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### Authors

Funke, Lena M  
Chakraborty, Romit  
Carsch, Kurtis M  
et al.

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# Assessment of Adsorbate $\pi$ -Backbonding in Copper(I) Metal–Organic Frameworks via Multinuclear NMR Spectroscopy and Density Functional Theory Calculations

Lena M. Funke, Romit Chakraborty, Kurtis M. Carsch, Martin Head-Gordon, Jeffrey R. Long, and Jeffrey A. Reimer\*



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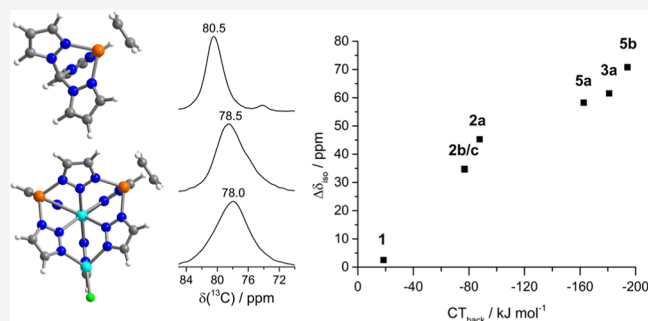
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**ABSTRACT:** We assess the binding of  $C_2H_4$  to the coordinately unsaturated copper(I) sites of the metal–organic frameworks Cu(I)-ZrTpmC\* and Cu(I)-MFU-4l via  $^{13}C$  solid-state nuclear magnetic resonance spectroscopy, density functional theory (DFT), and natural localized molecular orbital analysis. Using these methods, forward-donation and back-donation contributions between  $C_2H_4$  and the exposed Cu(I) are delineated, and high binding enthalpies are contextualized as a function of electronic changes upon site modification and adsorption. With the infrastructure for DFT and solid-state  $^{13}C$  NMR becoming more routine for scientists, we envision that these results will support the study of exposed electron-rich metal sites in a variety of chemical applications.



## INTRODUCTION

For applications such as gas separations, heterogeneous catalysis, and sensing, porous adsorbents offer an energy-efficient alternative to established technologies. In particular, metal–organic frameworks (MOFs) bearing coordinatively unsaturated metal sites can bind gas molecules with selectivities 1 or 2 orders of magnitude larger than traditional adsorbent materials that possess non-specific physisorption interactions. Through judicious choice of the metal ion and linker, one can tailor, for example, strong selective gas binding under a plethora of conditions extending into industrial gas separations, catalysis, and gas storage.<sup>1</sup> Unsaturated metal sites characteristic of some adsorbents—including those in MOFs and zeolites—are electronically Lewis acidic in nature with minimal  $\pi$ -backbonding capabilities. In contrast,  $\pi$ -basic metal sites afford the possibility of strongly adsorbing many substrates. Lewis  $\pi$ -basic sites in MOFs are less common and act either by accepting electrons in free orbitals or donating electrons into adsorbate accessible  $\pi^*$  orbitals, which are referred to as back bonding and forward donation, respectively.

An exemplary MOF hosting Lewis acid sites is Cu(I)-MFU-4l ( $Zn_5Cl_4(btd)_3$ ;  $btd^{2-}$  = bis[1,2,3-triazolato-[4,5-*b*],[4',5'-*i*]]dibenzo[1,4]-dioxin), which was reported in 2014 and features coordinatively unsaturated Cu(I) metal sites that adsorb  $\pi$ -acidic  $H_2$ ,  $O_2$ ,  $N_2$ , and  $C_2H_4$ .<sup>2</sup> In 2018, the MOF Cu(I)-ZrTpmC\* [Tpm\* = tris(3,5-dimethylpyrazolyl)-methane] was reported and observed to catalyze cyclopropanation reactions akin to those promoted by analogous

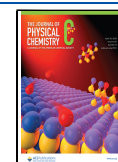
molecular complexes.<sup>3</sup> While theoretical approaches have improved to better understand adsorbent–adsorbate interactions involving forward and back donation at Lewis  $\pi$ -basic sites in MOFs,<sup>4,5</sup> experimental proof-of-impact of synthetic MOF manipulations according to those models is underdeveloped. Open questions include (1) the direction and intensity of charge transfer (CT) and (2) the influence of the chemical environment of the open metal site on the adsorbent–adsorbate interaction. Recently, Cu L-edge near-edge X-ray absorption fine structure measurements performed on Cu(I)-MFU-4l suggest that the energies of the X-ray transitions correlate with the energy levels of the isolated small-molecule adsorbates. The transition intensities were also found to be proportional to the binding energies of the guest molecules within Cu(I)-MFU-4l.<sup>6</sup>

To further understand the effects of guest binding on the structure, dynamics, and electron density distribution, we employ  $^{13}C$  and  $^1H$  NMR spectroscopy measurements of ethylene adsorbed within two MOFs with different Cu(I) metal sites and conduct DFT and natural localized molecular

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orbital (NLMO) analyses to better understand the NMR spectra. These analyses are further informed by computational simulations for other ethylene–metal complexes.

The overall nuclear-spin Hamilton operator for a solid is typically expressed as a sum of Hamilton operators,<sup>7</sup> yet herein we focus on just one of those Hamiltonians, chemical shielding, and in particular the differing chemical shielding between free and adsorbed ethylene. In our study, diamagnetic and paramagnetic effects contribute to the chemical shift and have the potential to impact the characteristic features of the <sup>13</sup>C NMR spectrum of ethylene adsorbed on different substrates (for a general description of chemical shift, see the Supporting Information).

