Organometallics **2007,** *26,* 609−616

Reactions of Cyclopropenes with Organoaluminum Compounds and Other Organometallic Compounds: Formation of Ring-Opened Products

Mark A. Smith and Herman G. Richey, Jr.*

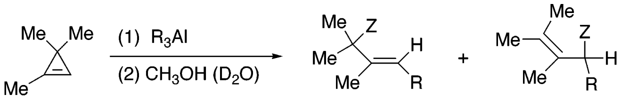
Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received August 23, 2006

Reactions of 1-ethylspiro[2.5]oct-1-ene and triethylaluminum furnish a product that results from addition of triethylaluminum to the double bond with opening of the three-membered ring to form an allylic organoaluminum compound and a second product that results from addition of this allylic organoaluminum compound to the cyclopropene double bond. Reactions of spiro[2.5]oct-1-ene with triethylaluminum furnish two products resulting from addition to the cyclopropene double bond, one of triethylaluminum and the other of an allylic organoaluminum compound formed by addition of triethylaluminum to the cyclopropene double bond with opening of the three-membered ring. Reactions of the spiro compounds with triethylboron, triethylgallium, diethylzinc, or diethylcadmium also furnish rearrangement products, but reactions with diethylmagnesium or ethyllithium furnish only addition products.

Introduction

Addition of 1,3,3-trimethylcyclopropene (**1**) to a hexane solution of *i*-Bu_3Al followed by quenching with methanol was found to produce **2a** and **3a**.[1] These products contain the elements of one **1** and one isobutane as expected for addition of *i*-Bu_3Al to **1**, but their formation involved a rearrangement. Hydrolysis with D_2O furnished **2b** and **3b**, indicating that allylic organoaluminum compounds were precursors of the products. Yields of these products were low, and additional products were formed that contained the elements of one isobutane and two **1**'s or that had even higher molecular weights. A related observation was formation of 2-methyl-2-(2,2-dimethylcyclopropyl)-*trans*-hex-3-ene from a reaction of 3,3-dimethylcyclopropene and Et_3Al.[2]



1

R = isobutyl

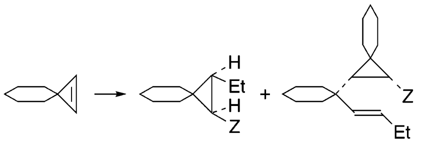
2a Z = H
2b Z = D

3a Z = H
3b Z = D

In this paper, we revisit this rearrangement, which provides information relevant to how organometallic compounds react with alkenes. Objectives were to more thoroughly investigate reactions of cyclopropenes and organoaluminum compounds and to determine whether reactions of cyclopropenes and organometallic compounds of other metals lead to similar rearrangements.

Results

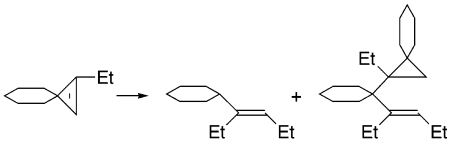
Reactions with Et_3Al. As cyclopropene substrates we chose **4** and **7**, which are less volatile than **1**, facilitating separation of the cyclopropenes and products of their reactions from routine solvents, such as hexane and diethyl ether. GC analysis of the products that resulted from adding a hexane solution of **4** to a hexane solution of Et_3Al followed by quenching with methanol showed only two significant peaks. ^{1}H NMR spectra indicated that the compounds responsible for these peaks are **5a** and **6a**. A trans stereochemistry for the double bond of **6a** was indicated by the vicinal coupling constant of 16.1 Hz between its two hydrogens.[3] ^{1}H NMR and mass spectra showed that the products were **5b** and **6b** when quenching was with D_2O. The values of the vicinal coupling constants between the two cyclopropyl hydrogens of the monodeuterated compounds (8.3 Hz for **5b**, 9.0 Hz for **6b**) indicate them to have a cis relationship.[4] GC analysis of similar reactions of **7** also showed just two significant products, and ^{1}H NMR spectra indicated their structures[5] to be **8** and **9**. Addition of Et_3Al to a solution containing equal amounts of **4** and **7** produced the products formed with **4** and with **7** alone, but the major product was **10**.[5] Addition of a



4

5a Z = H
5b Z = D

6a Z = H
6b Z = D



7

8

9

---

* To whom correspondence should be addressed. E-mail: hgr@chem.psu.edu.

(1) Richey, H. G., Jr.; Kubala, B.; Smith, M. A. *Tetrahedron Lett.* **1981**, *22*, 3471.

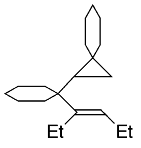
(2) Binger, P.; Schäfer, H. *Tetrahedron Lett.* **1975**, 4673.

(3) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon: Oxford, 1969; Chapter 4-2.

(4) Wiberg, K. B.; Barth, D. E.; Schertler, P. H. *J. Org. Chem.* **l973**, *38*, 378.

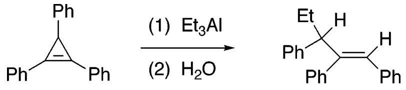
(5) The stereochemistry of the alkene function of **8**, **9**, **10**, **12**, or **21** is not known with certainty.

10.1021/om060766t CCC: $37.00



10

benzene−hexane (ca. 5:1 v/v) solution of Et_3Al to **11** produced **12** (87%).[5] Product **5** could result from routine syn addition[6−8] of Et_3Al to the cyclopropene, but formation of the other products involves rearrangements.



