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Correlation of Reactivities of Organocuprate(I) and Zincate(II) with d-Orbital Energies of Ate Complexes

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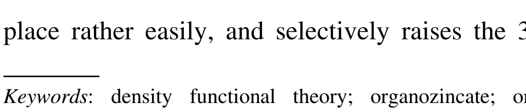
Abstract—Kohn–Sham orbital analysis of MeCu, Me_2Cu^-, Me_2Zn, Me_3Zn^- and Me_4Zn^{2-}, as well as the bent structures of Me_2Cu^-, has been performed with the density functional (B3LYP) method. It has been shown that the organozincates possess high-lying methyl carbon orbitals and low-lying d-orbitals, and hence are expected to behave as alkyl nucleophiles. On the other hand, the d-orbitals of the cuprate are at the same energy levels as the methyl carbon orbitals, and hence the cupretes react as metal-centered nucleophiles. The correlation between the bent geometry and the orbital energies of d-orbitals (z^2 and xz) was also found and has been related to the mechanistic difference between S_N2 alkylation reaction and conjugate addition reaction. © 2000 Elsevier Science Ltd. All rights reserved.

Copper and zinc lie side by side on the Periodic Table, yet the nucleophilic reactivities of their organometallic complexes differ very much. Organocopper(I) species are highly reactive nucleophiles, especially in their ate forms (e.g. R_2CuLi),[1] yet organozinc species are much less nucleophilic even in their ate forms (e.g. R_3ZnLi and R_4ZnLi_2).[2–4] While the difference has been well known among synthetic chemists, it has not received due theoretical attention. We previously studied the molecular orbitals of MeCu and Me_2Cu^-,[5] and found that the d-orbitals of the former is rather low lying and the addition of Me^- to MeCu (Eq. (1)) is necessary to make the d-orbitals sufficiently high for nucleophilic reactions. In the same vein, we can speculate that addition of Me^- to Me_2Zn (Eq. (2)) would raise the d-orbital levels. We have examined such a possibility with the aid of density functional calculations for model compounds, Me_2Zn, Me_3Zn^- and Me_4Zn^{2-}, as compared with the reference compounds, MeCu and Me_2Cu^-. We also examined how the geometry of Me_2Cu^- influences the d-orbital energies and found that bending of the linear Me–Cu–Me structure takes place rather easily, and selectively raises the $3d_{xz}$ orbital to make the cuprate species highly nucleophilic toward a π-acidic substrate.[6]

$$\mathrm{MeCu} \xrightarrow{\mathrm{Me}^-} \left[\mathrm{Me{-}Cu{-}Me}\right]^- \tag{1}$$



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Theoretical Methods and Chemical Models

We used the GAUSSIAN 94 program[7] for the density functional (B3LYP) calculations.[8] The B3LYP method has previously been shown to be suitable for analyses of organocuprate and organozinc reactions.[9–12] The basis set denoted as 631A, which consists of the Ahlrichs all-electron 'SVP' basis set[13] for Cu or Zn atom and 6-31G(d) for the rest.[14] Zero imaginary frequency for equilibrium structures was confirmed by normal coordinate analysis. The canonical and Kohn–Sham MO analyses were performed at the B3LYP levels for the B3LYP/631A structure, and the basis set used for these analyses (denoted as 6311B) consists of the Ahlrichs 'DZP' all-electron basis set for copper and zinc atoms,[13] and 6-311+G(d,p) for the rest. Kohn–Sham orbitals can offer qualitative interpretation of molecular orbitals.[15]

We examined (Fig. 2a and b) the total energy of Me_2Cu^- and the energies of several high-lying MOs as a function of the C–Cu–C angle (as in a Walsh diagram).[16] The linear molecule Me_2Cu^- was optimized under D_{3h} symmetry, and the bent one under C_{2v} symmetry.

The optimized structure of linear D_{3h} Me_2Cu^{-17-19} has been favorably compared with the crystal structure of Me_2Cu^-.[20] The stable linear C–Cu–C geometry of Me_2Cu^- is due to bonding participation of the copper d_{z^2} orbital. Analysis of the Boys localized MOs[21] and natural bond orbitals[22] of the linear Me_2Cu^- indicates that the C–Cu σ-bond is composed of the carbon s+p and the copper s+d_{z^2} orbitals. The copper

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Keywords: density functional theory; organozincate; organocuprate; d-orbital; conjugate addition.