The effective magnetic field  $B_{\text{eff}}$  at the site of the nucleus can be described in terms of the sum of the external and the induced magnetic fields  $B_{\text{eff}} = B_0 + B_{\text{ind}}$ . The induced field is described by the magnetic shielding anisotropy (CSA) tensor  $\vec{\sigma}$  interacting with  $B_0$

$$B_{\text{ind}} = \vec{\sigma} B_0 \quad (1)$$

with

$$\vec{\sigma} = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix} \quad (2)$$

The matrix elements  $\sigma_{xx}$ ,  $\sigma_{yy}$ , and  $\sigma_{zz}$  describe the strength of magnetic shielding along three directions in space. The CSA tensor  $\vec{\sigma}$  describes the shielding along the Cartesian directions in a principal axis coordinate system. The historical convention for the definition of the principal axis system<sup>8</sup> is

$$\delta_{\text{iso}} = -\sigma_{\text{iso}} = -1/3(\delta_{11} + \delta_{22} + \delta_{33}) \quad (3)$$

$$\delta_{ii} = -\sigma_{ii} + \delta_{\text{iso}}(\text{reference}) \quad (4)$$

with  $\delta_{\text{iso}}(\text{reference})$  being the chemical shift of a reference compound.

## METHODS

Cu(I)-MFU-4l was synthesized following previously reported procedures.<sup>2,9</sup> In particular, Cu(I)<sub>2.2</sub>Zn<sub>2.8</sub>(Cl/HCOO)<sub>1.8</sub>(btdd)<sub>3</sub> was prepared following thermolysis at 180 °C with subsequent conversion to Cu(I)<sub>2.2</sub>Zn<sub>2.8</sub>(Cl/H)<sub>1.8</sub>(btdd)<sub>3</sub> upon thermolysis at 230 °C, accompanied by evident off-gassing.<sup>3</sup> The compound Cu(I)-ZrTpmC\* was also prepared following previously reported procedures.<sup>3</sup> The ethylene isotherm for Cu(I)-MFU-4l at 298 K reveals an initial steep uptake (ca. 1.3 mmol/g below 1 mbar), attributed to ethylene coordination to open Cu(I) sites with approximately 70% of Cu sites occupied for stoichiometries of Cu(I)<sub>2.2</sub>Zn<sub>2.8</sub>(Cl/H)<sub>1.8</sub>(btdd)<sub>3</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)<sub>1.54</sub> and Cu(I)<sub>2.2</sub>Zn<sub>2.8</sub>(Cl/HCOO)<sub>1.8</sub>(btdd)<sub>3</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)<sub>1.54</sub>.<sup>6</sup> The discrepancy between the calculated and measured ethylene capacity is partially attributed to spectator Cu(II) sites, which have been spectroscopically observed with X-ray absorption spectroscopy and electron paramagnetic resonance spectroscopy.<sup>6,10</sup>

Isotopically labeled <sup>13</sup>CH<sub>2</sub>=<sup>13</sup>CH<sub>2</sub> (99 atom % <sup>13</sup>C) was purchased from Sigma-Aldrich, and propene (1-<sup>13</sup>C 99%) and 1-butene (1-<sup>13</sup>C 99%) were purchased from Cambridge Isotope Laboratories.

For NMR measurements, the fully activated MOF was loaded into a rotor in a home-built gas manifold<sup>11</sup> inside the

argon atmosphere of a glovebox and evacuated before dosing with the <sup>13</sup>C-labeled ethylene at ~1000 mbar. The rotor was closed within the manifold, and the samples transferred to a 11.7 T magnet were spun immediately under continuous N<sub>2</sub> flow and with compressed air at 16.4 T.

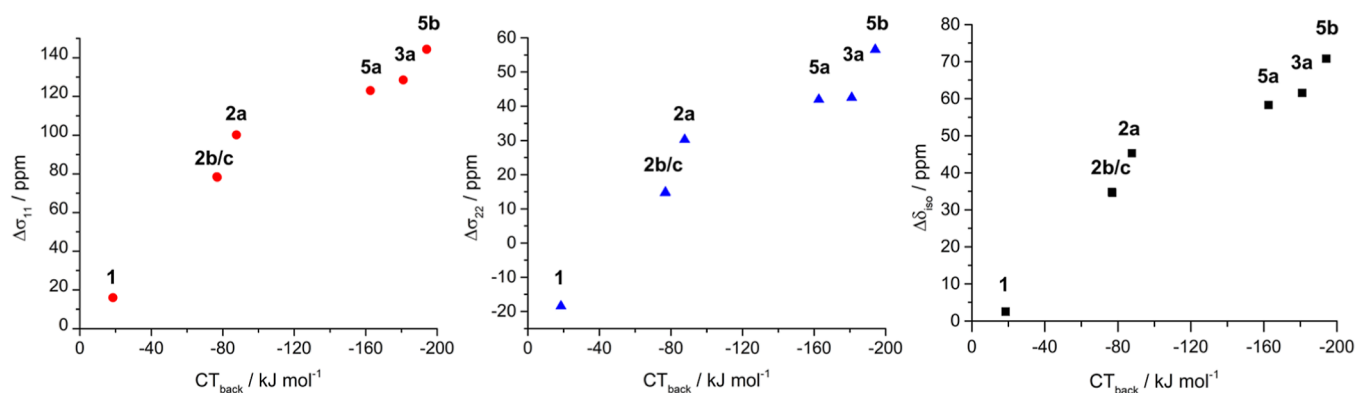
The magic angle ( $\theta = 54.74^\circ$ ) was set prior to the experiment using KBr. All NMR experiments were acquired at 11.7 T using Bruker 4 mm MAS probes and at 16.4 T using 3.2 mm MAS probes. All <sup>13</sup>C MAS NMR spectra were acquired using the <sup>13</sup>C{<sup>1</sup>H} cross-polarization experiment at room temperature without temperature control if not stated otherwise.

