1472 J. Org. Chem. 1982, 47, 1472–1474

Molecular Orbital Study of the Bonding and Structure of Organocuprates

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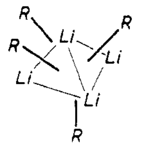
Received November 6, 1981

Structural characteristics of organocuprates were studied by performing molecular orbital calculations on $(CH_3)_4Li_4$, $(CH_3)_4Cu_4$, $(CH_3)_4Cu_2Li_2$, $(CH_3)_2(CH_3O)_2Cu_2Li_2$, and $(CH_3)_2(HC{\equiv}C)_2Cu_2Li_2$. It is found that organocuprates adopt planar structures, and alkyl groups or heteroligands of organocuprates are primarily bonded to copper instead of being equally coordinated to copper and lithium. An implication of these structural aspects of organocuprates on the selective addition to α,β-unsaturated carbonyls is briefly discussed.

Use of dialkylcopperlithium reagents in organic synthesis has flourished since the work of House et al.[1] and that of Corey and Posner.[2] These organocuprates are extremely useful because of the selectivity that they behave as reactive nucleophiles in conjugate addition to α,β-unsaturated carbonyl compounds but as poor nucleophiles in additions to nonconjugated carbonyl compounds.[3] An organocuprate transfers its alkyl groups without inverting the carbon configurations in addition[4] and displacement[5] reactions. So far reactions of organocuprates have been extensively investigated from a synthetic point of view. It has been difficult to study the mechanisms of organocuprate reactions due largely to the fact that these reagents are unstable, and hence little is known about their structures.

In the solid state, methyllithium is known to exist as a tetrameric unit $(CH_3)_4Li_4$ in which methyl groups are face-centered on the tetrahedral Li_4 cluster as shown in 1.[6] Initially, it was thought[2b,7] that dimethylcopperlithium



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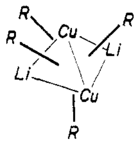

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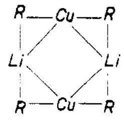
might exist as a dimeric unit $[(CH_3)_2CuLi]_2$ and have a structure similar to 1 as indicated in 2, which results when two Li atoms of 1 are replaced by two Cu atoms. Dimethylcopperlithium exists as a dimeric unit in solution, but ^1H and ^{13}C NMR studies[8] do not reveal any observable nonequivalence of the methyl groups anticipated from the structure 2. Pearson and Gregory concluded[8a] that the structure of dimethylcopperlithium is best described by the one with approximate D_{2h} symmetry as shown in 3, which has each methyl group edge-centered to a planar Cu_2Li_2 cluster. Thus 3 is similar in structure to organocopper tetramer R_4Cu_4 shown in 4.[9,10]



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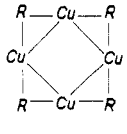

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A common structural feature of 1 and 4 is the presence of a tetranuclear cluster of metal ions, all with the formal oxidation state of 1. It is interesting to speculate if $R_4Cu_2Li_2$ might adopt a structure intermediate between the tetrahedral R_4Li_4 and the square-planar R_4Cu_4. In addition, it is important to examine whether or not the selective behavior of $R_4Cu_2Li_2$ in addition reactions can be attributed to its structure. To gain some insight into these questions, we have carried out molecular orbital (MO) calculations on R_4Li_4, R_4Cu_4, and $R_2R'_2Cu_2Li_2$ ($R = CH_3$, $R' = CH_3$, $C{\equiv}CH$, OCH_3) by employing the extended Hückel (EH) method.[11] For $(CH_3)_4Li_4$ ab initio SCF MO calculations were also performed.[12] The atomic parameters employed in our study are summarized in the Appendix. Unless stated otherwise, the standard bond lengths and bond angles[13] were used in our calculations.

Table I. Calculated Stability of the Square-Planar Structures of $(CH_3)_4Li_4$, $(CH_3)_4Cu_2Li_2$, and $(CH_3)_4Cu_4$ with Respect to Their Tetrahedral Structures

molecule	stability, kcal/mol
$(CH_3)_4Li_4$	−3.8,[a] 6.1,[b] −6.1[c]
$(CH_3)_4Cu_2Li_2$	−39[a]
$(CH_3)_4Cu_4$	−78[a]

[a] The extended Hückel calculations. [b] The ab initio SCF MO calculations with the STO-3G basis set. [c] The PRDDO calculations.[15]

Results and Discussion

A. Tetrahedral vs. Square-Planar Structures. In this section we will examine the relative stability of the square-planar and the tetrahedral structures for each of $(CH_3)_4Li_4$, $(CH_3)_4Cu_2Li_2$, and $(CH_3)_4Cu_4$. Our calculations are simplified by adopting the metal–metal and the metal–carbon bond lenghts of 2.56 and 2.28 Å, respectively, for all the three molecules.[14] For $(CH_3)_4M_4$ (M = Li, Cu),

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[‡] Camille and Henry Dreyfus Teacher-Scholar, 1980–1985.

