

## Correlation of Coordination Geometry of Copper Atom to Reactivities of Organocuprate. Molecular Orbital Analysis of Dimethylcuprate Anion

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**Abstract:** Kohn-Sham MO analysis of the bent structures of  $(\text{CH}_3)_2\text{Cu}^-$  has been performed with the B3LYP hybrid density functional method. In the linear conformer of  $(\text{CH}_3)_2\text{Cu}^-$ , which is the global minimum, the HOMO represents the copper s+d<sub>z2</sub> orbital, and the carbon s+p orbitals lie near this HOMO. These orbitals are responsible for the nucleophilic reactivities in the alkylation reaction of cuprates. Bending of the C-Cu-C angle pushes up the d<sub>xz</sub> orbital of the copper atom to mix it with the s+p orbitals of the carbon atom, generating a HOMO capable of interacting with the  $\pi^*$  orbital of acetylene and olefins. © 1999 Elsevier Science Ltd. All rights reserved.

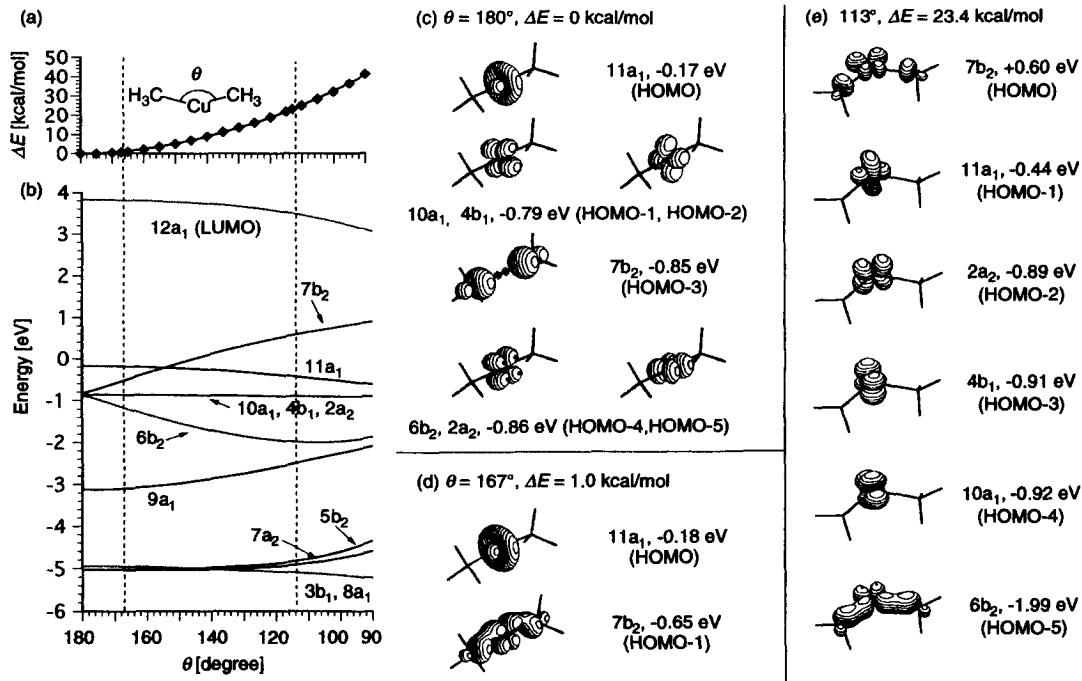
**Keywords:** density functional theory, organocuprate, conjugate addition, carbocupration, mechanism

Organocuprate(I) species play key roles in organic synthesis.<sup>1</sup> Structures of diorganocuprate(I) species determined in crystals<sup>2</sup> or by theory<sup>3,4,5</sup> have invariably indicated linear C-Cu-C coordination geometry as the most stable cuprate geometry, and mechanistic discussions have generally been made on the basis of such static reactant structures.<sup>6</sup> While the thermal energy will easily change the coordination geometry and the most stable geometry may not be ideal for all possible reactions, the correlation between the coordination geometry and the reactivities of organocuprates has so far never been investigated. We have examined the energy and the frontier molecular orbitals (FMOs) of a  $(\text{CH}_3)_2\text{Cu}^-$  molecule for various C-Cu-C angles to find that (near) linear geometry is suitable for an S<sub>N</sub>2-substitution reaction, while bent geometry is ideal for a  $\pi$ -complexation process.

We employed the B3LYP/631A method for geometry optimization, and B3LYP/6311A for single-point calculations.<sup>7,8</sup> The B3LYP method has previously been shown to be suitable for analysis of organocuprate reactions.<sup>9,10,11</sup> The cuprate was modeled as  $(\text{CH}_3)_2\text{Cu}^-$  for the sake of simplicity. We examined (Figure 1a, b) the total energy of  $\text{Me}_2\text{Cu}^-$  and the energies of several high-lying MOs as a function of the C-Cu-C angle (as in a Walsh diagram).<sup>12,13</sup> The linear molecule  $\text{Me}_2\text{Cu}^-$  is  $D_{3h}$  symmetric, and the bent one  $C_{2v}$  symmetric. As shown in Fig. 1a, the linear structure is the global minimum, and the energy increases gradually to 23.4 kcal/mol at  $\theta = 113^\circ$ .<sup>14</sup> Bending with this amount of energetic cost will easily take place under the thermal conditions (below 25°C) used in synthetic reactions of organocuprates.