The <sup>13</sup>C{<sup>1</sup>H} MAS NMR spectra at 16.4 T were recorded with 2 ms contact time,  $\tau_p(^1\text{H}) = 4.0 \mu\text{s}$  at  $\nu_r = 3 \text{ kHz}$  with SPINAL64 <sup>1</sup>H decoupling at  $\nu_{\text{rf}} = 63 \text{ kHz}$  <sup>1</sup>H radio-frequency field-strength. The <sup>13</sup>C{<sup>1</sup>H} heteronuclear correlation (HETCOR) NMR spectra were recorded with 100  $\mu\text{s}$  contact time,  $\tau_p(^1\text{H}) = 4.5 \mu\text{s}$  at  $\nu_r = 10 \text{ kHz}$  with TPPM decoupling ( $\nu_{\text{rf}} = 63 \text{ kHz}$ ).

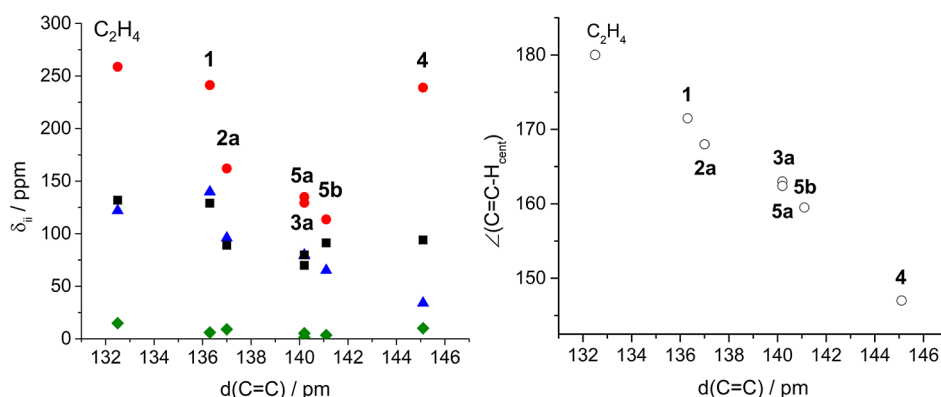
The <sup>13</sup>C{<sup>1</sup>H} MAS NMR spectra at 11.7 T were recorded with 2 ms contact time,  $\tau_p(^1\text{H}) = 5.0 \mu\text{s}$  at  $\nu_r = 3 \text{ kHz}$  with two-pulse phase-modulation (TPPM) <sup>1</sup>H decoupling ( $\nu_{\text{rf}} = 33\text{--}54 \text{ kHz}$ ). Contact times of 200  $\mu\text{s}$  and spinning speeds  $\nu_r = 2, 2.5, 5, \text{ and } 10 \text{ kHz}$  were tested as well. The variable-temperature <sup>13</sup>C{<sup>1</sup>H} MAS NMR spectra were recorded at 11.7 T with  $\tau_p(^1\text{H}) = 3.9 \mu\text{s}$  at  $\nu_r = 3 \text{ kHz}$  with TPPM <sup>1</sup>H decoupling ( $\nu_{\text{rf}} = 64 \text{ kHz}$ ). The temperature was calibrated based on the chemical shift  $\delta(^{79}\text{Br})$  of KBr at  $\nu_r = 5 \text{ kHz}$ . <sup>1</sup>H NMR spectra were recorded using a 90° pulse sequence at  $\nu_r = 3 \text{ and } 10 \text{ kHz}$  spinning speed with  $\tau_p(^1\text{H}) = 5.0 \mu\text{s}$  at a recycle delay of 2 s; <sup>13</sup>C and <sup>1</sup>H chemical shifts were referenced using adamantane to 38.5 ppm (tertiary carbon, left-hand resonance) and 1.8 ppm.

## RESULTS AND DISCUSSION

Motivated by experimental observations and chemical intuition that the degree of backbonding between a metal site and adsorbent may influence NMR chemical shifts, we first formulated a DFT protocol to probe the magnitude of backbonding for C<sub>2</sub>H<sub>4</sub> in various chemical environments using state-of-the-art energy decomposition analysis (EDA).<sup>4,5,12–14</sup> Similar EDA techniques have been used recently to delineate forward- and back-donating contributions for H<sub>2</sub> binding to Cu(I) in MFU-4l and to a V(II) center in a different MOF.<sup>9,15,16</sup> Here, we calculate the quantitative contributions of  $\sigma(\text{C}=\text{C})$ ,  $\pi(\text{C}=\text{C})$ , and  $\sigma(\text{C}-\text{H})$  to  $\sigma_{11}$ ,  $\sigma_{22}$ ,  $\sigma_{33}$ , and  $\delta_{\text{iso}}$  in six metal complexes and three molecules: [Ag( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)]<sup>+</sup> (1), Cu(I)-MFU-4l( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) (2a), Cu(I)-MFU-4l( $\eta^2$ -C<sub>3</sub>H<sub>6</sub>) (2b), Cu(I)-MFU-4l( $\eta^2$ -1-C<sub>4</sub>H<sub>8</sub>) (2c), [Pt(II)Cl<sub>3</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)]<sup>-</sup> (3a), [HB(3-(CF<sub>3</sub>),S-(Ph)Pz)<sub>3</sub>]Au(I)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) (5a), [MeB(Pz)<sub>3</sub>]-Au(I)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) (5b), C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, and 1-C<sub>4</sub>H<sub>8</sub>. The occupied orbitals contribute to  $\sigma_{ii}$  according to the energy difference with the unoccupied orbital of proper symmetry, i.e., when the products of irreducible representation of  $\psi_{\text{occ}}$ ,  $\psi_{\text{unocc}}$ , and  $\sigma_{ii}$  are non-zero. Tables S1–S3 summarize all values for ethylene, propylene, and 1-butylene, respectively. The main contribution to  $\sigma_{11}$  comes from the  $\sigma(\text{C}=\text{C})$  bond, and  $\sigma_{11}$  decreases with the rise of the  $\pi^*(\text{C}=\text{C})$  energy level, thereby reflecting backdonation. For Cu(I) and Pt(II), 81 and 82% of the changes can be attributed to these effects, demonstrating how back bonding strength is reflected in  $\sigma_{11}$ . The tensor component  $\sigma_{33}$  is unchanged from the gas phase molecules upon binding to the metal centers in Cu(I)-MFU-4l, consistent