(1) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966).

(2) (a) E. J. Corey and G. H. Posner, *J. Am. Chem. Soc.*, **89**, 3911 (1967); (b) *ibid.*, **90**, 5615 (1968).

(3) (a) G. H. Posner, *Org. React.*, **19**, 1 (1972), and references cited therein; (b) S. R. Krauss and S. G. Smith, *J. Am. Chem. Soc.*, **103**, 141 (1981), and references cited therein.

(4) G. M. Whitesides and P. E. Kendall, *J. Org. Chem.*, **37**, 3718 (1972).

(5) C. R. Johnson and G. A. Dutra, *J. Am. Chem. Soc.*, **95**, 7777, 7783 (1973).

(6) E. Weiss and E. A. C. Lucken, *J. Organomet. Chem.*, **2**, 197 (1964).

(7) G. M. Whitesides, W. F. Fischer, J. S. Filippo, R. W. Bashe, and H. O. House, *J. Am. Chem. Soc.*, **91**, 4871 (1969).

(8) (a) R. G. Pearson and C. D. Gregory, *J. Am. Chem. Soc.*, **98**, 4098 (1976); (b) R. L. Kieft and T. L. Brown, *J. Organomet. Chem.*, **77**, 289 (1974); (c) J. S. Filippo, Jr., *Inorg. Chem.*, **17**, 275 (1978).

(9) P. K. Mehrotra and R. Hoffmann, *Inorg. Chem.*, **17**, 2187 (1978).

(10) (a) J. A. J. Jarvis, B. T. Kilbourn, R. Pearce, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 475 (1973). (b) For systems with shorter Cu–Cu distances, a butterfly arrangement between a square-planar and a tetrahedral structure has been found. See: G. Van Koten and J. G. Noltes, *J. Organomet. Chem.*, **84**, 129 (1975).

(11) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(12) Our ab initio SCF MO calculations were performed by employing the MONSTER-GAUSS program developed by I. G. Csizmadia, M. R. Peterson, and R. A. Poirier at Department of Chemistry, University of Toronto.

(13) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).

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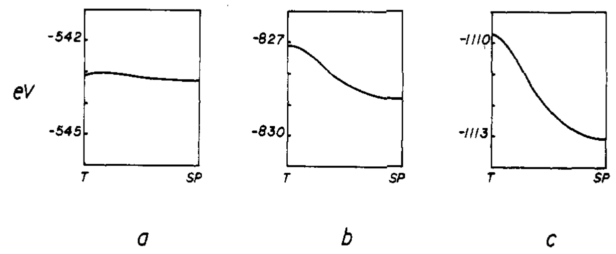
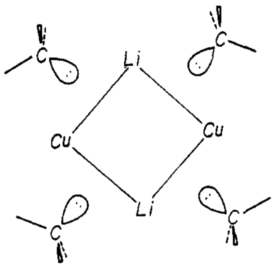


Figure 1. The calculated energies of (a) $(CH_3)_4Li_4$, (b) $(CH_3)_4Cu_2Li_2$, and (c) $(CH_3)_4Cu_4$ during the course of the structural transition from the tetrahedral (T) to the square-planar (SP) structure.

the methyl groups are arranged such that the threefold rotational axis of each methyl group coincides with the twofold (threefold) rotational axis of the M_4 cluster in the square-planar (tetrahedral) structure. The same arrangement of methyl group as the above was adopted for the square-planar and the tetrahedral structures of $(CH_3)_4Cu_2Li_2$ in our initial calculations. The results of the present calculations are summarized in Table I.

As in the case of the PRDDO calculations performed by Graham et al.[15] our EH calculations show that the square-planar structure is slightly favored over the tetrahedral structure in $(CH_3)_4Li_4$. However, the opposite is the case according to the present ab initio SCF MO calculations with the STO-3G basis set.[16] Nevertheless, it is quite evident that the stability difference between the two structures is small in $(CH_3)_4Li_4$. On the other hand, the planar structure is significantly more stable than the tetrahedral structure in $(CH_3)_4Cu_2Li_2$ just as in the case of $(CH_3)_4Cu_4$.[9,10] In order to examine if there exists any stable structure in between the square-planar and the tetrahedral structures of $(CH_3)_4Li_4$, $(CH_3)_4Cu_2Li_2$, or $(CH_3)_4Cu_4$, we may define a concerted structural transition from the tetrahedral to the square-planar structure as follows. The tetrahedral metal cluster is gradually flattened into the square-planar metal cluster by lengthening two opposite edges of the tetrahedron, while the remaining four edges are kept constant. This structural transformation of the metal cluster is coupled with the gradual motion of each methyl group. That is, one of the three metal–carbon distances associated with each methyl group of the tetrahedral structure is gradually lengthened, while the threefold rotational axis of each methyl group is gradually tilted at the same time. Figures 1a–c show the potential energy changes for $(CH_3)_4Li_4$, $(CH_3)_4Cu_2Li_2$, and $(CH_3)_4Cu_4$, respectively, during the course of the structural transition as defined above. Figure 1 clearly reveals that $(CH_3)_4Cu_2Li_2$ adopts a planar structure as $(CH_3)_4Cu_4$ does, and that the square-planar and the tetrahedral structures of $(CH_3)_4Li_4$ are nearly the same in stability in contrast to the case of either $(CH_3)_4Cu_2Li_2$ or $(CH_3)_4Cu_4$.