11 **12**

Results of some reactions of Et_3Al and **4** having different combinations of reactant ratio, temperature, and time are summarized in Table 1.[9] Reactions were rapid; some **4** was recovered only from reactions (entries 1 and 2) for 1 h at ≤−60 °C. The product composition from reactions at −30 °C (entries 3−6) was not greatly dependent on reaction time or reactant ratio. The yield of **6** did decrease over a long reaction period at 25 °C (entries 8−10), probably due to formation of higher molecular weight materials. The ratio of products depended only modestly on temperature (entries 4, 7, and 8). Results of some reactions of Et_3Al and **7** are summarized in Table 2.[9] These reactions also were rapid; **7** was recovered only from a reaction with insufficient Et_3Al. The **9**:**8** ratio decreased modestly with increasing temperature (entries 1, 4, 6, and 7), but was more sensitive to the Et_3Al:**7** ratio (entries 2, 4, and 5): an increase in this ratio from 0.3 to 3.0 led to a decrease in the **9**:**8** ratio from 2.2 to 0.4.[10] Reactions with **11** were much slower.[11]

Table 1. Compositions[a] of Products from Reactions of Et_3Al and 4 in Hexane

				yield, %		
entry	temp, °C	time, h	$[Et_3Al]_o/[\mathbf{4}]_o$[b]	**4**	**5**	**6**
1	−85	1.0	1	91	6	2
2	−60	1.0	1	22	24	47
3	−30	1.0	0.3[c]	0	22	57
4	−30	1.5	1.0	0	21	53
5	−30	1.5	3.0	0	15	51
6	−30	74	100[d]	0	15	58
7	0	1.5	1	0	33	71
8	25	1.5	1	0	21	84
9	25	3.0	1	0	23	79
10	25	45	1	0	24	1
11	−30[e]	1.5	1	0	26	71
12	25[e]	0.5	1	0	25	71

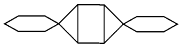
[a] Yields indicate the percentage of **4** that is incorporated into each product. [b] $[\mathbf{4}]_o$ = ca. 0.20 M except where otherwise noted. [c] $[\mathbf{4}]_o$ = 0.10 M. [d] $[\mathbf{4}]_o$ = 0.0088 M. [e] The aliquot that was analyzed after 1.5 h at −30 °C was allowed to warm to 25 °C and then after 0.5 h was reanalyzed.

Table 2. Compositions[a] of Products from Reactions of Et_3Al and 7 in Hexane

				yield, %		
entry	temp, °C	time, h	$[Et_3Al]_o/[\mathbf{7}]_o$[b]	**7**	**8**	**9**
1	−60	1.0	1.0	0	40	56
2	−35	1.5	0.3[c]	39	14	31
3	−35	13	0.3[c]	0	20	62
4	−35	1.5	1.0	0	42	54
5	−35	1.5	3.0[d]	0	56	22
6	0	1.5	1.0	0	50	35
7	25	1.5	1.0	0	58	30

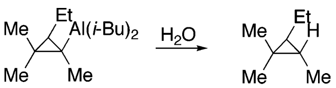
[a] Yields indicate the percentage of **7** that is incorporated into each product. [b] $[\mathbf{7}]_o$ = ca. 0.20 M except where otherwise noted. [c] $[\mathbf{7}]_o$ = 0.25 M. [d] $[\mathbf{7}]_o$ = 0.13 M.

Reactions of **4** with Et_3Al were much slower in hexane−diethyl ether (5:1 v/v) than in hexane. Significant amounts of products were not formed, for example, in a reaction (Et_3Al and **4** both ca. 0.4 M) at 25 °C, even after 2 h, conditions that led to complete reaction with comparable hexane solutions. After 44 h, however, small amounts of **5** (3%) and **6** (1%) were present along with a larger amount (28%) of a product identified as **13**.[12] A sample of **13** was prepared by adding $BF_3(Et_2O)$ to **4**, a procedure that has been used[2,13] to dimerize cyclopropenes.



13

Tetraalkylcyclopropylaluminum compound **14** was prepared to determine if a sterically hindered cycloprpopylaluminum compound might undergo ring-opening; hydrolysis after 10 min at ambient temperature furnished only **15**.[14]



14 **15**

Reactions with Other Organometallic Compounds. Some of the results of an exploratory study of reactions of **4** and **7** with ethyl compounds of other metals are summarized in Table 3. Reactions with compounds of other group 15 metals also produced rearrangement products. Et_3B and **4** rapidly produced **5** and **6**, as had reactions with Et_3Al.[15] Et_3Ga and **4** produced only rearrangement product **6**; addition product **5** was not found. Et_3Ga and **7** formed only **9**. Recovery of **4** and **7** when

---

(6) The following review many aspects of properties, preparations, and reactions of organoaluminum compounds. Mole, T.; Jeffery, E. A. *Organoaluminum Compounds*; Elsevier: Amsterdam, 1972. Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. A., Eds.; Pergamon: Oxford, l982; Vol. 1, Chapter 6. Eisch, J. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. A., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, l995; Vol. 1, Chapter 10.

(7) A review of carboalumination and other reactions of organoaluminum compounds with organic substrates: Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Abel, E. A., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, l995; Vol. 11, Chapter 6. A review of carbometalation by organoaluminum, organoboron, organomagnesium, organozinc, organocopper, and organolithium compounds: Knochel, P. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, l991; Vol. 4, Chapter 4.4.

(8) A review of current developments in cyclopropene chemistry including carbometalation and a source of references to other reviews: Rubin, M.; Rubina, M.; Gevorgyan, V. *Synthesis* **2006**, 1221.

(9) Material balances were generally good, although small amounts of higher molecular weight products were sometimes noted in GC traces.

(10) Yields of products from reactions in which the initial ratio of Et_3Al to **4** or **7** was 0.3 indicate that more than one ethyl group of Et_3Al became incorporated into the products.

(11) For example, no significant amount of product was observed from a reaction for 1 h at 0 °C (each reactant 0.15 M in benzene−hexane (5:1, v/v)); in a similar reaction at ambient temperature, product was still forming after 3 days.