**Figure 1.** Calculated  $^{13}\text{C}$  NMR parameters  $\Delta\sigma_{11} = \sigma_{11}(\text{complex}) - \sigma_{11}(\text{molecule})$  (left, red dots),  $\Delta\sigma_{22} = \sigma_{22}(\text{complex}) - \sigma_{22}(\text{molecule})$  (center, blue triangles), and  $\delta_{\text{iso}} = \delta_{\text{iso}}(\text{molecule}) - \delta_{\text{iso}}(\text{complex})$  (right, black squares) plotted against energy lowering on CT related to  $\pi$ -backbonding ( $\text{CT}_{\text{back}}$ ) for  $[\text{Ag}(\eta^2\text{-C}_2\text{H}_4)]^+$  (1),  $\text{Cu(I)-MFU-4l}(\eta^2\text{-C}_2\text{H}_4)$  (2a),  $\text{Cu(I)-MFU-4l}(\eta^2\text{-C}_3\text{H}_6)$  (2b),  $\text{Cu(I)-MFU-4l}(\eta^2\text{-1-C}_4\text{H}_8)$  (2c),  $[\text{Pt(II)Cl}_3(\eta^2\text{-C}_2\text{H}_4)]^-$  (3a),  $[\text{HB}(3\text{-}(\text{CF}_3)_2, 5\text{-}(\text{Ph})\text{Pz})_3]\text{Au(I)}(\eta^2\text{-C}_2\text{H}_4)$  (5a), and  $[\text{MeB}(\text{Pz})_3]\text{Au(I)}(\eta^2\text{-C}_2\text{H}_4)$  (5b). Experimental data for  $\delta_{ii}$  have been published for  $\text{C}_2\text{H}_4$ ,<sup>17,18</sup> and (3a)<sup>17,19,20</sup> and computational data for  $\delta_{ii}$  for  $\text{C}_2\text{H}_4$ , (1), and (3a).<sup>22</sup>



**Figure 2.** (Left) Computed  $^{13}\text{C}$  chemical shifts  $\delta_{11}$  (red dots),  $\delta_{22}$  (blue triangles),  $\delta_{33}$  (green diamonds), and  $\delta_{\text{iso}}$  (black squares) for  $[\text{Ag(I)}(\eta^2\text{-C}_2\text{H}_4)]^+$  (1),  $\text{Cu(I)-MFU-4l}(\eta^2\text{-C}_2\text{H}_4)$  (2a),  $[\text{Pt(II)Cl}_3(\eta^2\text{-C}_2\text{H}_4)]^-$  (3a),  $\text{Cp}^*_2\text{Ti(II)}(\eta^2\text{-C}_2\text{H}_4)$  (4),  $[\text{HB}(3\text{-}(\text{CF}_3)_2, 5\text{-}(\text{Ph})\text{Pz})_3]\text{Au(I)}(\eta^2\text{-C}_2\text{H}_4)$  (5a), and  $[\text{MeB}(\text{Pz})_3]\text{Au(I)}(\eta^2\text{-C}_2\text{H}_4)$  (5b) according to CSA tensor calculations. (Right) Computed C=C distance and (C=C-H<sub>cent</sub>) angle in  $\text{C}_2\text{H}_4$  uncoordinated and coordinated to metal centers for the same structures. Experimental data for  $\delta_{ii}$  have been published for  $\text{C}_2\text{H}_4$ ,<sup>17,18</sup> (3a),<sup>17,19,20</sup> and (4).<sup>21</sup> Computational data (left, right) for  $\text{C}_2\text{H}_4$ , (1), (3a), and (4) match well with ref 22.

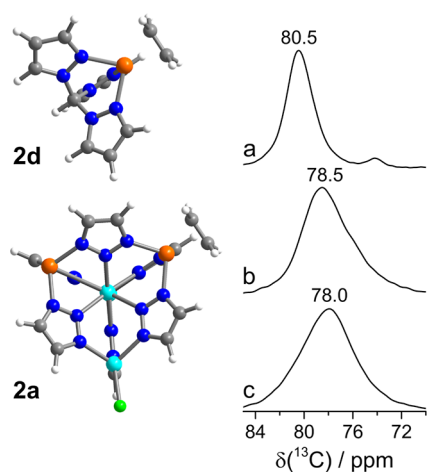
with experimental observations (vide infra). This absence of change is expected since a combination of the  $\sigma_{33}$   $B_{1g}$  symmetry and a large energy gap between the two perpendicular orbitals  $E(\sigma(\text{C}=\text{C})) - E(\sigma(\text{C}-\text{H}))$  leads to small shielding of ethylene, propylene, and butylene along the  $z$ -direction that is not expected to change upon binding. In other words,  $\sigma_{11}$ ,  $\sigma_{22}$ , and  $\delta_{\text{iso}}$  are related by  $-\sigma_{11} - \sigma_{22} = 3\delta_{\text{iso}} + \sigma_{33} \approx 3\delta_{\text{iso}} + 10$  ppm.

