

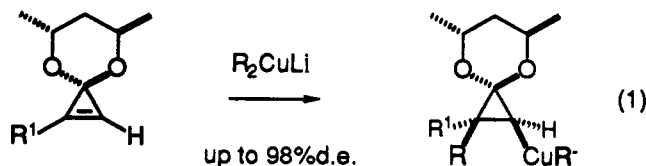
Theoretical Studies on Carbometalation of Cyclopropene. Transition Structures of Addition of Me⁻, MeLi, MeCu, and Me₂Cu⁻ and Origin of the High Reactivity of the Strained Double Bond

Eiichi Nakamura,^{*,†} Masaharu Nakamura,[†] Yoshimitsu Miyachi,[†] Nobuaki Koga,[†] and Keiji Morokuma^{*,†}

Contribution from the Department of Chemistry, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan, and Institute for Molecular Science, Myodaiji, Okazaki 444, Japan.
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Abstract: Comparative structural and energy decomposition analyses of the reaction of the additions of Me⁻, MeLi, MeCu, and Me₂Cu⁻ to ethylene and cyclopropene have provided general information on the mechanism of release of the ring strain and, consequently, reasons for the high reactivities of organocopper reagents to cyclopropenes. Analyses of structural parameters of the transition structures indicated that the Me⁻ and MeLi additions to cyclopropene involve an "earlier" transition state than the corresponding additions to ethylene, as expected from the higher exothermicity of the latter reaction. In contrast, the transition structures of the MeCu addition to cyclopropene is quite asynchronous, in that the overall nature of the TS is still early but the C=C bond cleavage is quite advanced. As a result of this advanced C=C bond cleavage, the olefinic carbons are significantly rehybridized so that the cyclopropene moiety experiences substantial orbital interaction with the vacant copper 4p orbital. Analysis of the localized molecular orbitals indicated that the filled copper 3d orbitals do not actively participate in the bond exchange in the transition state of the MeCu addition to ethylene.

High reactivities of strained small rings toward organometallics have been well-documented,¹ and the rapid cis-addition of nucleophilic organometallics² across the strained double bond of cyclopropene (olefinic strain = 24 kcal/mol)³ provides a typical example of the enhanced reactivities of strained olefins. On the other hand, addition of main-group organometallics (e.g., Et₂Mg) to ethylene takes place only at high temperatures,⁴ and 1,2-dialkyl-substituted olefin, which is a true nonstrained equivalent of cyclopropene, does not serve to accept organometallic additions. It was recently reported that the reaction of organocopper compounds is much more facile than that of main group organometallics, proceeding even in seconds at -78 °C.^{2d,5} The practical utility of the reaction resides in its high cis-stereoselectivity, and has been highlighted by the recent discovery of asymmetric addition of organocuprates to chiral cyclopropene **1** (eq 1).⁶ The



mechanistic understanding of this asymmetric induction is not yet available owing to the general lack of mechanistic information on such carbometalation reactions.

A simplistic mechanistic view of the carbometalation of cyclopropenes suggests that the transition state of this highly exothermic reaction may be quite reactantlike, and that a relatively small portion of the total strain energy may be released in the transition state. As to the role of the metals in the carbocupration reaction, conventional wisdom calls for the interplay of the strain energy and the metal d orbitals⁷ as key elements of the high reactivity of organocopper reagents toward cyclopropenes. However, it is unclear how copper differs from other main-group metals and how the ring strain and the d orbitals may cooperate to lower the activation barrier of the organocuprate reaction. Obviously, these are general problems in the transition-metal/strained-ring interactions. We have examined the problem with the aid of ab initio theoretical calculations by studying the addition of methyl anion (Me⁻), methyl lithium (MeLi), methylcopper

(MeCu), and dimethyl cuprate (Me₂Cu⁻) to cyclopropene (CP) and ethylene (ET).⁸ By systematic comparison of these two olefins for their activation energies and the transition structures (TSs), we have obtained a coherent view of the role of the strain and the orbital interactions in the strain-driven carbometalation of cyclopropenes.

Computational Methods

The geometries of reactants, complexes, and TSs were optimized with the Hartree-Fock method.⁹ For the copper atom, the

(1) Bishop, K. C., III. *Chem. Rev.* 1976, 76, 461.

(2) (a) PhLi: Applequist, D. E.; Saurborn, E. G. *J. Org. Chem.* 1972, 37, 1676. (b) Grignard reagent: Moiseenkov, A. M.; Czeskis, B. A.; Semenovskiy, A. V. *J. Chem. Soc. Chem. Commun.* 1982, 109. Lukina, M. Yu.; Rudashevskaya, T. Yu.; Nesmeyanova, O. A. *Dokl. Akad. Nauk. SSSR* 1970, 190, 1109. Rudashevskaya, T. Yu.; Nesmeyanova, O. A. *Izv. Akad. Nauk. SSSR* 1983, 1821. Nesmeyanova, O. A.; Rudashevskaya, T. Yu.; Dyachenko, A. I.; Savitova, S. F.; Nefedov, O. M. *Synthesis* 1982, 296. (c) Allylic metals are more reactive to cyclopropenes than alkyl, aryl, and vinyl metals. Allylmagnesium bromide: Lehmkuhl, H.; Mehler, K. *Liebigs Ann. Chem.* 1982, 2244. Lehmkuhl, H.; Mehler, K. *Liebigs Ann. Chem.* 1978, 1841. (d) Allylzinc bromide and propylcopper add to 1-trimethylsilyl-2-alkylcyclopropene: Stoll, A. T.; Negishi, E.-i. *Tetrahedron Lett.* 1985, 26, 5761. (e) Allylborane: Bubnov, N. Yu.; Kazanskii, B. A.; Nesmeyanova, O. A.; Rudashevskaya, T. Yu.; Mikhailov, B. M. *Izv. Acad. Nauk SSSR Ser. Khim.* 1977, 2545. Allyllithium and allylzinc reagents as well as some aryl Grignard reagent undergo addition to **1**: Isaka, M. unpublished results. (f) Reviews: Nakamura, E.; Isaka, M. *Organomet. News* 1990, 194. Halton, B.; Banwell, M. G. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; John Wiley: New York, 1987; p 1223.

(3) Defined as difference in strain between alkene and the corresponding alkane: Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1981, 103, 1891. Wiberg, K. B.; Artis, D. R.; Bonneville, G. *J. Am. Chem. Soc.* 1991, 113, 7969. Wiberg, K. B. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; John Wiley: New York, 1987; p 1.

(4) Cf.: Podall, H. E.; Fosters, W. E. *J. Org. Chem.* 1958, 23, 1848.

(5) Nakamura, E.; Isaka, M.; Matsuzawa, S. *J. Am. Chem. Soc.* 1988, 110, 1297.

(6) Isaka, M.; Nakamura, E. *J. Am. Chem. Soc.* 1990, 112, 7428.

(7) The proposed active participation of the filled 3d orbitals of copper assumes the formation of a Cu(III) intermediate as described by Corey for various reactions of cuprates involving carbocupration of acetylenes (Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* 1984, 25, 3063; 1985, 26, 6015). However, in this and our previous studies (ref 8), we found that MeCu and Me₂Cu⁻ react with olefins and acetylenes just like MeLi, in a manner expected for a nucleophilic addition of a methyl anion, rather than that of a metal nucleophile.