(12) Neither **4** nor **13** contained excess deuterium when a reaction was quenched with D_2O.

(13) Nefedov, O. M.; Dolgii, I. E.; Bulusheva, E. V.; Shteinshneider, A. Ya. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **l979**, 1422. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1979**, 1535.

(14) The stereochemistry of **14** or **15** is not known with certainty.

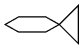
(15) Because of the difference in solvent, the rates of reactions with Et_3B and Et_3Al are not strictly comparable.

Table 3. Compositions of Products from Reactions of Ethyl Organometallic Compounds with 4 and 7

entry	reactants[a]	conditions[b,c]	**4**	**5**	**6**	**7**	**8**	**9**	**13**	**17**
1	**4**, Et_3B	A, 1.5 h, −50 °C		29	56					
2	**4**, Et_3Ga	B, 1 h			96					
3	**4**, Et_3Ga	B, 1 h, 0 °C	17		79					
4	**7**, Et_3Ga	B, 1 h, 0 °C						100		
5	**7**, Et_3Ga	B, 1.5 h, −60 °C	90					7		
6	**4**, Et_2Mg	C, 19 h	29	25						
7	**4**, Et_2Mg	D, 19 h	64	24					4	
8	**7**, Et_2Mg	E, 19 h				63				21
9	**4**, Et_2Zn	B, 10 h	16	46	22				11	
10	**4**, Et_2Zn	B, 44 h, −25 °C	87	12	1				2	
11	**4**, Et_2Zn	C, 20 h		26	14				48	
12	**7**, Et_2Zn	B, 46 h				44	5	27		
13	**7**, Et_2Zn	B, 4 h				85	15			
14[d]	**4**, Et_2Cd[e]	C, 70 h	12	41	7				17	
15	**7**, Et_2Cd[e]	C, 70 h				85	8	2		3
16	**4**, Et_2Hg	B, 96 h	96							
17	**4**, EtLi	F, 1 h, 0 °C	89	6						
18	**7**, EtLi	G, 1 h, 0 °C				83				3
19	**4**, Et_4Sn	A, 96 h, 70 °C	98							

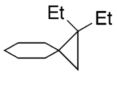
[a] Reactants used in approximately equimolar amounts or with a slight (ca. 10%) excess of the organometallic reactants. [b] The following solvents or solvent combinations were used: A, THF−hexane (1:5); B, hexane; C, Et_2O−hexane (1:5); D, THF−hexane (1:5); E, Et_2O−hexane (1:3); F, benzene−hexane (1:4); G, benzene−hexane (1:3); Et_2O−benzene−hexane (1:3:3). [c] Where temperature is not noted, it was ambient laboratory temperature, ca. 23 °C. [d] An additional compound identified as an isomer of **6** also was present. [e] The Et_2Cd contained a trace of Et_2O.

conditions were used that led to their disappearance in reactions with Et_3Al indicates that reactions with Et_3Ga are slower than with Et_3Al. Reactions of **4** with (2,3-dimethyl-2-butyl)BH_2 or (3-methyl-2-butyl)$_2$BH in THF−hexane produced only **16**.

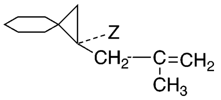


16

Reactions of group 12 compounds Et_2Zn and Et_2Cd with **4** and **7** produced both addition and rearrangement products (**17** is the addition product formed from **7**), although reactions of (methallyl)$_2$Zn in hexane produced only unrearranged addition products, **18a** (81%) and **18b** (98%). Group 2 compound Et_2Mg and **4** or **7**, however, furnished only addition products. Results of reactions with solutions containing both **4** and **7** confirmed that reactions of Et_2Mg, Et_2Zn, Et_2Cd, and (methallyl)$_2$Zn were faster with **4** than with **7**. Group 1 compound EtLi and **4** or **7** slowly produced addition products; failure of more addition to occur was not due to competing metalation of the cyclopropene since only 12% of the **7** recovered from a reaction (similar to that in Table 3, entry 18) that was quenched with D_2O had excess deuterium.

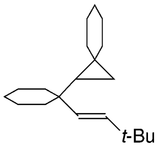


17

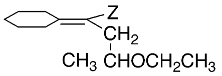


18a Z = H
18b Z = Et

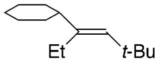
Reactions of *t*-Bu_2Zn and *t*-Bu_2Mg differed in part from those of their ethyl counterparts. A reaction (hexane−diethyl ether, 1:1 v/v; 52 h, 23 °C) of *t*-Bu_2Zn and **4** led to **19** (60%) and **20a** (19%). A similar reaction (19 h) of **7** led to **20b** (8%), **21** (36%), and **22** (45%).[5] Most of the **7** was recovered from reactions with *t*-Bu_2Mg (diethyl ether−hexane, 1:1 v/v) at 23 °C for as long as 115 h; the recovered **7** did not contain excess deuterium when quenching was with D_2O. A reaction (diethyl ether, 60 °C, 66 h) with much less hindered **23**, however, besides addition product **24** (15%) also produced **25** (17%).[16,17]



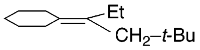
19



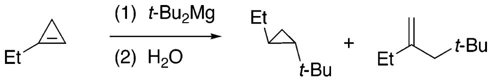
20a Z = H
20b Z = Et



21



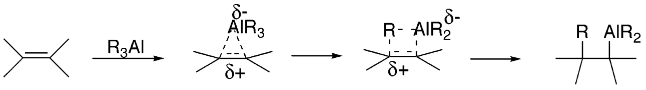
22



23 **24** **25**

Discussion

Reactions with Et_3Al. Addition of an organoaluminum compound to an alkene is thought to occur by electrophilic attack to form a π complex (**26**), which rearranges via a four-centered transition state (**27**) to the addition product. This mechanism,[18] due to Eisch, was based particularly on effects of structure on rates of additions to alkenes and alkynes and is supported by spectral evidence[19] for π-complex formation between alkenes and alkylaluminum functions.[20]