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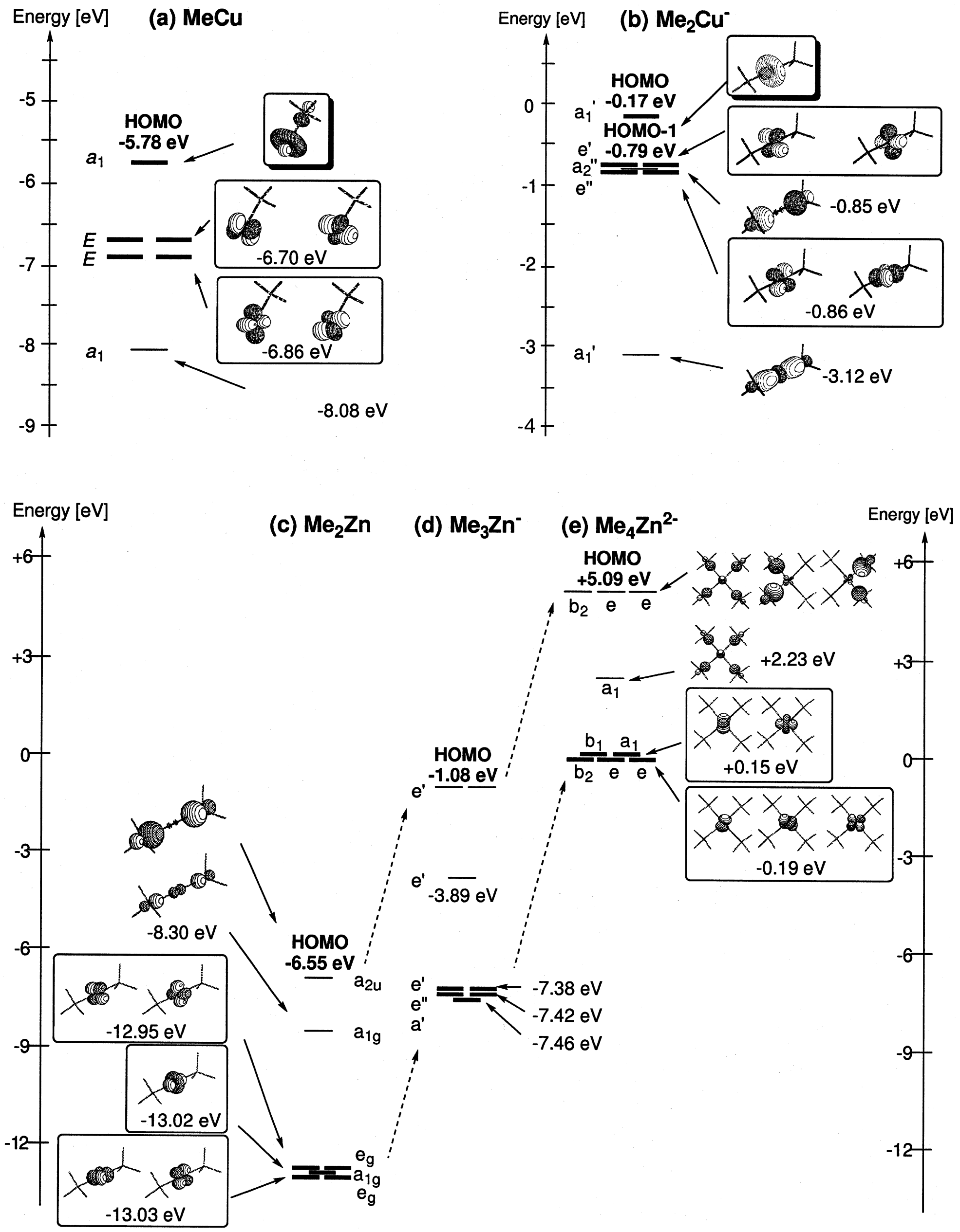

Figure 1. 3D Representation (0.1 e au^{-3}) of selected Kohn–Sham orbitals of (a) MeCu, (b) Me_2Cu^-, (c) Me_2Zn, (d) Me_3Zn^- and (e) Me_4Zn^{2-} the B3LYP/6311B//B3LYP/631A level. Methyl 2p-orbitals are shown in plain lines and metal d-orbitals in bold lines. Abnormally high energy levels of orbitals (e.g. HOMO of Me_4Zn^{2-}) are due to the absence of countercation (Li^+).

p-orbital plays little role in the C–Cu σ-bonding. At the B3LYP/6311B//B3LYP/631A level, the natural bond orbital of the C–Cu bond consists of 83% carbon electrons (s+p orbitals) and 17% copper electrons (85% s+15% d).

