen covalency.<sup>55</sup> To better understand the electronic structure of these molecules, **5-**<sup>CF3</sup>**Bn** and  $[9-^{CF3}$ **Bn** $]^-$  were characterized through solution electron paramagnetic resonance (EPR) in the X-band at room temperature and compared to that of **1**<sup>-</sup>. The data could be successfully modeled to obtain the *g*-factors ( $g_{avg}$ ) and hyperfine splitting constants ( $A_{avg}$ ) for these complexes (Table 2). All three EPR spectra display a ten-line

Table 2. g-factors and hyperfine splitting constants obtained from simulation of X-band EPR data of 1<sup>-</sup>, 5-<sup>CF3</sup>Bn and [9-<sup>CF3</sup>Bn]<sup>-</sup>

	1-	5- <sup>CF3</sup> Bn	[9- <sup>CF3</sup> Bn] <sup>-</sup>
gavg	2.095	2.069	2.069
A/G	35.0	34.3	35.3

pattern, as expected for delocalization of the unpaired spin over all the  $[Cu_3S]^{2+}$  core (Figure S20). Additionally, the similar hyperfine splitting constants across the series indicate that at room temperature the loss of symmetry in the ligand does not affect the delocalization of the unpaired spin in the core. Absence of <sup>19</sup>F hyperfine interactions also imply minimal delocalization of charge on to the benzyl group. We infer then that the electronic structure of the  $[Cu_3S]^{2+}$  core is insensitive to the modification of the BDI arm across the series  $1^-$ ,  $5^{-CF3}Bn$ , and  $[9^{-CF3}Bn]^-$ . We note, however, that spectra reflect the contribution of any thermally populated low-lying excited states at 298 K, rather than the electronic ground state exclusively.



Figure 11. Proposed pathway responsible for the release of bromoethylene and dihydrogen in the reaction of  $1^-$  with 1,2-dibromoethane (DBE).

# CONCLUSIONS

Reaction of the tricopper cyclophanates  $1^-$  and  $2^-$  with alkyl halides affords the corresponding complexes with one, and in a smaller yield, two, alkylated ligand arms. With this approach we have synthesized a family of alkyl modified copper chalcogenides, **5-R** and **7-R**, and supported the nucleophilic nature of this substitution reaction. Unexpectedly, when the ligand substitution contains unhindered  $\beta$ -hydrogens, such as the case of 1,2-dibromoethane, the product decomposes readily to release a small unsaturated hydrocarbon.

We have demonstrated that **5-R** can be deprotonated at the  $\gamma$ -position to afford the anionic family,  $[9-R]^-$ , which exhibits similar reactivity to the parent 1<sup>-</sup>. We posit that this deprotonation of **5-R** by another equivalent of 1<sup>-</sup> is responsible for enabling the second nucleophilic attack to alkyl halides, yielding the disubstituted family, **6-R**. Finally, X-band EPR measurements at ambient temperature suggest a similar spin delocalization for the series 1<sup>-</sup>, **5-**<sup>CF3</sup>Bn, and  $[9-^{CF3}Bn]^-$ .