(8) For the theoretical studies on carbometallation of acetylenes, see: Nakamura, E.; Miyachi, Y.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* 1992, 114, 6686.

[†] Tokyo Institute of Technology.

[‡] Institute for Molecular Science.

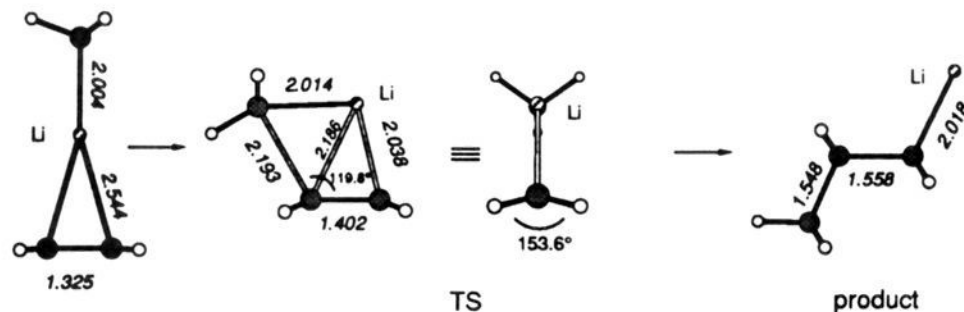


Figure 1. Reaction pathway of MeLi addition of ET (HF/3-21G, based on ref 19). Throughout Figures 1–7, bond lengths in *italics* are in angstroms.

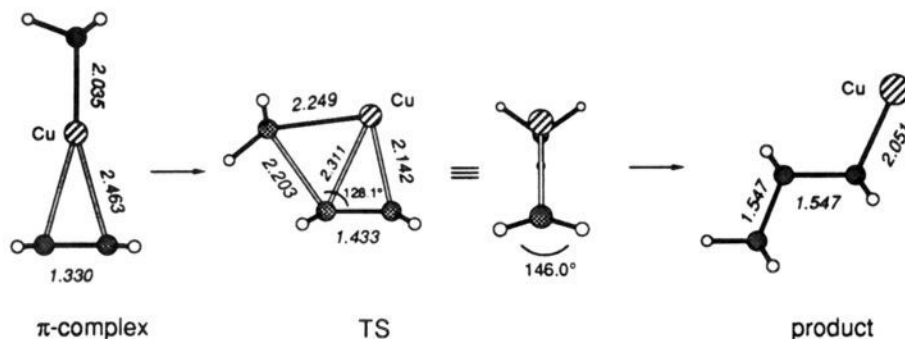


Figure 2. Reaction pathway of MeCu addition to ET (HF/3-21G).

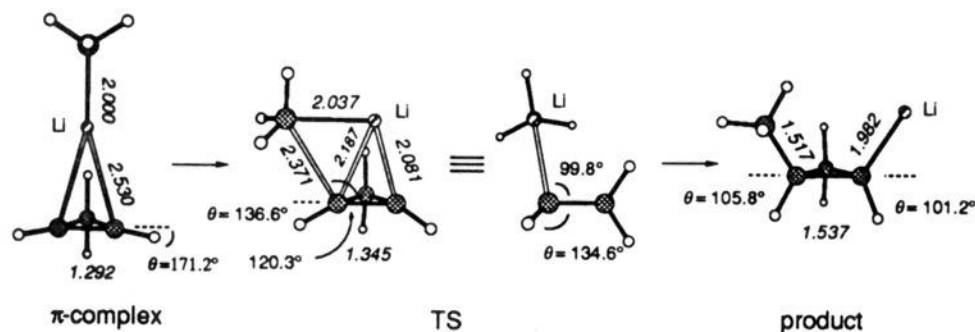


Figure 3. Reaction pathway of MeLi addition to CP. The dihedral angle (θ) is defined for the C=C bond between the indicated olefinic hydrogen and the plane defined by the three-membered ring (indicated by dotted line). These definitions also apply to other figures.

inner-shell (from 1s to 3p) electrons were replaced by an effective core potential (ECP). The potential parameters employed in our calculations are those given by Hay and Wadt.^{10,11} The remaining electrons were described by basis functions of double- ζ quality.¹² For all other atoms, the 3-21G basis set¹³ was used for geometry optimizations. In order to obtain better activation energies, energy calculations were also performed at the MP2(FC)¹⁴/6-31G*(5D)

level on the HF/3-21G optimized geometry (abbreviated also as MP2/6-31G**/HF/3-21G), for the structures involving copper, and at the MP2(FC)/6-31G*(6D) level on the HF/3-21G optimized geometry (also abbreviated as MP2/6-31G**/HF/3-21G), for other structures. In all cases reported in this article, the energy profiles of the reaction obtained with electron correlation at the MP2/6-31G* level were qualitatively the same as those at the HF/3-21G level.

The large number of calculations involved in the present studies necessitated dealing with only monomeric ligand-free MeCu and MeLi. A few important structures were also examined for the reaction of Me_2Cu^- for two reasons: first, because of the importance of organocuprates in actual experiments and, second, because the highly basic Me^- ligand on copper would serve as a model for probing ligand effects.

In order to alleviate the obvious deficiency of our models, we used a protocol to evaluate the structural and energetic parameters in a relative sense by taking the unstrained ET as a reference standard for CP. In this way, the deficiency with respect to the ligand and the aggregation state, which are most likely common for both the CP and ET reactions, would largely be cancelled.¹⁵

(9) (a) The following programs were used. GAUSSIAN 86: Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whitesides, R. A.; Schlegel, H. B.; Pople, J. A. GAUSSIAN 90, Revision: Frisch, J. M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1990. (b) C_s symmetry was assumed for the reactions of ET.

(10) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270, 284. For ECP parameters, see: Goddard, W. A., III; Kahn, L. R. *J. Chem. Phys.* **1972**, *56*, 2685. Melius, C. F.; Goddard, W. A., III. *Phys. Rev. A* **1974**, *10*, 1528.

(11) The procedure used in GAUSSIAN 86 on which the code was based has been described: Davidson, E. R.; McMurchie, L. E. *J. Comput. Phys.* **1981**, *44*, 289. The computational implementation is due to Martin, L. R.

(12) In specifying the level of calculation, the basis set for Cu, which is always DZ with ECP, will not be shown.

(13) (a) 3-21G basis set: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) 6-31G* basis set: Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(14) Binkley, J. S.; Pople, J. A.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.

(15) Although the absolute values of the activation energies of the MeCu addition are unrealistically high owing to the drastic simplification of the ligand environment of copper, studies of the *difference* between the CP and the ET reactions would thus give us a realistic estimate of the strain effects.