To compare with organocopper(I) compounds, we also examined several organozinc(II) compounds, Me_2Zn, Me_3Zn^- and Me_4Zn^{2-}. Crystal structures of neutral diorganozinc(II),[23] metal triorganozincate(II),[24] and metal tetraorganozincate(II)[25] indicate that these species are linear, planar, and tetrahedral, respectively. C–Zn bond length of Me_2Zn is 1.96 Å at the B3LYP/631A level, and this value is close to experimental values (1.93 Å) determined by the spectroscopy[26] and previous theoretical calculations.[19,27] C–Zn bond length of Me_4Zn^{2-} (2.22 Å) at the B3LYP/631A level is close to the experimental values (2.07 Å) and previous theoretical results.[19] Therefore, we modeled these species with Me_2Zn of linear D_{3h} symmetry, Me_3Zn^- of C_{3h} symmetry and Me_4Zn^{2-} of D_{2d} symmetry. The natural bond orbital of the C–Zn bond of Me_2Zn consists of 76% carbon electrons (s+p orbitals) and 23% zinc electrons (94% s+5% d).

Results and Discussion

In Fig. 1 are shown the energies of metal d-orbitals and of the methyl 2p-orbitals (which are always HOMO except in

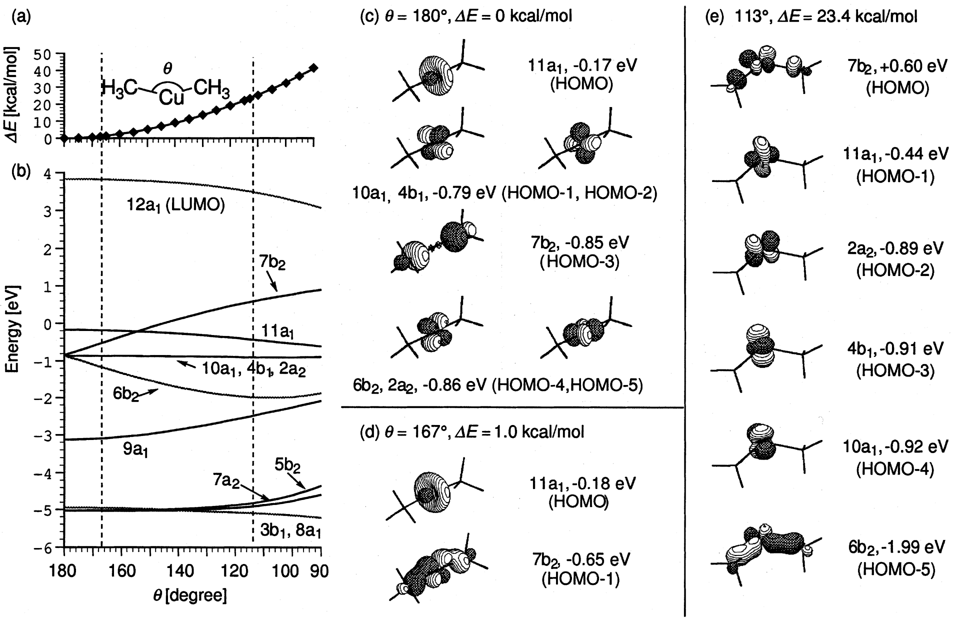

Figure 2. (a) Energy change (B3LYP/6311B//B3LYP/631A) of Me_2Cu^- as the function of the C–Cu–C angle (θ), (b) energy change of representative MOs, (c) the 3D surface (0.1 e·au^{-3}) of the MOs of Me_2Cu^- with $\theta=180°$, (d) with $\theta=167°$ and (e) with $\theta=113°$. Structures were optimized by fixing the C–Cu–C angle at 5° intervals between 90 and 180° as well as at 113 and 167°.