#### **EXPERIMENTAL DETAILS**

General Considerations. All reactions were performed in an N2or Ar-filled Vacuum Atmospheres Company glovebox (dioxygen level evaluated using a titanocene atmosphere test),<sup>57</sup> or using air-free Schlenk techniques unless otherwise specified. Tetrahydrofuran (THF), benzene, toluene, diethyl ether ( $Et_2O$ ), acetonitrile (MeCN), and n-hexane were purchased from Sigma-Aldrich, then dried through an Innovative Technologies Solvent Purification System, and stored over activated 3 Å molecular sieves at least 24 h prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, dried with CaH2 under reflux, then distilled, degassed, and stored over 3 Å molecular sieves (activated at 180 °C at 10 mTorr) in the glovebox. Neutral alumina was dried at 270 °C at 10 mTorr in a Schlenk flask for 2 d, and stored in the glovebox prior to use. <sup>1</sup>H NMR spectra were recorded on a 500 MHz Varian Inova spectrometer or a 400 MHz Bruker spectrometer. Chemical shifts were reported in  $\delta$  (ppm) and referenced to residual solvent resonances. Chemical shifts for <sup>19</sup>F-NMR spectra were referenced to 1,2 difluorobenzene (-140 ppm). Fourier Transform Infrared (FT-IR) spectra were recorded as solids or on drop-casted solution samples using the OMNIC software package (32 scans per sample at 1.0 cm<sup>-1</sup> resolution) on a Thermo Fisher iS6 spectrophotometer equipped with an ATR diamond crystal stage. Mass spectra (MS) were collected using an Agilent 6220 ESI-TOF instrument (175.0 V head voltage), housed in the Mass Spectrometry Research and Education Center at UF. Samples were loaded by direct injection using airtight Hamilton syringes and an external syringe pump. The ligand H<sub>3</sub>L and corresponding Cu complexes were synthesized as reported previously, unless otherwise stated.<sup>52,56,58</sup> UV-visible measurements were performed using an Ocean Optics Spectrophotometer and OceanView 1.6.5 software, and UV-visible kinetic and variable temperature (VT) experiments were performed using a Cary 50 spectrophotometer, equipped with a temperature-controlled Unisoku single-cell accessory and Scanning Kinetics and Scan software (Agilent Technologies, USA). All measurements were performed in screw capped or Schlenk-adapted quartz cuvettes with a 1 cm optical path length. Electron paramagnetic resonance data were recorded on a Bruker Elexsys E580 with a Bruker 4116DM resonator. Data were collected in the field from 2900 to 3900 G with the following parameters at 298 K: power = 2.000 mW; frequency = 9.789357 GHz; modulation frequency = 100.00 kHz; modulation amplitude = 5 G; gain = 60 dB; and scans = 4. Cyclic voltammetry data was recorded on a Princeton Applied Research Versastat II potentiostat, using a conventional three-electrode setup in a N2- filled glovebox.

**Synthesis of [K(THF)**<sub>3</sub>**·1.** This compound was synthesized as described previously,<sup>10</sup> except that Celite used to filter the complex

after reduction was neutralized with  $KN[Si(CH_3)_3]_2$  in THF and extensively rinsed with THF prior to use.

**Reaction of 1<sup>-</sup> with Brønsted Acids.** [K(18-crown-6)]·1 (10 mg, 8.2  $\mu$ mol, 1 equiv) was dissolved in acetonitrile (2 mL) and treated with 1.0 equiv of a proton source. 2,6-lutidinium triflate, Et<sub>3</sub>NHCl (or Et<sub>3</sub>NDCl), and the hydrochloride adduct of Proton Sponge afforded an color change from teal to blue upon mixing. Addition of excess acid resulted in conversion of blue species to the green Cu<sub>3</sub>SL within seconds, based on <sup>1</sup>H NMR data.

**Reaction of 1<sup>-</sup> with 1,2-Dibromoethane.** [K(18-crown-6)]·1 (10 mg, 8.2  $\mu$ mol, 1 equiv) was dissolved in MeCN- $d_3$  (450  $\mu$ L) and transferred to a J-Young NMR tube, and 1,2-dibromoethane (1.6 mg, 8.5  $\mu$ mol, 1.0 equiv) dissolved in MeCN- $d_3$  (50  $\mu$ L) added. The tube was then sealed and shaken vigorously. The mixture evolved to a deep blue solution within 10 min, and forest green over the next 24 h. The <sup>1</sup>H NMR spectrum at 72 h support generation of 1, ethylene, dihydrogen and bromoethylene.

Alkylation of 1<sup>-</sup> to 5-R and 6-R. In a typical reaction, a solution of alkyl halide (0.8 equiv) in MeCN or THF added dropwise to either  $[K(18\text{-crown-6})] \cdot 1$  or  $[K(THF)_3] \cdot 1$  (1 equiv) dissolved in MeCN or THF, respectively. For either complex, the color changes from teal to deep blue for alkyl chlorides (<5 h) and bromides, iodides, or triflates (<1 min). After stirring at ambient temperature for 24 h for chlorides and 2 min for all others, the mixture is filtered through Celite, and the solvent removed under reduced pressure. Composition of reaction mixtures, where noted, were evaluated by ESI-MS(+). The crude mixture corresponds to an inseparable mixture of 1, 5-R, and 6-R except for the R groups noted below. Efforts to optimize the conditions to improve the yield on 5-R by varying reaction time, temperature, and equivalents were unsuccessful and recrystallization of the mixture was ineffective to separate the products. Single crystals of 5-Bn suitable for XRD were obtained by slow evaporation of a saturated diethyl ether solution into toluene at -35 °C. ESI-MS(+) of the crude mixture where R= Bn showed ions at m/z values of 1040.2849 ([5-Bn+K]<sup>+</sup>, expected 1040.2890) and 1130.3335 ([6-Bn +K]<sup>+</sup>, expected 1130.3359), where R= Me showed ions at m/z values of 949.2248 ([5-Me+Na]<sup>+</sup>, expected 949.2916), and where R=  $CH_2^{Cy}Pr$  showed ions at m/z values of 988.1835 ([5- $CH_2^{Cy}Pr$ ]<sup>+</sup>, expected 988.3150).