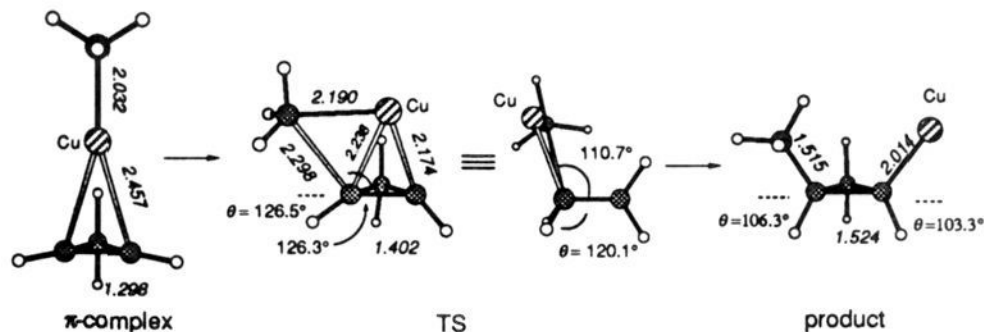


Figure 4. Reaction pathway of MeCu addition to CP (HF/3-21G).

Table I. Mulliken Overlap Populations (HF/3-21G) in the TSs of Carbometalations

reaction	C_α -M	C_β -M	C_β -CH ₃	CH ₃ -M
ET + MeLi	0.127	0.011	0.080	0.141
ET + MeCu	0.158	0.016	0.098	0.113
CP + MeLi	0.090	0.004	0.056	0.205
CP + MeCu	0.146	0.025	0.072	0.180

The power of this comparative protocol using monomeric MeLi and MeCu has recently been demonstrated by the successful reproduction of the experimental regioselectivity of carbometalation of substituted acetylenes.⁸ Moreover, such simplification may be justified in the light of the recent results that reactants and transition structures of the reaction of methyl lithium monomer and its dimers with formaldehyde¹⁶ and acetylenes¹⁷ share in common important features.

Results and Discussion

Structural Analysis. The HF/3-21G optimized structures of the reactants, CP,¹⁸ ET,¹⁹ MeLi,^{16,20} and MeCu,²¹ have been previously reported in the literature. Addition of MeLi to ET was previously studied with the ab initio method employing optimization with the HF/3-21G procedure (Figure 1).¹⁹ The reaction first gives a MeLi/olefin π complex, and then proceeds through a four-centered TS to give finally propyllithium.²²

As in the MeLi addition to ET, addition of MeCu to ET, MeLi to CP, and MeCu to CP have also been found (HF/3-21G) to proceed through a π complex and a four-centered TS (Figures 2-4) to give finally a substituted cyclopropyl metal.²³ Experimentally, kinetic studies of the addition of a Grignard reagent to a cyclopropene have been interpreted to yield a bimolecular mechanism involving a four-centered transition state.²⁴ Such a

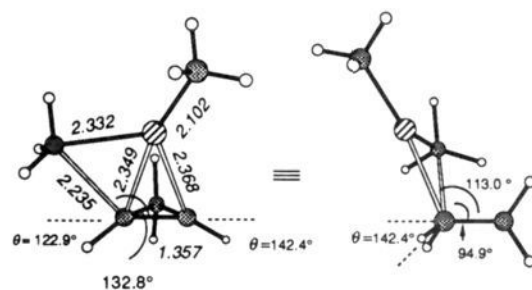


Figure 5. Transition structure of addition of Me₂Cu⁻ to CP (HF/3-21G).

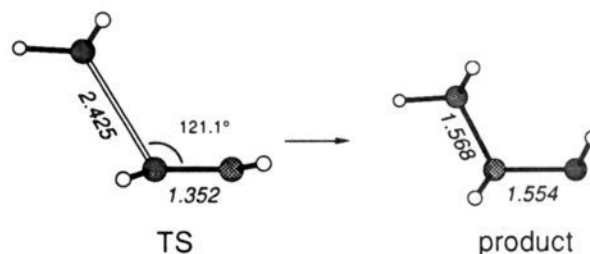


Figure 6. Reaction pathway of Me⁻ addition to ET (HF/3-21G).

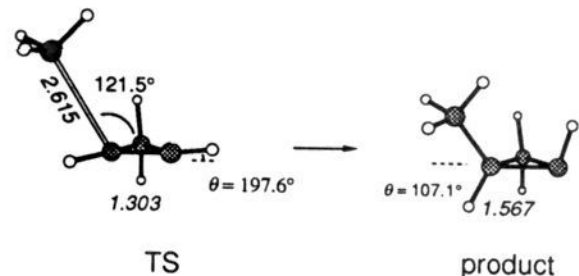


Figure 7. Reaction pathway of Me⁻ addition to CP (HF/3-21G).

(16) Kaufmann, E.; Schleyer, P. v. R.; Wu, Y.-D.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 5560. Bachrach, S. M.; Streitwieser, A. Jr. *J. Am. Chem. Soc.* **1986**, *108*, 3946.

(17) Unpublished results by the authors.

(18) Staley, S. W.; Norden, T. D.; Su, C.-F.; Rall, M.; Harmony, M. D. *J. Am. Chem. Soc.* **1987**, *109*, 2880. Yoshimine, M.; Pacansky, J.; Honjou, N. *J. Am. Chem. Soc.* **1989**, *111*, 2785.

(19) Houk, K. N.; Rondan, N. G.; Schleyer, P. v. R.; Kaufmann, E.; Clark, T. *J. Am. Chem. Soc.* **1985**, *107*, 2821.

(20) Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* **1987**, *109*, 5909.

(21) Dorigo, A. E.; Morokuma, K. *J. Am. Chem. Soc.* **1989**, *111*, 4635. Dorigo, A. E.; Morokuma, K. *J. Am. Chem. Soc.* **1989**, *111*, 6524.

(22) The conformationally stable trans product is shown in Figure 1, as the syn addition product formed directly without C-C bond rotation is a transition state of C-C bond rotation.

(23) Collins, J. B.; Dill, J. D.; Jemmins, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5419. Skancke, A.; Boggs, J. E. *J. Mol. Struct.* **1978**, *50*, 173. Clark, T.; Spitznagel, G. W.; Klose, R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 4412.

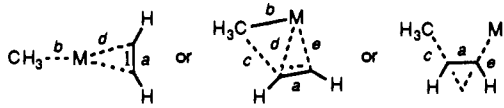
(24) (a) Richey, H. G., Jr.; Watkins, E. K. *J. Chem. Soc., Chem. Commun.* **1984**, 772. (b) Chamberlin, A. R.; Bloom, S. H.; Cervini, L. A.; Fotsch, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 4788. See also Hill, E. A. *Organomet. Chem.* **1975**, *97*, 7171. Dolzine, T. W.; Oliver, J. P. *J. Organomet. Chem.* **1974**, *78*, 165.

transition state is fully consistent with the rigorous cis-selectivity observed experimentally for the reaction of R₂CuLi to cyclopropenone acetals (eq 1).⁵

These "four-centered" TSs in Figures 1-4 may resemble a "metallacyclopropane" structure bearing a methyl anion appendage. The metal is located quite close to (2.04-2.31 Å) and nearly equidistant from the two olefinic carbons. The apparent metallacyclopropane-like structure, however, seems to be superficial. Mulliken overlap populations in the TSs of MeLi and MeCu additions (Table I) gave viable information on the electronic interactions between the metal (M) and the two olefinic carbons (C_α and C_β): the overlap population between M and C_α as well as between M and Me is quite large, while that between M and C_β is small. Thus, M and C_β appear to be simply forced to come closer by external requirements.²⁵ Further support of this view

(25) The large attack angle (<Me-C_β-C_α, Table II) and the strong Me-M-C_α bonding (Table I) appear to force the Me and C_β close to each other.