26 **27**

A *formal* sequence of steps that would lead to the products of the Et_3Al−**4** reactions is illustrated in Scheme 1. For ease of depiction, a structure of the type of **27** is replaced by **28**, which has full charges rather than the partial charges that actually must be present and which does not show the partial bond from an ethyl group to a cyclopropyl carbon. Attachment of an ethyl group to carbon would lead to **29**, which would produce **5** on quenching. A critical feature is that the amount of positive charge on carbon, although certainly less than the full charge shown in **28**, is sufficient to trigger the electrocylic ring-opening characteristic[21] of cyclopropyl cations to generate **30**; ethyl migration then would produce **31**, which would be in equilib-

---

(16) It was not determined if any **23** remained since its GC retention time was close to that of the solvent.

(17) Reactions of **23** and Et_3Al, even at −100 °C, produced mainly polymeric products.

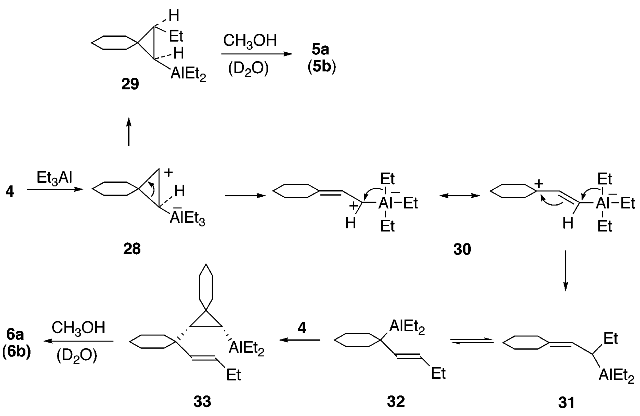
(18) A review: Eisch, J. J. *J. Organomet. Chem.* **1995**, *500*, 101.

(19) Hata, G. *Chem. Commun.* **1968**, *7*. Dolzine, T. W.; Oliver, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 1737. Dolzine, T. W.; Oliver, J. P. *J. Organomet. Chem.* **1974**, *78*, 165.

(20) For MO calculations about carboalumination of alkenes, see the following and references therein: Bundens, J. W.; Yudenfreund, J.; Francl, M. M. *Organometallics* **l999**, *18*, 3913.

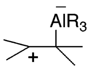
(21) Sankararaman, S. *Pericyclic Reactions−A Textbook*; Wiley-VCH: Weinheim, 2005; pp 32−37. Sorenson, T. S.; Rauk, A. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic: New York, l977; Vol. *2*, pp 3−19.

Scheme 1



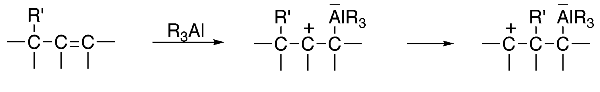
rium with its allylic isomer, **32**. Addition of **31**−**32** to **4** would generate **33**, which would produce **6** on quenching; this addition is rapid since quenching does not provide products of protonation of **31**−**32**. Of course **4** → **28**, **28** → **30**, and **30** → **31** *must be significantly concerted* rather than discrete steps.

In reactions of **7**, an unrearranged addition product (a homologue of **5**) was not formed. Besides **9** (a homologue of **6**), however, product **8** was obtained that resulted from protonation of homologues of **31** and **32**. The effect of the ethyl group of **7** on product structure and composition is consistent with the proposed mechanism. Since alkyl groups stabilize positive carbon, more of the developing positive charge must be at the alkene carbon bearing the ethyl group; as a result, subsequent ring-opening leads to the ethyl that migrates from aluminum, becoming attached to the unsubstituted alkene carbon, consistent with the placement of ethyl groups in **8** and **9**. Moreover, by enhancing the character depicted in **34** relative to that depicted in **27**, an ethyl group would increase the amount of rearrangement relative to addition without rearrangement. A steric effect of the ethyl group might also make a transition state for addition (**27**) more difficult to achieve.



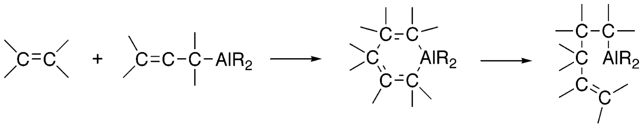
34

We suggest three reasons why rearrangements are observed in reactions of organoaluminum compounds with cyclopropenes but not with other alkenes. (1) Electrocyclic rearrangement of a cyclopropyl cation to an allylic cation may be inherently more facile than the usual Wagner−Meerwein rearrangements of carbocations, which require transfer of an organic group from one carbon to another. (2) The electrocyclic rearrangement does not *increase* separation of positive and negative charge as does Wagner−Meerwein rearrangement (**35** → **36**) of a cation formed by attack of a *neutral* electrophile. (3) For addition to occur, transfer of R from Al to C must to some degree be concerted with the attack by R_3Al; this seems feasible in a reaction with a cyclopropene, but difficult if a Wagner−Meerwein rearrangement (e.g., **35** → **36**) is shifting the positive charge from a β-carbon to a γ-carbon.



35 **36**

The products (**6**, **9**, and **10**) of addition of allylic organoaluminum compounds result from formation of the new C−C bond at the more substituted allylic carbon, as generally found for reactions[6,7,22] of unsymmetrical allylic organoaluminum compounds with electrophiles. Reactions of allylic organoaluminum compounds and alkenes are usually considered to proceed by six-centered transition states (**37**), a proposal consistent with formation of the new C−C bond at the more substituted allylic carbon (as in **6**, **9**, and **10**) even though aluminum resides predominantly at the less substituted allylic carbon and also consistent with additions to cyclopropenes occurring without ring-opening.