To further assess the  $\pi$ -backbonding contribution to the NMR chemical shift tensors, we calculated the energy lowering in kJ/mol on CT due to backbonding as distinct from overall CT for different diamagnetic metal centers. We found an increase in the normalized NMR parameters  $\sigma_{22}$ ,  $\sigma_{11}$ , and  $\delta_{\text{iso}}$  with an increase in CT related to backbonding ( $\text{CT}_{\text{back}}$ ). Figure 1 shows the changes in these parameters after subtracting the values of the adsorbed alkylene, respectively. This analysis suggests that the experimental values of  $\sigma_{22}$ ,  $\sigma_{11}$ , and  $\delta_{\text{iso}}$  reflect the extent of CT attributed to  $\pi$ -backbonding. In Figure 2, we examine these calculated parameters in the context of geometric changes in the ethylene molecule within these complexes. The righthand plot shows the C=C bond distance increasing linearly with a decreasing out-of-plane angle  $\angle(\text{C}=\text{C}-\text{H}_{\text{cent}})$  for metal complexes (the angle between the center of the two H on each side of the molecule in

relation to the C=C bond). While C=C distance information can be derived via IR spectroscopy, Figure 2 shows that the NMR parameters  $\sigma_{\text{iso}}$ ,  $\sigma_{11}$ , and  $\sigma_{22}$  are nonlinear with geometric changes and that DFT and NLMO calculations may be paired to give a more detailed description of geometric changes that occur in ethylene upon binding.

We measured  $^{13}\text{C}$  solid-state NMR spectra of three MOFs with coordinatively unsaturated Cu(I) sites (Figure 3). Upon dosing with ethylene, we measured a static  $^{13}\text{C}$  NMR spectrum for coordinated  $^{13}\text{C}_2\text{H}_4$  in  $\text{Cu(I)-MFU-4l}(\eta^2\text{-C}_2\text{H}_4)$  and  $\text{Cu(I)-ZrTpmC}^*(\eta^2\text{-C}_2\text{H}_4)$ . Analysis of the static NMR line shape is experimentally the most reliable way to extract  $\delta_{ii}$  ( $i = 1, 2, 3$ ). Alternatively, we turned to  $^{13}\text{C}$  MAS NMR and compared our experimental spectra with our DFT calculated (vide supra)  $\delta_{\text{iso}}$ ,  $\delta_{11}$ , and  $\delta_{22}$ .

Experimentally, we find different  $^{13}\text{C}$  isotropic chemical shifts for the frameworks  $\text{Cu(I)-ZrTpmC}^*(\eta^2\text{-C}_2\text{H}_4)$  and  $\text{Cu(I)-MFU-4l}(\eta^2\text{-C}_2\text{H}_4)$ , as well as for the two  $\text{Cu(I)-MFU-4l}(\eta^2\text{-C}_2\text{H}_4)$  variants with the Zn site coordinated to a mixture of  $\text{Cl}^-/\text{HCOO}^-$  or a mixture of  $\text{Cl}^-/\text{H}^-$  (for static  $^{13}\text{C}$  NMR spectra, see Figure S5). Briefly,  $\text{Cu(I)-MFU-4l}$  was prepared following the literature procedures,<sup>2,9</sup> with  $\sim 85\%$  of the peripheral chloride anions exchanged for formate anions, as quantified through  $^1\text{H}$  NMR spectroscopy following dissolu-



**Figure 3.** (Left) Complexes of Cu(I)-ZrTpmC\*( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) (**2d**) and Cu(I)-MFU-4l( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) (**2a**) used for calculations in this study. (Right) <sup>13</sup>C MAS NMR spectra of (a) [Cu(I)-ZrTpmC\*( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)] (**2d**), (b) Cu(I)<sub>2.2</sub>Zn<sub>2.8</sub>(Cl/HCOO)<sub>1.8</sub>(btdd)<sub>3</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) (**2e**), and (c) Cu(I)<sub>2.2</sub>Zn<sub>2.8</sub>(Cl/H)<sub>1.8</sub>(btdd)<sub>3</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) (**2f**). Cyan, orange, green, blue, gray, and white spheres represent Zn, Cu, Cl, N, C, and H atoms, respectively. Full frequency range <sup>13</sup>C MAS NMR spectra are depicted in Figure S4.

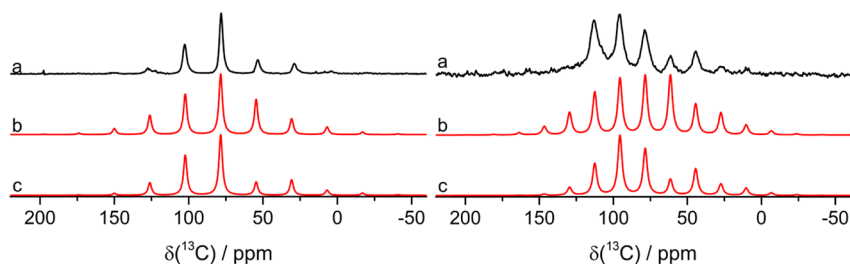
tion in DMSO-*d*<sub>6</sub>/D<sub>2</sub>SO<sub>4</sub>. Thermolysis at 180 °C for 1 h under vacuum afforded a mixture of chloride and formate anions at the Zn sites, whereas further thermolysis at 230 °C for 3 h afforded zinc–formate decomposition to yield a mixture of chloride and hydride anions at the Zn sites.