Table II. Structural Parameters (HF/3-21G) of the Various Stationary Points of Carbometalation



	a^b	b^c	c^d	d	e	$\langle \text{CH}_3\text{-C}_\beta\text{-C}_\alpha \text{, deg}$
CH ₃ Li		2.001 (100)				
CH ₃ Cu		2.040 (100)				
ethylene (ET)	1.315 (0)					
Me ⁻ (TS)	1.352 (15.5)		2.425 (154.6)			121.1
Me ⁻ (product)	1.554 (100)		1.569 (100)			
CH ₃ Li (π complex)	1.325 (3.7)	2.004 (100.1)		2.544		
CH ₃ Li (TS)	1.402 (31.8)	2.014 (100.6)	2.193 (141.7)	2.186	2.038	119.8
CH ₃ Li (product)	1.588 (100)		1.548 (100)		2.018	
CH ₃ Cu (π complex)	1.330 (5.8)	2.035 (99.8)		2.463	2.463	
CH ₃ Cu (TS)	1.433 (45.4)	2.249 (110.2)	2.203 (142.5)	2.311	2.142	128.1
CH ₃ Cu (product)	1.575 (100)		1.546 (100)			
cyclopropene (CP)	1.282 (0)					
Me ⁻ (TS)	1.303 (7.4)		2.615 (170.6)			121.5
Me ⁻ (product)	1.567 (100)		1.533 (100)			
CH ₃ Li (π complex)	1.292 (3.9)	2.000 (100.0)		2.530		
CH ₃ Li (TS)	1.345 (24.7)	2.037 (101.9)	2.371 (156.3)	2.187	2.083	120.3
CH ₃ Li (product)	1.537 (100)		1.517 (100)		1.982	
CH ₃ Cu (π complex)	1.298 (6.6)	2.032 (99.6)		2.457		
CH ₃ Cu (TS)	1.402 (49.6)	2.190 (107.4)	2.298 (151.7)	2.238	2.174	126.3
CH ₃ Cu (product)	1.524 (100)		1.515 (100)		2.015	

^a For definition of C_β and C_α , see Table I. ^b Numbers in parentheses refer to percent bond elongation with $\{(a \text{ in product}) - [a \text{ in starting material}]\}$ as 100% reference standard in respective reaction. ^c Numbers in parentheses refer to the percent bond elongation with the starting Me-metal length as standard. ^d Numbers in parentheses refer to the bond length relative to the one in the product expressed in percentage.

has been provided by the analysis of localized molecular orbital of the TS, wherein relatively small electron density is found between M and C_β (vide infra).

The TS of the addition of Me_2Cu^- was in some way found to be more advanced than that of the MeCu reaction, but may also be viewed quite similar to that of the MeCu addition in spite of the presence of a powerful Me^- ligand on the metal (Figure 5). This observation suggests that the presence of a ligand on the metal may not drastically change the TSs.

The TSs of the Me^- additions to ET and CP (Figures 6 and 7) are quite dissimilar to those of the Me-metal additions, in that these reactions take an anti addition course so that negative charge on the cyclopropene develops on the side opposite to the incoming Me^- group.²⁶

The incoming angles of the Me group were found to fall into a small range of 120–128° irrespective of the olefin structure or the nature of the incoming Me nucleophile (Table II). These angles are much larger than those found in the experimental Bürgi–Dunitz trajectory²⁷ or in the calculated MeLi and LiH additions to carbonyl compounds.¹⁶

To make more quantitative comparisons, important bond lengths have been evaluated by setting an appropriate standard for each reaction parameter (Table II). Thus, for the cleaving double bond (parameter a), difference of the bond lengths in the starting olefin and the product was taken as a standard (100%), and the degrees of bond stretching in the complex and the TS are indicated as respective percentiles. For the cleaving Me-metal bond (parameter b) and the forming Me-C bond (parameter c), percentiles are defined by taking the starting Me-metal and the fully formed Me-C length as a standard, respectively. These values for each reaction intermediate are shown in parentheses in Table II.

In addition, to investigate strain effects, the data shown in Table III were also evaluated. In this table, the three structural parameters a – c in the CP reaction were compared with those of the corresponding ET reaction in each series of the Me^- , MeLi , and

Table III. Structural Differences in the π Complexes and in the TSs of the CP and ET Reactions for Various Methyl Nucleophiles (HF/3-21G)^a

	Me^- (%)	MeLi (%)	MeCu (%)
π complex			
$a_{\text{CP}} - a_{\text{ET}}^b$	e	+0.2	+0.7
$b_{\text{CP}} - b_{\text{ET}}^c$	e	-0.1	-0.2
TS			
$a_{\text{CP}} - a_{\text{ET}}^b$	-8.1	-7.1	+4.2
$b_{\text{CP}} - b_{\text{ET}}^c$	e	+1.3	-2.8
$c_{\text{CP}} - c_{\text{ET}}^d$	+16.0	+14.6	+9.2

^a The x_{CP} and x_{ET} parameters ($x = a, b, \text{ and } c$) refer to the percentiles shown in the parentheses in Table II for the respective Me^- nucleophilic addition to the CP and ET. Thus, an $x_{\text{CP}} - x_{\text{ET}}$ value indicates the relative magnitude of bond formation or cleavage for each parameter in the CP TS against the ET reference standard, serving thereby as a measure of the position of the TS of the CP reaction in the reaction coordinate relative to the ET reaction. ^b The a parameter being associated with bond cleavage, negative values for TS suggest that the CP TS is "earlier" than the ET TS. ^c Similarly, negative b values suggest the CP TS being "earlier". ^d The c parameter associated with bond formation; positive c values suggest the CP TS being "earlier". ^e Not definable.

MeCu additions. This way of using an ET reaction as a non-strained reference standard should significantly reduce the deficiency of our model treatment of metal's ligand environment, which is likely shared in common by both the ET and the CP reactions.

The structural parameters of the Me-metal/olefin π complexes (Table II) indicate that complexation little changes the Me-metal length (parameter b , 99.6–100.1%), and slightly elongates the double bond (parameter a , 3.7–6.6%). Very small difference between the ET and CP reactions for their bond stretching indices for a and b (-0.2 to +0.7%, Table III) indicates that there is little strain effect surfacing at the π -complex stage.

Unlike the π complexes, the TSs showed marked dependence on the olefinic substrate as well as on the metal. For the Me^- addition, the $\text{C}=\text{C}$ double bond (parameter a , Table III) is less stretched (-8.1%) and the forming Me-C bond (c) is longer (+16.0%) in the CP reaction than in the ET reaction, indicating that the TS is "earlier" in the former than in the latter. This agrees with an expectation based on the much higher exothermicity of

(26) (a) This is against what has generally been observed experimentally for organometallics (refs 2, 5, and 6). (b) For the reasons for such trans bending, see: Fukui, K.; Fujimoto, H. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2116. Strozio, R. W.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 1340.