37

Reaction of **4** with **31**−**32** must be faster than with Et_3Al since more product results from addition of **31**−**32** than of the much larger amount of Et_3Al. Similarly, substantial amounts of the allylic organoaluminum compounds formed in reactions of Et_3Al with **7** react with **7** in competition with reaction with Et_3Al. Could the allylic organoaluminum compounds result from rearrangements of cyclopropylaluminum compounds (e.g., **29**) that were initial products rather than during the addition process? Cyclopropylaluminum compounds are not known to isomerize to their more stable allylic isomers, but it is conceivable that extensive alkylation might (e.g., due to steric crowding) accelerate ring-opening. That tetraalkylcyclopropylaluminum compound **14** did not open and that yields of **5**, a product of protonation of a trialkylcyclopropylaluminum compound, were similar from reactions having different times indicate that ring-opening was not significant.[23] Rearrangement to allylic compounds must occur *during* rather than after addition.

Formation of **10** as the major product from reactions with mixtures of **4** and **7** indicates that addition of Et_3Al is significantly faster to **7** than to **4**, but also that subsequent addition of the allylic species formed from **7** may be faster to **4** than to **7**. In reactions of **4** alone, addition of allylic species **31**−**32** is more rapid than addition of Et_3Al, since increased Et_3Al/**4** reactant ratios did not greatly enhance yields of **5**. In reactions of **7**, however, an increase in the Et_3Al/**7** ratio led to a significant decrease in the **9**/**8** ratio. A molecule of **7** can react either with Et_3Al, forming allylic isomers similar to **31**−**32**, or with the allylic isomers, forming a product similar to **33**. The rates are such that both reactions ordinarily are significant, but reaction with Et_3Al increases significantly with increasing Et_3Al concentration.[24]

Reactions of Et_3Al with **4** are slower when the solvent is diethyl ether rather than hexane, in accord with observations

---

[22] Attachment at the more substituted carbon is also often observed for allylic compounds of other metals, e.g., zinc: Nakamura, M; Inoue, T.; Sato, A.; Nakamura, E. *Org. Lett.* **2000**, *2*, 2193, and references therein.

[23] If the products from **7** resulted from ring-opening of a cyclopropylaluminum compound, they should have different structures than are observed: addition to **7** should place[6,7] aluminum at the less-substituted alkene carbon and isomerization then would lead to a different placement of ethyl groups in the product than is observed.

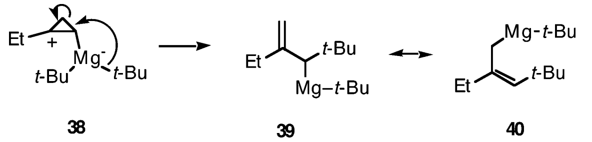
[24] Could addition of the allylic organoaluminum compound be so extremely rapid that addition products result from reactions of the first-formed allylic isomer rather than from an equilibrium mixture of the allylic isomers? That cannot be the case in the reactions of **4** since the results indicate that addition of an allylic species is similar in rate to addition of Et_3Al, which is not extremely fast since some **4** is recovered from reactions at low temperatures.

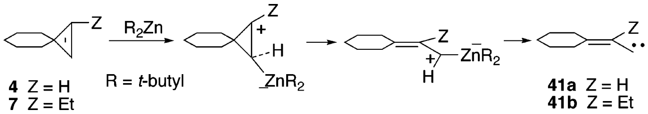
that other reactions[6,7] of organoaluminum compounds are slower in ethers than in hydrocarbons. The concentration of free Et_3Al, the reactive species, must be less in diethyl ether solutions, in which $Et_3Al(OEt_2)$ is the dominant species, than in hydrocarbon solutions, in which Et_3Al dimer is the major species. Formation of some **13** was observed when the solvent was diethyl ether. Similar dimerizations of other cyclopropenes by Et_3Al in diethyl ether and also by BF_3, $AlCl_3$, or Et_3B in that solvent have been reported.[2,13]

Reactions with Other Organometallic Compounds. Reactions of cyclopropenes and ethyl compounds of boron, gallium, zinc, and cadmium all led to at least some rearrangement.[25] We propose that attack of these organometallic compounds also develops sufficient positive charge on an alkene carbon to trigger an electrocyclic rearrangement. By contrast, only unrearranged addition products were obtained with the ethyl compounds of lithium and magnesium.[26]

Lewis acid strength of the metal may be one factor determining product composition. Metals (Li and Mg) in the ethyl compounds that gave only addition products are less electronegative than those in the ethyl compounds that gave rearrangement products. Decreased electronegativity would be associated with reduced Lewis acidity of the metal and increased anionic character of the alkyl group, both favoring nucleophilic attack by the alkyl group over electrophilic attack by the metal. Even if attack by Et_2Mg or EtLi has initially a strong electrophilic component, transfer of R must occur before sufficient positive charge to trigger a rearrangement develops. In contrast to the rearrangement products formed in reactions of **4** with Et_3B, reactions with R_2BH compounds produced only unrearranged hydroboration products,[28] indicating that formation of positive charge on a double-bond carbon never becomes sufficient to trigger rearrangement.[29]