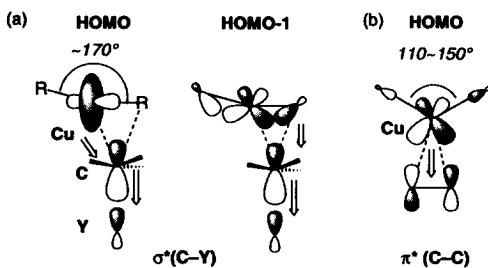
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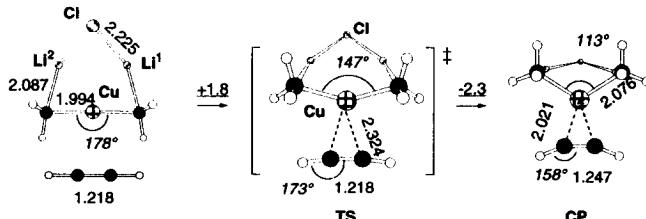
**Figure 1.** (a) Energy change (B3LYP/6311A/B3LYP/631A) of  $(\text{CH}_3)_2\text{Cu}^-$  as a function of the C-Cu-C angle ( $\theta$ ). (b) Energy change of representative MOs, (c) the 3D surface ( $0.1 \text{ e}^{-\text{a}u^{-3}}$ ) of the MOs of  $(\text{CH}_3)_2\text{Cu}^-$  with  $\theta = 180^\circ$ , (d) with  $\theta = 167^\circ$ , and (d) with  $\theta = 113^\circ$ . Structures were optimized by fixing the C-Cu-C angle at a  $5^\circ$  intervals between  $90^\circ$  and  $180^\circ$  as well as at  $113^\circ$  and  $167^\circ$ .

Several high-lying Kohn-Sham orbitals of the linear conformer of  $(\text{CH}_3)_2\text{Cu}^-$  ( $\theta = 180^\circ$ ) are shown in Fig. 1c.<sup>15</sup> The  $11a_1$  HOMO represents the copper  $s+d_{z2}$  orbitals as expected for a linear  $d^{10}$  complex,<sup>16</sup> the  $7b_2$  HOMO-3 the carbon  $s+p$  orbitals, and the  $2a_2$  HOMO-4 the  $3d_{xz}$  orbital. Bending of the C-Cu-C bond does not much change either the energy of the  $s+d_{z2}$  orbital (Fig. 1b) or the orbital mixing ( $11a_1$  in Fig. 1d and 1e). On the other hand, even a little bending (e.g.,  $167^\circ$ ) causes mixing of the  $b_2$  carbon  $s+p$  and the  $b_2$  copper  $3d_{xz}$  orbitals to create two new orbitals  $7b_2$  (Fig 1e, out-of-phase mixing) and  $6b_2$  (in-phase), whose energies split precipitously upon further bending (e.g.,  $\theta = 113^\circ$ , Fig. 1b). The former still remains lower in energy (HOMO-1) than the latter (HOMO) at  $\theta = 113^\circ$ ,<sup>14</sup> but rises to the HOMO energy at angles smaller than ca.  $150^\circ$ . As shown for  $\theta = 113^\circ$  in Fig. 1e, the new HOMO ( $7b_2$ ) represents out-of-phase mixing of the carbon  $s+p$  and the copper  $3p_z+3d_{xz}$  orbitals.<sup>16,17</sup>



**Figure 2.** Orbital interactions between  $\text{R}_2\text{Cu}^+$  and substrates in (a) interactions of the HOMO and the HOMO-1 of the cuprate with alkyl halide ( $\text{CH}_3\text{-Y}$ ) in the alkylation with alkyl halide, and (b)  $\pi$ -complexation to acetylene or olefin.

back-donation,<sup>20</sup> which will compensate the energy loss due to bending. Indeed, complexation of  $(\text{CH}_3)_2\text{CuLi} \cdot \text{LiCl}$  to acetylene (Figure 3) takes place with a small activation energy<sup>21</sup> despite the energy loss of several kcal/mol estimated for the  $147^\circ$  C-Cu-C angle in the transition structure of complexation (TS). With this bending angle, the cuprate moiety in TS must have already acquired the ability to donate d-electrons to the  $\pi^*$ -orbital of acetylene. Thus, these results conclusively demonstrated that dialkylcuprate(I) reagents behave as transition metal organometallics.



**Figure 3.** Complexation of  $(\text{CH}_3)_2\text{CuLi} \cdot \text{LiCl}$  with acetylene. Bond lengths are in angstroms, angles in italic are in degree, and energy changes underlined above arrows are in kcal/mol.

The Kohn-Sham MO analysis of the organocuprate(I) geometry has shed new light on the role of the bent geometry in organocuprate reactions.<sup>22</sup> The above discussions provide an FMO basis for understanding the mechanisms of the addition and alkylation reactions of lithium dimethylcuprate clusters. The present MO analysis is fully consistent with the previous localized molecular orbital analysis of the complexes and transition states found on the reaction pathways.<sup>9,10,11</sup> The present studies make it clear now that the static crystal structures or the time-averaged solution structures of cuprates do not always give us good information on their reactive conformations in solution, and that high level theoretical calculations play vital roles in the studies of the organometallic species in action.

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The above analysis demonstrates strong correlation between the geometry and the nucleophilic reactivities of cuprate anion. Thus, for C-Cu-C angles up to ca.  $154^\circ$  the high-lying cuprate orbitals will have symmetry suitable for donative interactions with C-Y  $\sigma^*$  orbital.<sup>18</sup> As illustrated in Fig 2a, both HOMO and HOMO-1 of a slightly bent structure (e.g.,  $\theta = 167^\circ$ ) will interact strongly with an alkylating agent.<sup>19</sup> Alternatively, for angles smaller than ca.  $150^\circ$ , the HOMO will have good interactions with the  $\pi^*$ -orbital of an acetylene or an olefin as shown in Fig. 2b. Such an interaction will create a typical case of Dewar-Chatt-Duncanson d- $\pi^*$

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