(27) Bürgi, H. B.; Dunitz, J. D.; Lehn, J. M.; Wipff, G. *Tetrahedron* **1974**, *30*, 1563.

Table IV. Energies Relative to Reactants ([ET + Nu⁻] or [CP + Nu⁻])^a

	Nu ⁻ = Me ⁻	MeLi	MeCu
[ET + Nu ⁻] ^b	-116.840 391 317 2	-124.353 469 492 9 (-125.446 168 80)	-167.406 930 918 (-168.621 248 98)
π complex ($\Delta E_{\pi(ET)}$)	<i>b</i>	-12.10 (-12.33)	-13.25 (-17.07)
TS ($\Delta E_{TS(ET)}$)	-1.32	11.48 (4.22)	39.30 (34.62)
product ($\Delta E_{P(ET)}$)	-28.47	-18.75	-19.22
actvn energy ($\Delta E^*_{(ET)}$)		23.58 (16.55)	52.55 (51.69)
[CP + Nu ⁻] ^b	-154.401 408 318	-161.914 486 493 (-163.365 557 01)	-204.967 947 918 (-206.540 637 19)
π complex ($\Delta E_{\pi(CP)}$)	<i>b</i>	-9.84 (-9.94)	-10.72 (-14.36)
TS ($\Delta E_{TS(CP)}$)	-6.03	4.37 (-1.41)	28.10 (21.80)
product ($\Delta E_{P(CP)}$)	-66.48	-53.05	-50.73
actvn energy ($\Delta E^*_{(CP)}$)		14.21 (8.53)	38.82 (36.16)

^aEnergies were obtained at the HF/3-21G level and expressed in kcal/mol except as noted. Energies in parentheses were obtained at the MP2/6-31G*//HF/3-21G level. ^bEnergies in hartree. ^cNot determined.

Table V. Energy Differences between the CP and ET Reactions^a

	Me ⁻	MeLi	MeCu
$\Delta E_{\pi(CP)} - \Delta E_{\pi(ET)}$		+2.26 (+2.40)	+2.54 (+2.71)
$\Delta E_{TS(CP)} - \Delta E_{TS(ET)}$	-4.71	-7.11 (-5.63)	-11.20 (-12.82)
$\Delta E_{P(CP)} - \Delta E_{P(ET)}$	-38.01	-34.30	-31.52
$\Delta E^*_{(CP)} - \Delta E^*_{(ET)}$		-9.27 (-7.88)	-13.65 (-15.42)

^aEnergies were obtained at the HF/3-21G level and expressed in kcal/mol except as noted. Energies in parentheses were obtained at the MP2/6-31G*//HF/3-21G level.

the CP reaction. Similarly, for the MeLi addition, the TS of the CP reaction is also "earlier" as judged by the parameters *a* (-7.1% shorter) and *c* (+14.6% longer).²⁸

In contrast to the Me⁻ and MeLi additions, the structural changes in the MeCu addition to CP, as compared with those in the addition to ET, are unique. The forming Me-C bond (*c*, 9.2% longer for CP than for ET, Table III) and the little stretched Me-Cu bond (*b*, only 7.4% elongated in its absolute magnitude, Table II, and 2.8% shorter than for ET, Table III) do indicate that the CP TS is earlier. However, the cleaving C=C bond (*a*, 4.2% longer for CP than for ET, Table III) in turn suggests a more advanced transition state. This positive value of +4.2% makes a sharp contrast to the less advanced C=C bond cleavage in the Me⁻ (-8.1%) and MeLi (-7.1%) additions (Table III).

The specific advancement of the C=C bond cleavage in the TSs of CP reactions is also seen from the sp²-to-sp³ rehybridization of the olefinic carbons, as measured by the dihedral angle θ between the two C-H (or C _{α} -CH₂) bonds in the projection perpendicular to the C _{α} =C _{β} axis (see Table I for the definition of C _{α} and C _{β}). In the MeLi and MeCu additions to ET (Figures 1 and 2), the olefinic protons are pushed down from the original olefin plane only by 13.2° and 17.0°, respectively. On the other hand, rehybridization proceeded much more extensively with the CP reactions. In the MeLi addition, the olefinic protons are 45.4° ($\theta = 134.6^\circ$; for definition, see Figure 3) down from the cyclopropene plane, and in the MeCu addition (Figure 4), the angle is 59.90° ($\theta = 120.1^\circ$), which is already quite close to the 80° angle in the product ($\theta = 101-103^\circ$). Thus, the cyclopropene region of the CP TS may be viewed as productlike rather than reactantlike. In summary, there was found unique and marked asynchrony in the TS of the MeCu addition to CP as opposed to other reactions.

Energy Analysis. Because of the ring strain release, the Me⁻, MeLi, and MeCu additions to CP were found to be exothermic by 66.48, 53.05, and 50.73 kcal/mol, respectively, at the HF/3-21G//HF/3-21G level (Table IV). Such exothermicity is much larger than those of the ET reaction by 38.01, 34.30, and 31.52 kcal/mol, respectively (Table V), and much of this energy difference can be attributed to the release of the olefinic strain.³

Interestingly, however, we found no sign of strain release in the Me-metal/olefin π -complexation stage. In fact, stability of

the π complex in the CP reaction ($\Delta E_{\pi(CP)}$) is even less than that in the ET reaction ($\Delta E_{\pi(ET)}$) by 2.39 and 2.71 kcal/mol at the MP2/6-31G*//HF/3-21G level for MeLi and MeCu, respectively (Table V).

In contrast to the π -complex stage, the TS energies were found to be subject to the ring-strain effect. To investigate this point, the TS energies (relative to reactants, ΔE_{TS} , Table IV) were compared between CP and ET for each methyl nucleophile ($\Delta E_{TS(CP)} - \Delta E_{TS(ET)}$, Table V). The ΔE_{TS} of the Me⁻ addition to CP was found to be 4.71 kcal/mol lower in energy than that to ET at the HF/3-21G//HF/3-21G level, and this value was found to be of the same magnitude (7.11 kcal/mol; 5.63 kcal/mol at MP2/6-31G*//HF/3-21G) for the MeLi reaction. In sharp contrast, the ΔE_{TS} of the MeCu addition to CP is conspicuously lower in energy (by 11.20 kcal/mol; 12.82 kcal/mol at MP2/6-31G*//HF/3-21G) than that to ET. In the light of the 24 kcal/mol olefinic strain³ of cyclopropene, it may be estimated that nearly half of the olefinic strain of CP is already released in the TS of the MeCu addition to CP, while only one-fourth is released in the Me⁻ and MeLi additions. This energetic trend is also observed in the activation energies ($\Delta E^* = \Delta E_{TS} - \Delta E_{\pi}$, the last row in Table IV), and is in good agreement with the asynchronous TS of the MeCu addition to CP found by the structural analysis.