Increased steric hindrance could favor rearrangement over addition by making a four-centered transition state necessary for addition without rearrangement more difficult to achieve. Several observations suggest that steric factors are significant. (1) The steric effect of the ethyl group of **7** may be a factor contributing to why reactions of Et_3Al and **7** produced no product of addition without rearrangement (corresponding to **5** obtained from reactions with **4**). (2) Although t-Bu_2Mg did not react with **7**,[30] it did react with much less hindered **23**. Product **24** resulted from a syn addition; attachment of the *tert*-butyl group was to the *less substituted* carbon of **23**, which is the reverse of the usual orientation of additions of polar organometallic compounds to alkenes but an orientation that has been observed for additions to other alkenes of hindered organometallics, including a *tert*-butyl Grignard reagent.[31] The other product of this reaction, **25**, could result from electrophilc attack and rearrangement (**38** → **39** → **40**) as proposed for reactions with Et_3Al. (3) Reactions of t-Bu_2Zn and **4** did not produce an addition product corresponding to **5**, one of the products obtained with Et_2Zn. Products **19** and **21** are *tert*-butyl counterparts of **6** and **8** (**22** is an allylic isomer of **21**).[32] The additional products, **20a** and **20b**, may have resulted from reactions with the diethyl ether solvent of carbenes[33] **41a** and **41b**, formed as shown.[34] Steric demands of a transition state for addition of the bulky *tert*-butyl group may permit competing elimination of t-Bu_2Zn to form a carbene to become a significant pathway.[35]





Experimental Section

NMR spectra were recorded at 200−MHz except where noted. Absorption positions are reported relative to internal Me_4Si (or to a standard calibrated against Me_4Si) and using the following notations: s, singlet; d, doublet; t, triplet; q, quartet; m, a more complex multiplet; c, complex overlapping absorptions. Mass spectra were obtained by electron impact (70 eV). The m/z values (and relative intensities) are listed of the molecular ion, M^+, and of any other ions with intensities $\geq$ 10% of the base peak. Low-temperature reactions were done in a liquid cooler that maintained temperature to ±1 °C. A vacuum-jacketed spinning band column with a Teflon band was used for some distillations. Elemental analyses were performed by Midwest Microlab, Ltd. Melting points were taken in capillary tubes and are uncorrected. Nitrogen was purified by passing through columns of manganese oxide oxygen scavenger and molecular sieves (4 Å). The solvents used for reactions of cyclopropenes with organometallic compounds were refluxed over sodium (diethyl ether, THF, hexane) or CaH_2 (benzene) and then distilled.

---

(25) In this work, allylic organometallic compounds always added to cyclopropenes without ring-opening. Some reactions of cyclopropenes with allylboranes, however, are reported to produce acyclic addition products that could have formed by a mechanism similar to that proposed for formation of the products of reactions with Et_3Al. Bubnov, Yu. N.; Nesmeyanova, O. A.; Rudashevskaya, T. Yu.; Mikhailov, B. M.; Kazansky, B. A. *Tetrahedron Lett.* **1971**, 2153. Mikhailov, B. M.; Bubnov, Yu. N.; Nesmeyanova, O. A.; Kieselev, V. G.; Rudashevskaya, T. Yu.; Kazansky, B. A. *Tetrahedron Lett.* **1972**, 4627. Bubnov, Yu. N.; Nesmeyanova, O. A.; Rudashevskaya, T. Yu.; Mikhailov, B. M.; Kazanskii, B. A. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1973**, *43*, 125; *Zh. Obshch. Khim.* **1973**, *43*, 127. Bubnov, Yu. N.; Nesmeyanova, O. A.; Rudashevskaya, T. Yu.; Mikhailov, B. M.; Kazanskii, B. A. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1973**, *43*, 132; *Zh. Obshch. Khim.* **1973**, *43*, 135. Bubnov, Yu. N.; Kazanskii, B. A.; Nesmeyanova, O. A.; Rudashevskaya, T. Yu.; Mikhailov, B. M. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **l979**, 2358; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 2538.

(26) Addition of organomagnesium compounds to cyclopropenes without rearrangement is well known. Ref 27 and Richey, H. G., Jr. In *Inorganic Reactions and Methods;* Hagen, A. P., Ed.; VCH: New York, 1989; Vol. 10, Section 5.4.2.5.1.

(27) Watkins, E. K.; Richey, H. G., Jr. *Organometallics* **1992**, *11*, 3785.

(28) Reactions of diborane and cyclopropenes have been observed to give addition (but no rearrangement) products: Köster, R.; Arora, S.; Binger, P. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 205. Zimmerman, H. E.; Nuss, J. M.; Tantillo, A. W. *J. Org. Chem.* **1988**, *53*, 3792.

(29) For MO calculations about hydroboration see: Wang, X.; Li, Y.; Wu, Y.-D.; Paddon-Row, M. N.; Rondan, N. G.; Houk, K. N. *J. Org. Chem.* **1990**, *55*, 2601, and references therein.

(30) t-Bu_2Mg in THF did add to spiro[2.4]hept-1-ene.[27]

(31) For example: Lehmkuhl, H.; Olbrysch, O.; Reinehr, D.; Schomburg, G.; Henneberg, D. *Liebigs Ann. Chem.* **1975**, 145. Also see: Lehmkuhl, H.; Bergstein, W.; Henneberg, D.; Janssen, E.; Olbrysch, O.; Reinehr, D.; Schomburg, G. *Liebigs Ann. Chem.* **1975**, 1176.

(32) A product corresponding to **9** was not observed, indicating that the allylic precursors of **21** and **22** did not add to the more hindered alkene function of **7**.

(33) For carbene insertion into C−H bonds see: Smith, M. B.; March, J. *March's Advanced Organic Chemistry*, 5th ed.; Wiley: New York, 2001; pp 251 and 788−791.

(34) Insertion exclusively at the methylene of diethyl ether rather than also at the methyl indicates considerable selectivity by the carbene.

(35) Greater steric demands may be another factor contributing to more rearrangement in reactions with trivalent compounds (B, Al, Ga) than with divalent compounds (Mg, Zn, Cd).