We find small differences in  $\delta_{\text{iso}}(^{13}\text{C}) = 78.0\text{--}79.0$  ppm upon ethylene coordination in Cu(I)-MFU-4l and 80.5 ppm for ethylene coordination in Cu(I)-ZrTpmC\*( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) (see Table 1). For hydride substituents in Cu(I)<sub>2.2</sub>Zn<sub>2.8</sub>(Cl/

**Table 1. Experimental and Calculated <sup>13</sup>C NMR Chemical Shifts of <sup>13</sup>C<sub>2</sub>H<sub>4</sub> in Different Cu(I)-Containing MOFs**

$\delta_{ii} (^{13}\text{C})/\text{ppm}$	$\delta_{\text{iso}}$	$\delta_{11}$	$\delta_{22}$	$\delta_{33}$
Experimental <sup>a</sup>				
Cu(I)-ZrTpmC*( $\eta^2$ -C <sub>2</sub> H <sub>4</sub> ) ( <b>2d</b> )	80.5			
Cu(I) <sub>2.2</sub> Zn <sub>2.8</sub> (Cl/HCOO) <sub>1.8</sub> (btdd) <sub>3</sub> ( $\eta^2$ -C <sub>2</sub> H <sub>4</sub> ) ( <b>2e</b> )	78.5	113	113	~10
Cu(I) <sub>2.2</sub> Zn <sub>2.8</sub> (Cl/H) <sub>1.8</sub> (btdd) <sub>3</sub> ( $\eta^2$ -C <sub>2</sub> H <sub>4</sub> ) ( <b>2f</b> )	78.0			
CSA Simulations <sup>b</sup>				
C <sub>2</sub> H <sub>4</sub> (molecule, solid-state)	126	253	116	9
Cu(I) <sub>2</sub> Zn <sub>3</sub> (Cl)(btdd) <sub>3</sub> ( $\eta^2$ -C <sub>2</sub> H <sub>4</sub> ) cluster	80	152	85	4

<sup>a</sup>Recorded at room temperature; experimental error:  $\Delta\delta_{\text{iso}} = \pm 0.1$  ppm. <sup>b</sup>See the Supporting Information for computational details.

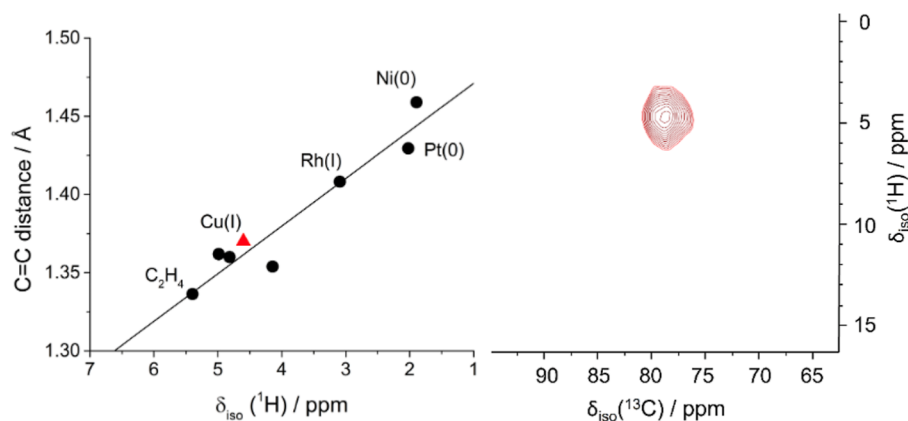


**Figure 4.** <sup>13</sup>C MAS NMR spectra of Cu(I)-MFU-4l( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) (**2a**) at (left) 11.7 T and (right) 16.4 T. (a) Experimental; (b,c) simulated two-spin system with a <sup>13</sup>C=<sup>13</sup>C distance and CSA as simulated for the benzotriazole-truncated Cu(I)<sub>2</sub>Zn<sub>3</sub>(Cl)<sub>2</sub>(N<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>6</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> with  $d(\text{C}=\text{C}) = 137$  pm: (b) resting and (c) with C<sub>2</sub>H<sub>4</sub> spinning around C<sub>3</sub> axis of the Cu(I)-MFU-4l Cu(I) site.