Energy Decomposition Analysis. The foregoing analyses based on structures and total energies indicated the exceptional character of the MeCu/CP combination as compared with other combinations. In order to investigate the energetic elements that form the background of this singularity, energy decomposition analysis (EDA) of the TS energies was carried out using the Kitaura-Morokuma scheme.²⁹

In Table VI is shown the EDA of the four TSs of the addition of MeLi and MeCu (indicated as M) to ET and CP (as O) as well as that of the TS of the Me₂Cu⁻ addition to CP.³⁰ The earlier nature of the CP TSs is reflected by the generally smaller deformation components (DEF) and the exchange repulsion terms

(29) Kitaura, K.; Morokuma, K. *Int. J. Quantum Chem.* 1976, 10, 325. Morokuma, K. *Acc. Chem. Res.* 1977, 10, 294.

(30) (a) The EDA procedure will be described briefly in this footnote, while the details of the theory²⁹ and an application to closely related investigations have been described elsewhere.^{8,21} With this procedure, the olefin component (O) and the Me-metal (M) in the TS are considered separately, and the energy of the transition state relative to the reactants, ΔE_{TS} , is formally divided into two parts, deformation energy (DEF) and interaction energy (INT) (eq 2). The former is the sum of the deformation energy of

$$\Delta E_{TS} = \text{DEF} + \text{INT} \quad (2)$$

O and M components, the energy required to deform them from their equilibrium geometry to those of the transition state. The latter consists of electrostatic (ES), exchange (EX), and CTPLX_(O-M) and CTPLX_(M-O), and residual (R) terms (eq 3). The CTPLX_(O-M) and CTPLX_(M-O) terms

$$\text{INT} = \text{ES} + \text{EX} + \text{CTPLX}_{(O-M)} + \text{CTPLX}_{(M-O)} + \text{R} \quad (3)$$

represent "donative orbital interaction" from O to M and M to O, respectively. The DEF and EX terms generally come out as positive (i.e., repulsive) and the ES and CTPLX terms as negative (i.e., attractive). Energies are those determined at the HF/3-21G level of theory. (b) The qualitative results of EDA is known to be relatively insensitive to the level of the basis set employed.

(28) The cleaving Me-Li bond (parameter *c*) is slightly elongated. However, this parameter is a much less reliable index than the others, since this is most susceptible to the ligand effects of methylmetal species.

Table VI. Energy Decomposition Analysis of MeLi, MeCu, and Me₂Cu⁻ Additions to ET and CP^a

reaction	ΔE_{TS}	DEF				INT				
		O	M	total (O + M)	total	ES	EX	CTPLX		R
								O→M	M→O	
MeLi + ET	11.47	14.83	9.28	24.11	-12.64	-76.65	143.53	-31.22	-61.18	12.88
MeLi + CP	4.36	12.38	3.31	15.69	-11.33	-49.51	87.00	-16.79	-36.65	4.62
MeCu + ET	39.30	22.63	17.44	40.07	-0.77	-49.65	146.05	-43.66	-52.98	-0.53
MeCu + CP	28.10	27.83	7.59	35.42	-7.32	-37.19	109.56	-34.22	-45.48	0.01
Me ₂ Cu ⁻ + CP	31.83	16.00	15.53	31.53	0.30	-50.66	119.68	-22.45	-49.35	3.08

^a $\Delta E_{TS} = \text{DEF} + \text{INT}$. See text and ref 30 for abbreviations.

Table VII. Differential EDA of MeLi and MeCu Additions to ET and CP^a

term = ΔE_{TS}	ΔE_{TS}	DEF				INT				
		O	M	total (O + M)	total	ES	EX	CTPLX		R
								O→M	M→O	
$\Delta[\text{term}]_{\text{Li}}$	-7.11	-2.45	-5.97	-8.42	1.31	27.14	-56.53	14.43	24.53	-8.26
$\Delta[\text{term}]_{\text{Cu}}$	-11.20	5.20	-9.85	-4.65	-6.55	12.46	-36.49	9.44	7.50	0.54
$\Delta\Delta[\text{term}]_{\text{Cu-Li}}$	-4.09	7.65	-3.88	3.77	-7.86	-14.68	20.04	-4.99	-17.03	8.80

^a See footnote a in Table VI.

Table VIII. Energy Decomposition Analysis of MeLi Additions to ET' and CP'^a

reaction	ΔE_{TS}	DEF				INT				
		O	M	total (O + M)	total	ES	EX	CTPLX		R
								O→M	M→O	
ET' + MeLi	12.03	22.62	9.28	31.90	-19.87	-77.04	142.09	-32.62	-65.60	13.30
CP' + MeLi	6.54	27.83	3.31	31.14	-24.61	-50.87	84.62	-18.44	-44.22	4.30

^a See footnote a in Table VI.

(EX) as compared with the corresponding ET reactions. However, the DEF term in the MeCu/CP combination is quite large (i.e., later TS). Inspection of each component in the interaction (INT) terms indicates that, in the MeLi reactions, the electrostatic (ES) terms contributes more toward lowering the TS energy (ΔE_{TS}) than the orbital terms (CTPLX), while the reverse is true for the MeCu reactions. Comparison of the CTPLX terms for the MeLi/ET and MeCu/ET reactions reveals an interesting point.³¹ In the MeLi reaction, $\text{CTPLX}_{(\text{M} \rightarrow \text{O})}$ is larger than $\text{CTPLX}_{(\text{O} \rightarrow \text{M})}$, indicating that strong donation from MeLi (namely, from methyl anion) to ET. In the MeCu reaction, on the other hand, $\text{CTPLX}_{(\text{O} \rightarrow \text{M})}$ becomes bigger while $\text{CTPLX}_{(\text{M} \rightarrow \text{O})}$ slightly decreases. The same trend was also noted in carbometalation of acetylenes.³² Apparently, the metal center of MeCu acts as a soft Lewis acid through its 4p vacant orbital.

Inspection of the INT terms for the Me₂Cu⁻/CP reaction (Table VI) indicates that the nature of this nucleophile falls between that of MeLi and MeCu. The less extensive sp²-to-sp³ rehybridization (Figure 5 and supported by the small DEF term of the olefinic moiety) also corroborates with less extensive orbital interactions.

Because of inadequate treatment of the ligand environment in the present models, further comparison of the MeLi and MeCu reactions appears fruitless. To cope with this problem, we performed differential evaluation of the EDA by setting the ET reactions as a nonstrained reference standard to evaluate the CP reactions. For this evaluation, we have considered three parameters for each terms of EDA: $\Delta[\text{term}]_{\text{Li}}$, $\Delta[\text{term}]_{\text{Cu}}$, and $\Delta\Delta[\text{term}]_{\text{Cu-Li}}$. The first parameter refers to the MeLi additions for its difference of each EDA term between the ET and the CP reactions (CP value - ET value); a negative value indicates that this term contributes toward lowering of the TS energy of the CP reaction as compared with that of the ET reaction. The second parameter refers to the similar difference in the MeCu series. In these two new set of EDA parameters, problems due to inadequate modeling of the metal environment may largely be cancelled. The last one refers to the difference between the first and the second parameters for each term (Cu - Li). The EDA was carried out

using the 3-21G basis set^{30b} and the data are summarized in Table VII.