Representative Reactions of Cyclopropenes and Organometallic Compounds. Some reactions were carried out in three-necked flasks containing a magnetic stirring bar and fitted with a pressure-equalizing addition funnel, a nitrogen gas inlet, and a rubber septum. Glassware was stored at 120 °C prior to use and assembled while hot under a stream of dry nitrogen. Gastight syringes were used to transfer anhydrous solvents and solutions of organometallic compounds. The cyclopropene solution was added dropwise from the addition funnel. For competition reactions, the order of addition was reversed. A positive pressure of nitrogen was maintained throughout the course of a reaction. Some small-scale reactions were carried out in a similar fashion but using glass vials containing a magnetic stirring bar and capped by a rubber septum through which two needles were inserted. The vial was flushed by nitrogen entering through one needle and exiting through the other. Solutions were added to the vial by syringe, and reactions were carried out under a static nitrogen atmosphere. Organoaluminum reactions were quenched by adding methanol followed by water; other reactions were quenched with just water. The quenched reaction was filtered if solids were present, the layers were separated, and the organic phase was dried (K_2CO_3). Products were isolated by "preparative" GC and product compositions determined by analytical GC. Yields are reported on the basis of the amount of the cyclopropene reactant incorporated into each product. Any significant deviations from these procedures are noted in descriptions of particular reactions.

Et$_3$Al and 4. A hexane solution of **4** (4.20 mL, 0.355 M, 1.41 mmol) was added to a hexane solution of Et_3Al (1.70 mL, 0.81 M, 1.38 mmol) at −30 °C. After 1.5 h, the reaction was worked up. GC analysis showed the presence of two products. The first was identified as **5a** (21%). ^1H NMR (CCl_4): δ 0.25 (m, 1 H of cyclopropane ring). 0.19−0.33 (c, 2 H's of cyclopropane ring), 0.89 (t, $J = 7.2$ Hz, CH_3), 1.00−1.34 (c, (CH_2CH_3 and 2 $(CH_2)_5$). EIMS: m/z (rel intensity) 139 (5), 138 (41), 109 (100), 96 (47), 95 (24), 82 (48), 81 (79). EIHRMS: m/z 138.1403 (M^+ calcd for $C_{10}H_{18}$ 138.1408). The second was identified as **6a**. ^1H NMR (CCl_4): δ 0.16 (c, CH_2 of cyclopropane ring), 0.37 (d of d, $J = 6.3$ and 9.0 Hz, CH of cyclopropane ring), 0.89 (t, $J = 7.3$ Hz, CH_3), 1.19−1.63 (c, $(CH_2)_5$), 1.93 (d of q, $J = 6.4$ and 7.3 Hz, CH_2CH_3), 5.00−5.24 (c, CH═CH). EIMS: m/z (rel intensity) 246 (1), 151 (13), 150 (100), 135 (15), 121 (46), 108 (12), 107 (26), 95 (29), 94 (24), 93 (18), 91 (12), 83 (13), 81 (34), 79 (28), 69 (14). EIHRMS: m/z 246.2333 (M^+ calcd for $C_{18}H_{30}$ 246.2347).

A similar reaction was quenched with D_2O (2 mL) and samples were again collected. The first product was identified as **5b**. ^1H NMR ($CDCl_3$): δ 0.28 (d, $J = 8.3$ Hz, CHD of cyclopropane ring), 0.35−0.46 (c, CHEt), 0.97 (t, $J = 7.2$ Hz, CH_3), 1.1−1.6 (c, $(CH_2)_5$ and CH_2CH_3). The second product was identified as **6b**. ^1H NMR ($CDCl_3$): δ 0.17 (d, $J = 9.0$ Hz, CHD of cyclopropane ring), 0.45 (d, $J = 9.0$ Hz, CH), 0.97 (t, $J = 7.4$ Hz, CH_3), 1.27−1.73 (c, 2 $(CH_2)_5$), 1.96−2.10 (c, CH_2CH_3), 5.11 (d, $J = 16.1$ Hz, CH═CHCH$_2$), 5.22−5.36 (c, ═CHCH$_2$). EIMS: m/z (rel intensity) 248 (0.19), 247 (0.89), 164 (14), 151 (15), 150 (100), 121 (27), 107 (17), 95 (18), 94 (18), 82 (11), 81 (23), 79 (14), 69 (11), 68 (18), 67 (18).

Other reactions used hexane−diethyl ether solvent mixtures. Diethyl ether (1.00 mL) was added to a stirred hexane solution of Et_3Al (1.00 mL, 0.81 M, 0.81 mmol) at ambient temperature. After 10 min a hexane solution of **4** (4.0 mL, 0.170 M, 0.68 mmol) was added. GC analysis of a quenched aliquot removed after 2.5 h showed no significant amount of any product. GC analysis of an aliquot quenched after 44 h showed it to contain **4** (35%), **5** (3%), **6** (1%), and **13** (28%). GC/MS analysis of a similar aliquot that had been quenched by addition of D_2O showed no excess D in either **13** or recovered **1**.