B. Nature of Metal–Ligand Bonding in Organocuprates. So far our calculations on the square-planar structure of $(CH_3)_4Cu_2Li_2$ assumed that the sp^3 lone pair of each methyl carbanion is equally shared by copper and lithium as shown in 5. Because of the different coordination capabilities of copper and lithium, the real arrangement of each methyl carbanion is expected to deviate from that shown in 5. Our calculations reveal that the lone pair of each methyl carbanion is almost exclusively bonded to copper as shown in 6. The lone pairs of the four methyl carbanions in $(CH_3)_4Cu_2Li_2$ are found to interact with the four low-lying acceptor orbitals of the planar $(Cu_2Li_2)^{4+}$ cluster, which are made up of Cu 4s and Cu 4p orbitals as shown in 7. Consequently, the bonding nature of $(CH_3)_4Cu_2Li_2$ may be best represented by 8. The optimization of the valence angle of α in 8 shows that the Cu_2Li_2 metal cluster does not deviate from the square-planar structure to any significant degree. The perpendicular structure 9 is an alternative to 8 but is calculated to be less stable than 8 by about 21 kcal/mol.



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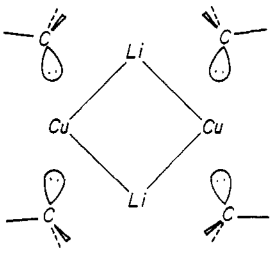

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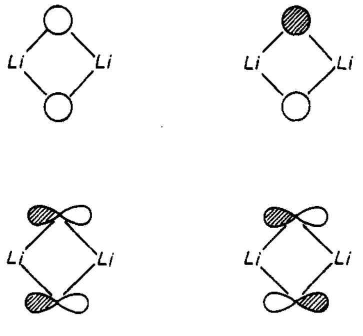

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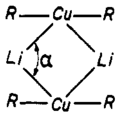

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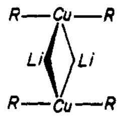

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Synthetically more useful organocuprates are those that contain not only alkyl anions but also "heteroligands" such as alkoxide, thiophenoxide, and acetylide anions.[17] These

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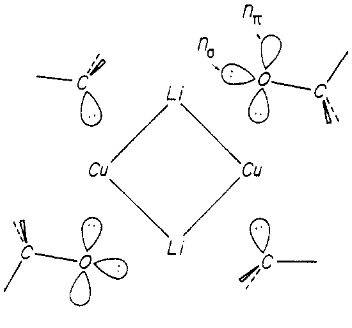
[14] The choice of these bond lengths was made on the basis of the crystal structure of $(CH_3)_4Li_4$[6] and the work of Mehrotra and Hoffmann[9] on $(CH_3)_4Cu_4$.

[15] G. Graham, S. Richtsmeier, and D. A. Dixon, *J. Am. Chem. Soc.*, **102**, 5759 (1980).

[16] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

[17] (a) G. H. Posner, C. E. Whitten, and J. J. Sterling, *J. Am. Chem. Soc.*, **95**, 7788 (1973); (b) E. J. Corey and R. H. Wollenberg, *ibid.*, **96**, 5581 (1974).

mixed organocuprates selectively transfer their alkyl groups in displacement and addition reactions. In order to study how the bonding capability of a heteroligand differs from that of an alkyl anion, we performed MO calculations on $(CH_3)_2(HC{\equiv}C)_2Cu_2Li_2$ and $(CH_3)_2(CH_3O)_2Cu_2Li_2$. Given the square-planar Cu_2Li_2 cluster, the CH_3O^- and $HC{\equiv}C^-$ anions are found to tilt as indicated in **10** and **11**, respectively.[18] The tilting of the $CH_3O^-(HC{\equiv}C^-)$ anion in **10**(**11**) in the other direction is found to result in destabilization. Thus it is the n_π lone pair of CH_3O^- and the n_σ lone pair of $HC{\equiv}C^-$ that primarily interact with the acceptor orbitals of copper in **10** and **11**, respectively. The n_σ lone pair of CH_3O^- and the π electron pair of $HC{\equiv}C^-$ are directed toward the lithium sites in **10** and **11**, respectively, and hence provide additional bonding interactions not present in the case of simple alkyl carbanions. Therefore in mixed organocuprates the alkyl groups are expected to be less tightly bound to the Cu_2Li_2 cluster than the heteroligands. This may be responsible for the preferential alkyl transfer in the reactions of mixed organocuprates.