As mentioned in the previous section, a larger negative energy for $\Delta[\Delta E_{TS}]_{\text{Cu}}$ (-11.2 kcal/mol) than for $\Delta[\Delta E_{TS}]_{\text{Li}}$ (-7.11 kcal/mol) is a manifestation of the favorable interaction between MeCu and CP. Analysis of the EDA components in Table VI elucidated a remarkable background of this favorable gain. In the MeLi series, the gain for the CP reaction comes from the DEF term (-8.42 kcal/mol; i.e., less deformation and earlier TS for CP), while in the MeCu series, it is mainly due to the INT term (-6.55 kcal/mol). The uniquely positive $\Delta[\text{DEF}]_{\text{Cu}}$ for the olefinic component (5.2 kcal/mol) indicates that the CP component is more deformed, which corroborates nicely with the structural analysis (vide supra).

The data for the $\Delta\Delta[\text{term}]_{\text{Cu-Li}}$ illustrates the above points even more clearly. Thus, the overall energy gain ($\Delta\Delta[\Delta E]_{\text{Cu-Li}}$) of -4.09 kcal/mol is derived from the gain in the INT term, of which the CTPLX terms (-4.99 and -17.03 kcal/mol) play the most important role.

The differential EDA results may be viewed in an alternative way so that one can obtain a more concrete chemical idea about the role of copper atom in the strain-driven reactions. In the region near the TS, deformation of the olefin toward the product (sp² and sp³) should generally favor orbital interaction between the olefin and the Me-metal, if the latter is indeed capable of such interaction. Thus, the balance between the energetic loss due to olefin deformation and the gain due to orbital interactions determines the balance of the TS energies, since the ES and EX interactions between the olefin and the Me-metal would be relatively independent of the exact structure of the former so far as the deformation is relatively small. The EDA along this line gave a full support to our chemical intuition.

Thus, we considered a hypothetical TS of MeLi addition to an olefin (ET and CP), wherein (only) the olefinic moiety of the TS is deformed toward the product. We have taken the geometry in the TS of the corresponding MeCu addition (indicated as ET' and CP') as such an olefin geometry. The differential EDA was carried out in the usual manner except that comparison was made for the pairs of ET/ET' and CP/CP'. The raw data for the hypothetical TSs are shown in Table VIII. The difference between the real and the hypothetical TSs for the ethylene pair

(31) This comparison is appropriate since the magnitudes of EX terms are nearly the same. For the equal EX protocol, see ref 8 and references therein.

(32) Compare Tables IV and V in ref 8.

Table IX. Differential EDA of MeLi Additions to ET and ET^a

term	DEF				INT					
	ΔE_{TS}	O	M	total	total	ES	EX	CTPLX		R
								O→M	M→O	
$\Delta[\text{term}]_{ET}$	0.56	7.79	0	7.79	-7.23	-0.39	-1.44	-1.40	-4.42	0.42
$\Delta[\text{term}]_{CP}$	2.17	15.45	0	15.45	-13.28	-1.36	-2.38	-1.65	-7.57	-0.32
$\Delta\Delta[\text{term}]_{CP-ET}$	1.61	7.56	0	7.56	-6.05	-0.97	-0.94	-0.25	-3.15	-0.74

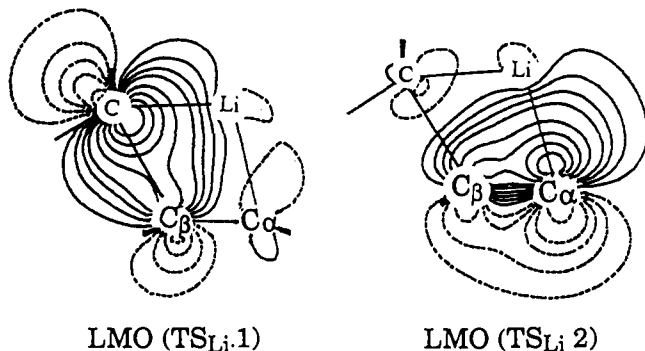
^aSee footnote a in Table VI.

Figure 8. Boys' LMOs of MeLi addition to ET (HF/3-21G).

($\Delta[\text{term}]_{ET}$) and the cyclopropene pair ($\Delta[\text{term}]_{CP}$) are shown in Table IX. As logically expected, the total TS energy of the hypothetical TSs became higher for both ET and CP. It is because the energy loss in the DEF component (e.g., 7.79 kcal/mol for ET) cannot be offset by the INT components (e.g., -7.23 kcal/mol). The small change of the ES and EX terms fully supports our intuitive expectation (vide supra). Inspection of the difference between $\Delta[\text{term}]_{ET}$ and $\Delta[\text{term}]_{CP}$ (i.e., $\Delta\Delta[\text{term}]_{CP-ET}$) indicates that there is energetic loss on going from ET to CP (e.g., 1.61 kcal/mol) in the hypothetical TS of the MeLi addition, which stands in contrast to the gain in the real case (i.e., for ET and CP; -7.11 kcal/mol in Table VI). Clearly, this is due to very small favorable contribution from the CTPLX terms (-0.25 and -3.15 kcal/mol), which cannot make up the large loss in the DEF term (7.56 kcal/mol). It is thus evident that, for MeLi, deformation of the CP component does not help increase the orbital interactions, since lithium is incapable of having strong orbital interactions with the forming sp^3 carbon center. Conversely, it is the orbital interactions that bring about stabilization of the TS in the MeCu/CP combination.

Finally, the role of the copper orbitals was examined for the MeCu addition to ET. As mentioned at the outset, the copper 3d orbitals have been considered important for the understanding of the nucleophilic reactivities of alkylcopper(I) species. The copper atom has occupied 3d orbitals, and their energies are similar to the partially breaking C-C π bonds and forming C-C σ bonds in the TS of this reaction. Consequently, in the conventional canonical (RHF) MOs, the copper d orbitals and the carbon centered orbitals undergo mixing regardless of existence of real interactions, to make the analysis of the wave function difficult. We therefore analyzed the wavefunction of the TSs of the MeCu addition with the aid of Boys' localized molecular orbitals (LMOs).³³ The merit of the LMO analysis resides in that orbitals actually involved in interaction and nonbonding orbitals can be separated, making the analysis much simpler.

For the purpose of comparison, we first calculated the LMOs of the TS of the MeLi addition to ET. In Figure 8 are shown the two important LMOs, which are responsible for the four-centered interaction; these LMO are occupied by the four electrons which take part in the bond exchange in this reaction. In LMO(TS_{Li} 1), one can see that the Me-Li σ bond interacts with the polarized π^* olefinic orbital leading to the formation of the

Scheme I. Schematic Representation of the Electron Flow in the MeLi Addition to an Olefin



Me-C _{β} σ bond (for definition of C _{α} and C _{β} , see Table I). We can find a complementary polarization in LMO(TS_{Li} 2), wherein the olefinic π orbital is polarized toward the C _{α} in such a way that the π electrons of ET interact with the Li metal. Such a picture is fully consistent with the EDA results in that the carbometalation may be roughly viewed as simultaneous addition of the methyl nucleophile and the metal electrophile in a push-pull manner.