Me_2Cu^-) of the copper(I) and zinc(II) compounds in their neutral and ate forms. The molecular orbitals of MeCu and Me_2Cu^- are shown in Fig. 1a and b. The 3d-orbitals of MeCu lie between −6.70 and −6.86 eV, and the addition of a Me^- group (Me_2Cu^-) pushes them by ca. 7 eV to the level between −0.17 and −0.86 eV. In contrast to these high-lying d-orbitals, the d-orbitals of zinc compounds are quite low-lying (Fig. 1c–e). In Me_2Zn, the 2p carbon orbital represents the HOMO of Me_2Zn (−6.55 eV) and the five 3d-orbitals at energies between −12.95 and −13.03 eV. In Me_3Zn^-, the d-orbitals rise by ca. 6 eV to the levels between −7.38 and −7.46 eV, while the methyl 2p-orbitals go up to −1.08 eV. Upon further addition of a Me^- group generating Me_4Zn^{2-}, the d-orbitals are pushed up further to the levels between 0.15 and −0.19 eV, and the methyl 2p-orbitals to +5.09 eV.

A few interesting observations surfaced from the data. First, the charge of the center metal has profound effects on the d-orbital level. Thus, comparison of the neutral counterparts, MeCu(I) and Me_2Zn(II), indicates that the metal d-orbital energies of the zinc(II) ion lie far below those of the copper(I) ion, whereas the energies of the methyl 2p-orbitals are much less influenced by the nature of the metal. As a result, the methyl 2p-orbitals and the metal d-orbitals in Me_2Zn are far more separated from each other in energy (ca. 6.5 eV) than in MeCu (ca. 1 eV). Second, addition of a methyl anion equally raises the energy levels of all orbitals. The orbital energy increase for each addition of one methyl group is rather uniform (4–6 eV) for both d-orbitals and the methyl 2p-orbitals. Third, what is unique to Me_2Cu^- is that the energy levels of the 3d-orbitals and the methyl 2p-orbitals are comparable so that these filled orbitals will mix together to generate even higher lying orbitals. Such mixing will be impossible for organozincates since the methyl 2p- and the d-orbitals are far separated from each other (a typical Main Group property).

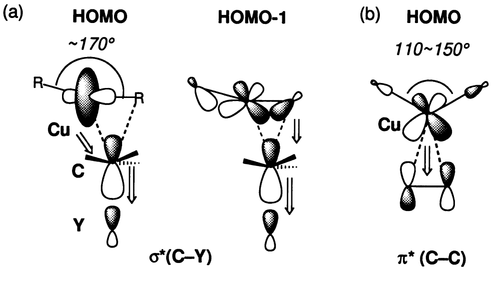

Figure 3. Orbital interactions between R_2Cu^- and substrates in (a) interactions of the HOMO and the HOMO-1 of the cuprate with alkyl halide (CH_3–Y) in the alkylation with alkyl halide, and (b) π-complexation to acetylene or olefin.

To explore the possibility of such orbital mixing, we examined the correlation of the deformation of Me_2Cu^- to the orbital properties of the molecule. To this end, we changed the Me–Cu–Me angle of Me_2Cu^- under C_{2v} symmetry constraint. As shown in Fig. 2a, the linear structure is the global minimum, and the energy increases gradually to 23.4 kcal/mol at $\theta=113°$.[28] Bending with this amount of energetic cost will easily take place under the thermal conditions (below 25°C) used in synthetic reactions of organocuprates.

Several high-lying Kohn–Sham orbitals of the linear conformer of Me_2Cu^- ($\theta=180°$) are shown in Fig. 2c. The $11a_1$ HOMO represents the copper $p_x + d_{z^2}$ orbitals as expected for a linear d^{10} complex,[29] 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 $p_x + d_{z^2}$ orbital (Fig. 2b) or the orbital mixing ($11a_1$ in Fig. 2d and e). On the other hand, even a little bending (e.g. 167°) causes mixing of the b_2 carbon s+p and the b_2 copper $3d_{xz}$ orbitals to create two new orbitals $7b_2$

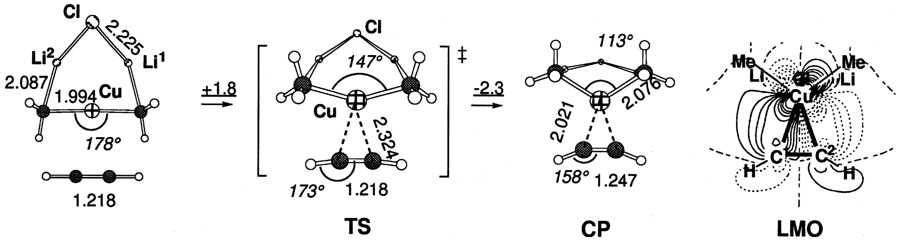

Figure 4. Complexation of $Me_2CuLi{\cdot}LiCl$ with acetylene. Bond lengths are in angstroms, angles in italic are in degree, and energy changes underlined above arrows are in kcal/mol. LMO: Localized Kohn–Sham orbital of **CP** representing back donation from copper to acetylene.