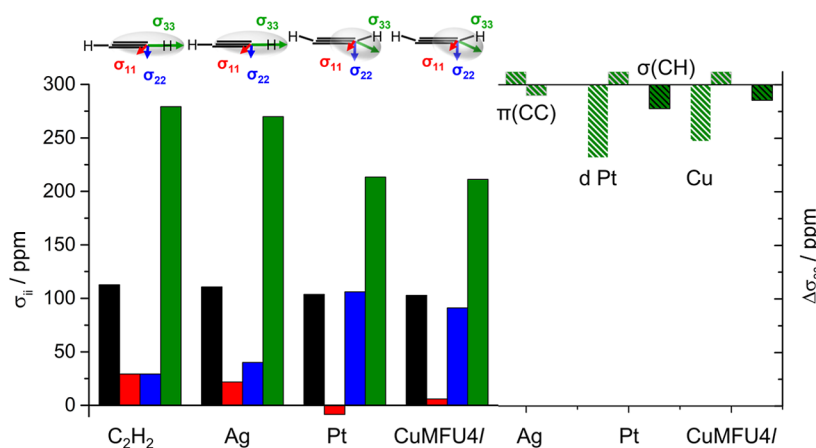
H)<sub>1.8</sub>(btdd)<sub>3</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>), the <sup>13</sup>C shifts are slightly higher with 78.0 ppm (HCOO<sup>-</sup>: 78.5 ppm), indicating stronger binding for the electron-donating hydride compared to the bulkier chloride ligand, and with the bidentate formate ligand falling in the intermediary range. This emphasizes the sensitivity of the <sup>13</sup>C NMR spectra for detecting small changes in the MOF that can impact the nature of adsorbate binding, for example, showing slightly stronger  $\pi$ -backbonding. The <sup>13</sup>C MAS NMR data portend that electron-donating groups coordinated to neighboring Zn(II) sites can measurably increase the binding energy of ethylene to Cu(I). The isotropic chemical shift of  $\delta_{\text{iso}}(^{13}\text{C}) = 78$  ppm compared to 126 ppm for pure ethylene reflects the electronic changes upon  $\pi$ -backbonding. DFT and NLMO analyses allow us to assign the origin to decreasing  $\delta_{ii}(^{13}\text{C})$  ( $i = 1, 2$ ) when  $\pi^*(\text{C}=\text{C})$  rises in energy compared to  $\sigma(\text{C}=\text{C})$  and  $\sigma(\text{C}-\text{H})$ , respectively.

To elucidate the response of the guest to confinement at the Cu(I) site, we measured <sup>13</sup>C NMR spectra as a function of temperature and magnitude of magnetic field (Figure 4). At both 11.7 and 16.4 T, good fits were obtained with the CSA and <sup>13</sup>C–<sup>13</sup>C dipole–dipole coupling parameters, as derived from DFT. At lower temperatures (see Figure S2), the spinning side bands observed at low ppm increase in relative intensity, indicating a slight increase in  $\delta_{11}$ , while the center of the spectrum shifts to larger chemical shifts (i.e.,  $\delta_{\text{iso}}$  decreases, see Figure S3). The best fit simulating (c in Figure 4) the experimental data in Figure 4a illustrates that from room temperature down to 255 K (see Figure S2), the line shape of ethylene is best fit with a model that assumes the ethylene molecule rapidly rotates when bound to the metal center and effectively averages  $\sigma_{11}$  and  $\sigma_{22}$ . This is consistent with a small rotation barrier height of 2.0 kJ/mol obtained from DFT simulations (see Figure S1). Thus, via <sup>13</sup>C MAS NMR combined with DFT calculations, we find that ethylene is adsorbed at the Cu(I) center while spinning around the C<sub>3</sub> z-axis in Cu(I)-MFU-4l, effectively averaging out anisotropy in the xy plane.

To discern the isotropic <sup>1</sup>H NMR chemical shift of C<sub>2</sub>H<sub>4</sub> in Cu(I)-MFU-4l( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>), we turned to <sup>13</sup>C{<sup>1</sup>H} HETCOR spectroscopy. This double resonance NMR experiment transfers magnetization from protons (<sup>1</sup>H) to adjacent <sup>13</sup>C nuclear spins. As dipole–dipole coupling decreases with the third power of the internuclear distance  $\propto r(\text{C}-\text{H})^{-3}$ , the final 2D spectrum at short contact times (100  $\mu\text{s}$ ) features those <sup>1</sup>H in direct proximity of <sup>13</sup>C, for example, the protons in <sup>13</sup>C<sub>2</sub>H<sub>4</sub>. Figure 5 (left) shows the linear fit of the C=C distance in ethylene as a function of the <sup>1</sup>H chemical shifts of different metal complexes. The distance for Cu(I)-MFU-4l derived from our DFT calculations agrees well with the distance predicted



**Figure 5.** (Left)  $^1\text{H}$  NMR isotropic chemical shifts of  $\text{C}_2\text{H}_4$  in metal complexes<sup>23</sup> and  $\text{Cu(I)-MFU-4l}(\eta^2\text{-C}_2\text{H}_4)$  (2a) (red triangle). (Right)  $^{13}\text{C}\{^1\text{H}\}$  HETCOR spectrum of  $\text{Cu(I)}_{2.2}\text{Zn}_{2.8}(\text{Cl}/\text{H})_{1.8}(\text{btdd})_3(\eta^2\text{-C}_2\text{H}_4)$  (2f).



**Figure 6.** (Left) CSA tensor components in acetylene according to DFT  $\sigma_{11}$  (red),  $\sigma_{22}$  (blue),  $\sigma_{33}$  (green), and  $\sigma_{\text{iso}}$  (black); at the top are principal axes relative to the molecular frame. (Right) Orbital contributions attributed to a decline in  $\sigma_{33}(^{13}\text{C})$  (green) according to NLMO calculations of  $^{13}\text{C}_2\text{H}_2$  in metal complexes:  $[\text{Ag(I)}(\eta^2\text{-C}_2\text{H}_2)]^+$  (1b),  $[\text{Pt(II)}\text{Cl}_3(\eta^2\text{-C}_2\text{H}_2)]^-$  (3b), and  $\text{Cu(I)-MFU-4l}(\eta^2\text{-C}_2\text{H}_2)$  (2g):  $\pi(\text{CC})$  in  $\text{C}_2\text{H}_2$  (green-yellow striped), d orbital of Pt and s/p orbitals of Cu metal (green-white striped  $d(\text{Pt})$  and Cu), and  $\pi(\text{CC})$  in  $\text{C}_2\text{H}_2$  (green-black striped).

by the  $^1\text{H}$  NMR shift from the site-resolved  $^{13}\text{C}\{^1\text{H}\}$  HETCOR experiment (right). This observation suggests that the isotropic  $^1\text{H}$  NMR chemical shift is a good predictor of the geometrical changes in ethylene, specifically the C=C distance and the  $\angle(\text{C}=\text{C}-\text{H}_{\text{cent}})$  angle. This also applies to the MOF  $\text{Cu(I)-MFU-4l}$ .