A surprisingly similar picture was obtained for the MeCu addition. Of the two LMOs shown on the top in Figure 9, LMO(TS_{Cu} 1) represents the forming Me-C _{β} bond, and LMO(TS_{Cu} 2) represents the polarized π bond. It is especially notable that there is found little contribution of 3d orbitals in the former. Since this LMO represents the bond formation due to electron donation from the Me-Cu bond to the polarized π^* orbital, it can be concluded that the copper 3d orbitals are not responsible for the electron donation to the olefin. The in-plane copper 3d orbitals, which might well be expected to take part in the bond formation, are represented by LMO(TS_{Cu} 3) and LMO(TS_{Cu} 4), but these orbitals are seen to be entirely isolated from the bond-forming orbital interactions. This is in full agreement with the above analysis of LMO(TS_{Cu} 1). This conclusion is also supported by the LMO analysis of the MeCu itself. Thus, the LMO(MeCu) shown on the bottom right of Figure 9 is largely 4s in nature. The copper 3d orbitals being small in size, much smaller than the 4s orbital,³⁴ cannot directly take part in the bond-exchange interactions.

Conclusion

From the analyses of structure and energies, the following conclusions about the reaction course of the carbometalation of cyclopropene and, more generally, the nature of the strain-driven reactions may be drawn.

(1) The addition of a methyl nucleophile to CP is a highly exothermic reaction. However, in contrast to what has generally been felt, the ring strain is not released at the π -complex stage regardless of the nature of the metal, but released only in the transition state. (2) In consonance with the high exothermicity, the Me⁻ and MeLi additions to CP involve quite early TSs, as characterized by the four important structural parameters in Table II.³⁵ (3) Comparable analysis of these parameters (Table III) reveals a particularly asynchronous nature of the MeCu addition to CP. This asynchronousness is also evident from the extensive rehybridization of the CP olefinic carbons in the MeCu addition. This observation may provide useful insights to the mechanistic interpretation of the asymmetric induction shown in eq 1.⁶ (4) The energetic consequence of such asynchronous structural change was also evident in the activation energies and in the EDA results.

(34) The radii of maximum charge density calculated by the numerical Hartree-Fock method are 0.32 and 1.2 Å for 3d and 4s, respectively: Fraga, S.; Saxena, K. M. S.; Karwowski, J. *Handbook of Atomic Data*; Elsevier: Amsterdam, 1976.

(35) The TS of the addition of MeMgCl to CP shares essentially the same structural features with the TS of the MeLi addition and is markedly different from that of the MeCu addition. TSs for various metals other than Li and Cu will be reported in a due course.

(33) Boys, S. F. In *Quantum Theory of Atoms, Molecules, and the Solid State*; Lowdin, P. O., Ed.; Academic Press: New York, 1968.

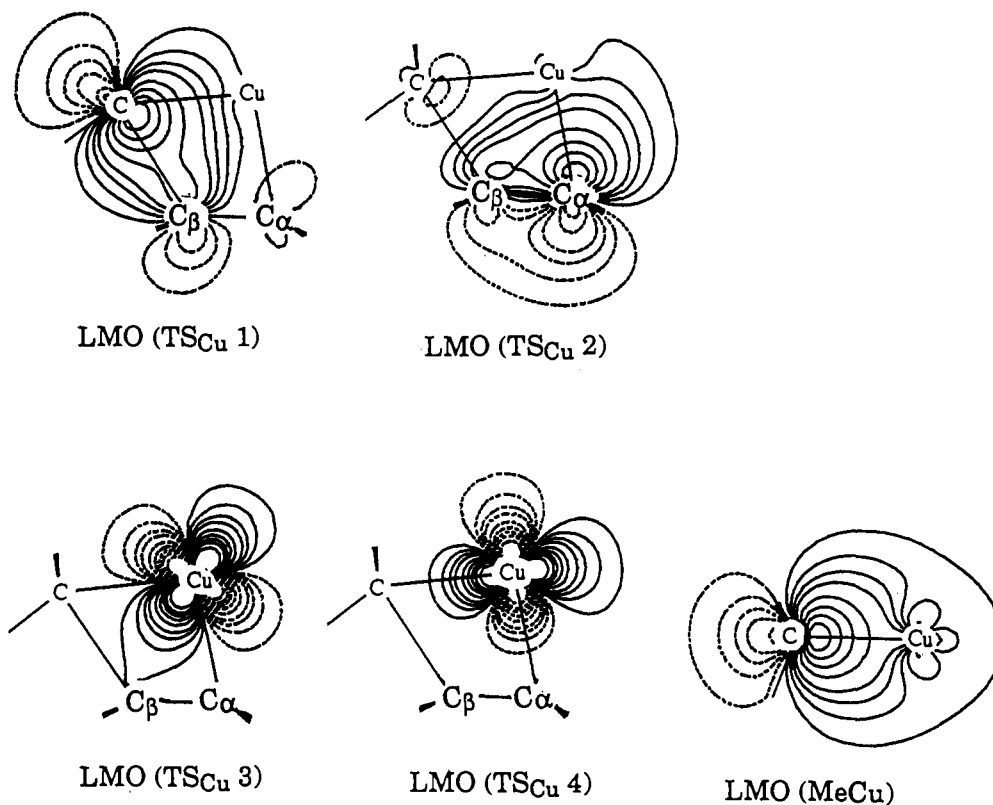


Figure 9. Boys' LMOs of MeCu and the TS of its addition to ET (HF/3-21G).

Scheme II. Schematic Representation of the Electron Flow in the MeCu Addition to an Olefin



Being very early in nature, the TSs of the Me^- and the MeLi additions experience only small strain release (of the total). On the other hand, the MeCu reaction experiences significantly more strain release, since the olefin and the copper benefit through orbital interactions involving the extensively rehybridized cyclopropyl carbon and the vacant 4p orbital. LMO analysis indicated the unimportance of the filled copper 3d orbitals for the bond exchange in the transition state of MeCu addition. The contrasting characteristics of the electron flow in the TSs of the MeLi and MeCu additions to an olefin may thus be viewed, in an extreme representation, as depicted in Schemes I and II. Structure and EDA indicate that Me_2Cu^- does not deviate too much from the framework of chemistry defined for MeLi and MeCu, presumably because the Me^- donor ligand is not directly involved in the bond exchange.

In summary, the *dynamic* effects of orbital interactions suggest that it is necessary to reformulate the conventional view of strain effects,¹ which is largely based on *static* metal/strained-bond

interactions. The results of differential EDA suggested the necessity to consider two types of effects in the strain-driven organometallic reactions. The first, which may be called "primary strain effect" is due to a simple strain effect which drives a molecule to deform to a more stable structure. It is the force that is ubiquitous in any strain-driven reactions independent of the nature of the metal. The MeCu/CP combination illustrates a "secondary strain effect", which is dependent on the nature of the metal component involved in the reaction. Thus, in the copper case, the (soft) metal further assists deformation by its favorable orbital interactions with the rehybridized carbon center. Qualitatively speaking, the copper atom acts as a soft Lewis acid to assist the electron flow from the methyl anion to the olefin. This is the most intriguing strain effect which may be highly dependent on the nature of the metal component involved in the reaction.

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Supplementary Material Available: Tables of optimized geometries (Z-matrices) and energies of the TSs (4 pages). Ordering information is given on any current masthead page.