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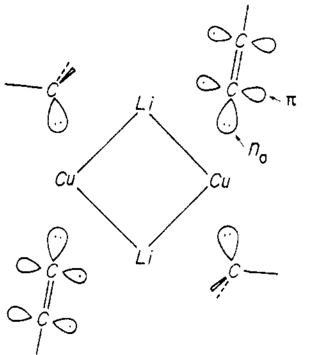

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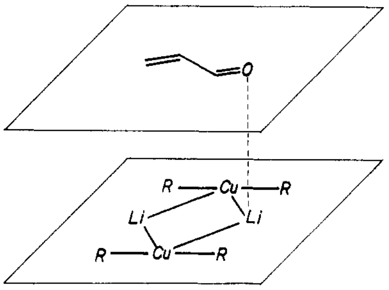
Concluding Remarks

According to our calculations discussed in the previous sections, organocuprates adopt planar structures. In addition, either alkyl groups or heteroligands of organocuprates are not equally bonded to copper and lithium but primarily bonded to copper. Such a preferential coordination makes the lithium sites more electropositive than the copper sites. This supports the observation of House and Chu[19] that complexation of an α,β-unsaturated carbonyl to an organocuprate, a necessary first step in the conjugate addition reaction,[19,20] occurs through the coordination of the carbonyl oxygen to a lithium atom of the Cu_2Li_2 metal cluster. The planar organocuprate **8** has empty Cu 4p orbitals perpendicular to the Cu_2Li_2 metal plane, and these empty orbitals may provide additional stabilization by interacting with available electron pairs. Thus the conjugate addition reaction might involve a stacked arrangement of an α,β-unsaturaged carbonyl and an organocuprate as depicted in **12**, which is consistent with an intermediate complex recently proposede by Krauss and Smith.[3b]

Table II[a,b]

χ_μ	ζ_μ	ζ'_μ	$H_{\mu\mu}$, eV
Cu 4s	2.2		-11.4[13]
Cu 4p	2.2		-6.06
Cu 3d	5.95 (0.5933)	2.30 (0.5744)	-14.0
C 2s	1.625		-21.4
C 2p	1.625		-11.4
O 2s	2.275		-32.3
O 2p	2.275		-14.8
Li 2s	0.65		-5.4
Li 2p	0.65		-3.5
H 1s	1.3		-13.6

[a] The d orbitals are given as a linear combination of two Slater-type orbitals,[21] and each is followed in parentheses by the weighting coefficient. [b] A modified Wolfsberg-Helmholz formula was used to calculate $H_{\mu\nu}$.[22]



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Acknowledgment. This work is in part supported by Research Corporation through a Cottrell Research Program and by Camille and Henry Dreyfus Foundation through a Teacher-Scholar award to M.-H. Whangbo.

Appendix

The exponents (ζ_μ) and the valence-shell ionization potentials ($H_{\mu\mu}$) of the Slater-type orbitals (χ_μ) employed in our study are summarized in Table II.

Registry No. $(CH_3)_4Li_4$, 20670-26-2; $(CH_3)_4Cu_4$, 66758-40-5; $(CH_3)_2Cu\,Li$, 15681-48-8; $CH_3(CH_3O)Cu\,Li$, 80822-52-2; $CH_3(HC{\equiv}C)CuLi$, 80822-53-3.

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[18] A concerted structural transition from the tetrahedral to the square-planar structures was also examined for $(CH_3)_2(HC{\equiv}C)_2Cu_2Li_2$ as in the case of $(CH_3)_4Cu_2Li_2$ to confirm that the square-planar structure is more stable than the tetrahedral structure in mixed organocuprates as well. A planar mixed organocuprate may adopt a configuration in which the heteroligands are arranged such that the point group symmetry of the molecule is C_{2v} rather than C_{2h} as shown in **10** and **11**. Our calculations with $(CH_3)_2(HC{\equiv}C)_2Cu_2Li_2$ reveal that the C_{2h} and C_{2v} configurations are very similar in stability. In a mixed organocuprate the C_{2h} configuration provides the least steric hindrance between the heteroligands.

[19] H. O. House and C.-Y. Chu, *J. Org. Chem.*, 41, 3083 (1976).

[20] H. O. House, *Acc. Chem. Res.*, 9, 59 (1976).

[21] H. Basch and H. B. Gray, *Theoret. Chim. Acta*, 4, 367 (1966).

[22] J. H. Ammeter, H.-B. Bürgi, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 3686 (1978).