To measure the contribution of the metal center to forward electron donation, we chose acetylene in lieu of ethylene. Computing the  $^{13}\text{C}$  chemical shielding anisotropy tensors of acetylene, we found  $\sigma_{33}$  reflects the metal orbital contribution to forward bonding electron donation.

Figure 6 shows how the orientation of  $\sigma_{33}$  slightly tilts from the  $\text{C}\equiv\text{C}$  axis for  $[\text{Pt(II)}\text{Cl}_3(\eta^2\text{-C}_2\text{H}_2)]^-$  and  $\text{Cu(I)-MFU-4l}(\eta^2\text{-C}_2\text{H}_2)$ . The NLMO analysis (Figure 6, right) highlights the orbital contribution to the paramagnetic component of  $\sigma_{33}$  and the origin of the decrease of  $\sigma_{33}$  upon binding. In  $[\text{Ag}(\eta^2\text{-C}_2\text{H}_2)]^+$ ,  $\sigma_{33}$  stays almost constant compared to  $\text{C}_2\text{H}_4$  as the two contributions of  $\pi(\text{C}\equiv\text{C})$  (see Figure 6, right) cancel each other out. In  $[\text{Pt(II)}\text{Cl}_3(\eta^2\text{-C}_2\text{H}_2)]^-$  and the complex of  $\text{Cu(I)-MFU-4l}(\eta^2\text{-C}_2\text{H}_2)$ , the metal orbital contributions decrease  $\sigma_{33}$ . This observation suggests that with  $\sigma_{33}$  almost parallel to  $\text{C}\equiv\text{C}$ , the  $^{13}\text{C}$  solid-state NMR spectrum of  $^{13}\text{C}_2\text{H}_2$  adsorbed on a metal center should probe the forward donation contribution of the metal center. Our NMR computations show that the  $^{13}\text{C}$ -acetylene NMR shifts serve as a probe for

ranking metal centers based on their forward donating contribution.

## CONCLUSIONS

Carbon-13 NMR chemical shift simulations predict orbital contributions of the metal base/ $\pi$ -acid interactions in MOFs. We find that  $\pi$ -backbonding dominates the interaction as discerned from the  $^{13}\text{C}$  chemical shielding anisotropy. While the  $^{13}\text{C}$  NMR spectrum of ethylene is almost uninfluenced by forward donation— $\sigma_{11}$ ,  $\sigma_{22}$ , and  $\sigma_{33}$  only depend on  $E(\sigma(\text{C}=\text{C}))$ ,  $E(\pi^*(\text{C}=\text{C}))$ ,  $E(\sigma(\text{C}-\text{H}))$ —the extent of forward donation can best be evaluated by considering the  $^{13}\text{C}$  NMR spectrum of acetylene. The  $^1\text{H}$  NMR spectrum of ethylene reflects the overall physical changes upon binding with the isotropic shift, directly correlating with  $d(\text{C}=\text{C})$  and  $\angle(\text{C}=\text{C}-\text{H}_{\text{cent}})$ . In the future, such observations of the electronic structure may help in the design of metal sites with enhanced backbonding interactions in porous materials for gas separation. We envision our approach to be broadly relevant to the study of catalysis and gas adsorption involving alkenes and alkynes in porous framework materials.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.3c00462>.

Additional remarks on chemical shielding; computational details of NMR parameters; details of DFT calculations on structural refinement, CT, and the C<sub>3</sub> axis rotation of ethylene bound to Cu(I) in MFU-4l; details of fitting the <sup>13</sup>C MAS NMR line shape; orbital contributions to chemical shielding anisotropy of ethylene, propylene, and 1-butylene; calculated energy lowering on CT in metal complexes due to forward donation and backbonding; and extended complementary NMR spectroscopic experimentation (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

Jeffrey A. Reimer – Department of Chemical and Biomolecular Engineering, University of California Berkeley, Berkeley, California 94720, United States; Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-8099, United States; Email: [reimer@berkeley.edu](mailto:reimer@berkeley.edu)

### Authors

Lena M. Funke – Department of Chemistry, University of California Berkeley, Berkeley, California 94720, United States; Department of Chemical and Biomolecular Engineering, University of California Berkeley, Berkeley, California 94720, United States; [orcid.org/0009-0003-7489-9557](https://orcid.org/0009-0003-7489-9557)

Romit Chakraborty – Department of Chemistry, University of California Berkeley, Berkeley, California 94720, United States; Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-8099, United States

Kurtis M. Carsch – Department of Chemistry, University of California Berkeley, Berkeley, California 94720, United States; [orcid.org/0000-0003-4432-7518](https://orcid.org/0000-0003-4432-7518)

Martin Head-Gordon – Department of Chemistry, University of California Berkeley, Berkeley, California 94720, United States; Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-8099, United States; [orcid.org/0000-0002-4309-6669](https://orcid.org/0000-0002-4309-6669)

Jeffrey R. Long – Department of Chemistry, University of California Berkeley, Berkeley, California 94720, United States; Department of Chemical and Biomolecular Engineering, University of California Berkeley, Berkeley, California 94720, United States; Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-8099, United States; [orcid.org/0000-0002-5324-1321](https://orcid.org/0000-0002-5324-1321)

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.jpcc.3c00462>

### Notes

The authors declare no competing financial interest.

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