**5-CF<sub>3</sub>Bn and 6-CF<sub>3</sub>Bn.** As described above using the typical reaction conditions and [K(18-crown-6)]·1 (32.0 mg, 26.3  $\mu$ mol, 1 equiv) in MeCN (8 mL), a solution of *p*-trifluoromethyl benzyl chloride (4.1 mg, 21.1  $\mu$ mol, 0.8 equiv) in MeCN (0.5 mL). To isolate the product, the blue residue was redissolved in Et<sub>2</sub>O and loaded on a neutral alumina column. The column was eluted with Et<sub>2</sub>O, then THF, then MeCN to obtain three fractions. The Et<sub>2</sub>O fraction was confirmed to be 1 (5.2 mg, 5.7  $\mu$ mol, 22% based on 1<sup>-</sup>) through single crystal XRD and <sup>1</sup>H NMR spectroscopy. The THF fraction corresponds to 5-<sup>CF3</sup>Bn (12.6 mg, 11.8  $\mu$ mol, 45% based on 1<sup>-</sup>), and the MeCN fraction to 6-<sup>CF3</sup>Bn. Characterization of 5-<sup>CF3</sup>Bn: <sup>19</sup>F{<sup>1</sup>H}-NMR (377 MHz, Toluene-*d*<sub>8</sub>)  $\delta$  (ppm) –62.21. ATR-IR ( $\nu$ , cm<sup>-1</sup>): 1633 (m, diketimine C = N). UV–visible ( $\lambda_{max}$ , nm): 580, 756 nm. ESI-MS(+): 1069.2773 ([5-<sup>CF3</sup>Bn]<sup>+</sup>, expected 1069.3126). Characterization of 6-<sup>CF3</sup>Bn: ESI-MS(+): 1228.3404 ([6-<sup>CF3</sup>Bn +H]]<sup>+</sup>, expected 1228.3548).

**7-Bn and 8-Bn.** Reaction was performed as described for alkylation of 1<sup>-</sup>, except [K(18-crown-6)]·2 (15.0 mg, 11.9  $\mu$ mol, 1 equiv) in MeCN (3 mL) and a solution of benzyl bromide (1.5 mg, 8.8  $\mu$ mol, 0.75 equiv) in MeCN (20  $\mu$ L) were used. The resultant blue residue (7.2 mg) was extracted into minimal Et<sub>2</sub>O and filtered through Celite. This product mixture contains 1, 7-Bn, and 8-Bn based on a combination of <sup>1</sup>H NMR and ESI-MS(+) data. Efforts to optimize the conditions to improve the yield on 7-Bn were unsuccessful. Recrystallization of the mixture was ineffective to separate the products. ESI-MS(+) of rod-shaped crystals of this sample grown by slow evaporation of Et<sub>2</sub>O at -35 °C showed ions at m/z values of 1049.2571 ([7-Bn]<sup>+</sup>, expected 1049.2697) and 1139.3149 ([8-Bn]<sup>+</sup>, expected 1139.3167).

**7-Me and 8-Me.** Reaction was performed as described for alkylation of  $1^-$ , except [K(18-crown-6)] **2** (10.0 mg, 7.9  $\mu$ mol, 1

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All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

Authors acknowledge the following: support from the US Department of Energy (no. DE-SC022174); an instrumentation award by National Institutes of Health award (NIH S10 OD021758-01A1) to the Mass Spectrometry Facility; and S.N. MacMillan for the XRD data collection and analysis. M.V.L.O. would also like to acknowledge University of Florida, College of Liberal Arts and Sciences, for a Graduate Research Fellowship, and Titto S. John for help with experiments.

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equiv) in MeCN (2 mL) and MeI (1.2 mg, 8.5  $\mu$ mol, 1.05 equiv) in MeCN (30  $\mu$ L) were used. After 2 min, the solvent was removed under reduced pressure, and the remaining blue residue (5.9 mg) was extracted into minimal Et<sub>2</sub>O and filtered through Celite. As for 7-Bn and 8-Bn, this crude mixture could not be further purified and contained 1, 7-Me, and 8-Me. Efforts to optimize the conditions to improve the yield on 7-Me through reaction time, temperature, and equivalents were unsuccessful. ESI-MS(+) of this crude mixture showed ions at m/z values of 973.2356 ([7-Me]<sup>+</sup>, expected 973.2384) and 988.2630 ([8-Me+H]<sup>+</sup>, expected 988.2619).