(Fig. 2e, out-of-phase mixing) and $6b_2$ (in-phase), whose energies split rapidly upon further bending (e.g. $\theta=167^\circ$, Fig. 2b). The former still remains lower in energy (HOMO-1) than the latter (HOMO) at $\theta=113^\circ$[28] but rises to HOMO at angles smaller than ca. 150°. As shown for $\theta=113^\circ$ in Fig. 2e, the new HOMO ($7b_2$) represents out-of-phase mixing of the carbon s+p and the copper $3p_x+3d_{xz}$ orbitals.[29,30]

The above analysis demonstrates that the 3d-orbital and the methyl 2p-orbital of Me_2Cu^- mix readily upon slight change of Me–Cu–Me geometry, which occurs with thermal energy provided at room temperature. Thus, for C–Cu–C angles up to ca. 154° the high-lying cuprate orbitals will have symmetry suitable for donative interactions with C–Y σ^* orbital.[31] As illustrated in Fig. 3a, both HOMO and HOMO-1 of a slightly bent structure (e.g. $\theta=167^\circ$) will interact strongly with an alkylating agent.[32] Alternatively, for angles smaller than ca. 150°, the HOMO will have good interactions with the π^*-orbital of an acetylene or an olefin as shown in Fig. 3b. Such an interaction will create a typical case of Dewar–Chatt–Duncanson d–π^* back-donation,[6] which will compensate the energy loss due to bending.

In consonance with the above analysis, complexation of $Me_2CuLi{\cdot}LiCl$ to acetylene (Fig. 4) takes place with a small activation energy[33] despite the energy loss of several kcal/mol estimated for the 147° C–Cu–C angle in the transition structure of complexation (**TS**). With this bending angle, the cuprate moiety in **TS** possesses the ability to donate d-electrons to the π^*-orbital of acetylene (Cf. LMO in Fig. 4).

Conclusion

In the above paragraphs, we have demonstrated that organozincates(II) possess high-lying methyl carbon orbital and low-lying d-orbital, and hence are expected to behave as an alkyl nucleophile and not as a metal-centered nucleophile.[34] On the other hand, organocuprates(I) will behave as a transition metal organometallics, since the d-orbitals in dialkylcuprates(I) (R_2Cu^-) are intrinsically high-lying. The d-orbitals can be further pushed up through orbital mixing with the R ligand orbital. High-lying d-orbitals thus provide theoretical support for the nucleophilic reactivity of cuprates.

The orbital energies of the alkyl ligands on the zincates have been found to lie far above the 3d-orbitals of the center metal. This orbital energy profile is very different from that of diorganocuprate, and suggests that the organozincate species will act as a carbon nucleophile rather than as a metal centered nucleophile. Obviously, further studies will be necessary to understand the apparent similarity between zincate and cuprate sometimes observed in synthetic chemistry.

The linear and bent geometries of R_2Cu^- control the relative energies of the d-orbitals (z^2 and xz) and result in the mechanistic difference between conjugate addition reaction[10] and S_N2 alkylation reaction.[11] This analysis agrees with the localized molecular orbital analysis of the complexes and transition states found on the reaction pathways of conjugate addition and carbocupration reactions.[9–11] The present studies also made it clear that the static crystal structures or the time-averaged solution structures of cuprates do not necessarily give us good information on their reactive conformations in solution, and that the high level theoretical calculations play vital roles in the studies of the organometallic species in action.[35]

Acknowledgements

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33. Activation barrier of Gibbs free energy from reactants to **TS** is 11.2 kcal/mol at 25°C and 1 atm at the B3LYP/631A level.

34. Another approach to view this summary is that the nucleophilic action of a zinc(II) centered nucleophile must generate an unlikely Zn(IV) intermediate.

35. 3D pictures and coordinates will be found on: http://www.chem.s.u-tokyo.ac.jp/~common/TH1999/title.html.