**Deprotonation of 5-R to** [9-R]<sup>-</sup>. In a typical reaction, 5-R (1 equiv., specifically for R = <sup>CF3</sup>Bn: 16.7 mg, 15.6  $\mu$ mol) was dissolved in THF (2 mL) and solid 18-crown-6 (1.05 equiv., specifically for R = <sup>CF3</sup>Bn: 4.3 mg, 16.4  $\mu$ mol) and either solid LiN[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>, or KN[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub> were added in one portion (1.05 equiv. in all cases, specifically for R = <sup>CF3</sup>Bn: 3.2 mg, 16.4  $\mu$ mol of KN[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>), resulting in a seafoam green solution upon mixing. The reaction was stirred at ambient temperature for 5 min, the solvent then removed under reduced pressure, and the seafoam green residue washed with hexanes to obtain the product, **M**·[9-**R**] (M = [Li(THF)<sub>4</sub>]<sup>+</sup>, [K(18-crown-6)]<sup>+</sup>, specifically for R = <sup>CF3</sup>Bn, 20.0 mg, 14.6  $\mu$ mol, 93%). Single crystals of [K(18-crown-6)]·[9-<sup>CF3</sup>Bn] suitable for XRD were obtained by pentane diffusion into a saturated THF solution at ambient temperature. <sup>19</sup>F{<sup>1</sup>H}-NMR (377 MHz, THF-*h*<sub>8</sub>),  $\delta$  (ppm) –62.53 and -62.54 (M = [K(18-crown-6)]<sup>+</sup> and [Li(THF)<sub>4</sub>]<sup>+</sup> respectively). ESI-MS(–) of this product showed ions at *m*/*z* 1068.2950 ([9-<sup>CF3</sup>Bn]<sup>-</sup> expected 1068.3048).

Oxidation of  $[9-R]^-$  to 9-R. In a typical reaction,  $[9-R]^-$  (1) equiv., specifically for  $R = CH_2^{Cy}Pr$  and cation =  $[Li(THF)_4]^+$ : 10.0 mg, 7.4  $\mu$ mol) in THF (1.5 mL) and precooled to -35 °C was reacted with AgBr (1.09 equiv., specifically for  $R = CH_2^{Cy}Pr$  and cation =  $[Li(THF)_4]^+$ : 1.5 mg, 8.0  $\mu$ mol), resulting in a color change from teal to dark brown-green upon mixing. After stirring for 1 min, the reaction was filtered through a Hirsch funnel fitted with a 0.2  $\mu$ m Nylon filter, and the solvent removed from the filtrate under reduced pressure to afford the crude product as a green residue (specifically for  $R = CH_2^{Cy}Pr$  and cation =  $[Li(THF)_4]^+$ : 7.4 mg, 6.9  $\mu$ mol, 95%). Characterization for 9-<sup>CF3</sup>Bn: <sup>1</sup>H NMR (500 MHz, Benzene- $d_{\delta}$ )  $\delta$ (ppm): 7.34 (d, J = 7.8 Hz, 2H, <sup>CF3</sup>PhCH<sub>2</sub>-), 4.90 (s, 2H, NCCHCN), 4.43 (s, 5H, BnCCNCH<sub>2</sub>Ph), 4.38 (m, 9H, CHCNCH<sub>2</sub>Ph), 3.72 (s, 2H, <sup>CF3</sup>PhCH<sub>2</sub>-), 2.74 (d, J = 18.6 Hz, 10H,  $-CH_2CH_3$ ), 2.68 (q, J = 7.7 Hz, 5H,  $-CH_2CH_3$ ), 2.02 (s, 12H, N(CH)CCH<sub>3</sub>), 1.98 (s, 6H, NC(CBn)CH<sub>3</sub>), 1.15 (dt, J = 15.2, 7.3 Hz, 18H,  $-CH_2CH_3$ ). <sup>19</sup>F{<sup>1</sup>H}-NMR (377 MHz, THF- $h_8$ ),  $\delta$  (ppm) -62.73.

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.4c01613.

<sup>1</sup>H NMR, UV–visible, ESI-MS, EPR spectra, and calculations for BDFE (PDF)

#### **Accession Codes**

CCDC 2349667 and 2349668 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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