Et$_3$Al and 7. A hexane solution of **7** (5.0 mL, 0.103 M, 0.52 mmol) was added to a hexane solution of Et_3Al (0.64 mL, 0.81 M, 0.52 mmol) at −60 °C. After 1 h, the reaction was worked up. GC analysis showed the presence of two products. The first was identified as **8** (40%). ^1H NMR ($CDCl_3$): δ 0.94 (t, $J = 7.6$ Hz, 2 CH_2CH_3), 1.08−1.75 (c, $(CH_2)_5CH$), 2.00 (m, 2 CH_2CH_3), 5.05 (t, $J = 7.0$ Hz, ═CH). EIMS: m/z (rel intensity) 167 (3), 166 (27), 137 (72), 124 (15), 123 (17), 109 (12), 95 (88), 83 (17), 82 (29), 81 (100), 79 (13), 69 (32). EIHRMS: m/z 166.1728 (M^+ calcd for $C_{12}H_{22}$ 166.1721). The second was identified as **9**. ^1H NMR ($CDCl_3$): δ 0.31−0.47 (c, all H's of cyclopropane ring), 0.95 (t, $J = 7.5$ Hz, 2 CH_3C═), 1.00 (t, $J = 7.6$ Hz, other CH_3), 1.11−1.61 (c, >CHCH_2CH_3 and 2 $(CH_2)_5$), 1.98−2.14 (c, 2 CH_2CH═), 5.00 (t, $J = 7.0$ Hz, ═CH). EIMS: m/z (rel intensity) 302 (2), 273 (39), 219 (11), 206 (22), 191 (26), 178 (12), 177 (59), 166 (12), 165 (90), 164 (32), 163 (25), 149 (43), 137 (12), 136 (11), 135 (28), 123 (38), 121 (18), 111 (18), 109 (77), 107 (26), 105 (12), 97 (24), 95 (100), 93 (27), 91 (22), 83 (92), 81 (90), 79 (35), 77 (11), 69 (55). EIHRMS: m/z 302.2961 (M^+ calcd for $C_{22}H_{38}$ 302.2973).

Other reactions used hexane−diethyl ether solvent mixtures. Diethyl ether (1.00 mL) was added to a stirred hexane solution of Et_3Al (0.64 mL, 0.81 M, 0.52 mmol), and the resulting solution was cooled to −60 °C. A hexane solution of **7** (5.0 mL, 0.103 M, 0.52 mmol) was added. GC analysis of an aliquot quenched after 1 h showed it to contain **7** (91%) and no significant amounts of other compounds.

Et$_3$Al, 4, and 7. A hexane solution of Et_3Al (1.20 mL, 0.135 M, 0.162 mmol) was added slowly to a solution prepared by combining hexane solutions of **4** (1.00 mL, 0.170 M, 0.170 mmol) and **7** (1.00 mL, 2.78 M, 0.278 mmol) and maintained at −75 °C. After 1.5 h, the reaction was worked up. GC analysis showed the presence of **5** (14%), **6** (22%), **7** (39%), **8** (8%), **9** (3%), and an additional product that was identified as **10** (69% and 43%, these yield figures indicating the amounts of **4** and of **7**, respectively, that were incorporated into **10**). ^1H NMR ($CDCl_3$): δ 0.10−0.43 (c, all H's of cyclopropane ring), 0.96 (t, $J = 7.5$ Hz, 1 CH_3), 1.00 (t, $J = 7.6$ Hz, 1 CH_3), 1.18−1.68 (c, 2 $(CH_2)_5$), 1.98−2.15 (2 CH_2CH_3), 5.00 (t, $J = 7.0$ Hz, ═CH). EIMS: m/z (rel intensity) 274 (1), 245 (29), 179 (30), 178 (100), 165 (10), 164 (37), 163 (26), 150 (57), 149 (95), 136 (49), 135 (95), 123 (33), 122 (74), 121 (95), 109 (68), 108 (49), 107 (94), 105 (17), 97 (35), 96 (48), 95 (92), 94 (40), 93 (93), 91 (29), 83 (55), 82 (31), 81 (91), 80 (14), 79 (72), 69 (34), 67 (82), 55 (77), 48 (11), 46 (17). EIHRMS: m/z 274.2676 (M^+ calcd for $C_{20}H_{34}$ 274.2660).

A similar reaction at −60 °C for 50 min gave **4** (85%), **5** (9%), **6** (5%), **7** (96%), **8** (8%), **9** (2%), and **10** (3% and 1%, these yield figures indicating the amounts of **4** and of **7**, respectively, that were incorporated into **10**). When reactions were attempted using a greater excess of **4** and **7**, the material balances were poor. In one instance a solid residue remained after removing all volatile components at reduced pressure; its ^1H NMR spectrum had a very broad peak at δ 0.3 and several broad peaks between δ 1.0 and 2.3.

Et$_3$Al and 11. A benzene solution of **11** (20 mL, 0.186 M, 3.7 mmol) was added to a hexane solution of Et_3Al (4.4 mL, 0.81 M, 3.6 mmol) at ambient temperature. After 133 h, the reaction was quenched by addition of water. The solvent was removed from the organic phase at reduced pressure, leaving a yellow solid that was identified as **12** (0.96 g, 87%). Recrystallization from MeOH gave a flaky, white solid (mp 69−72 °C).[36] ^1H NMR ($CDCl_3$): δ 0.97 (t, $J = 7.3$ Hz, CH_3), 1.90 (m, CH_2), 3.55 (t, $J = 7.5$ Hz, >CHPh), 6.56 (s, ═CH), 6.78−7.29 (H's of phenyl groups). The NMR spectra of the crude and recrystallized materials were identical. EIMS: m/z (rel intensity) 300 (2), 299 (21), 298 (82), 270 (21), 269 (92), 192 (18), 191 (100), 179 (14), 178 (23), 165 (10), 91 (45). Anal. Calcd for $C_{23}H_{22}$: C, 92.57; H, 7.43. Found: C, 92.35; H, 7.35. An aliquot of the reaction worked up after 71 h was a

---

[36] This compound has been reported before, but no mp was given. Boche, G.; Buckl, K. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 284.

mixture of **11** and **12**. No products were observed and **11** was recovered (80%) from a reaction for 1 h at 0 °C.

Et$_3$B and 4. A THF solution of Et$_3$B (0.22 mL, 1.0 M, 0.22 mmol) was added to a hexane solution of **4** (1.00 mL, 0.20 M, 0.20 mmol) at −50 °C. After 1.5 h, the reaction was quenched by addition of a small amount of acetic acid and then worked up in the usual way. The product composition for this reaction is given in Table 3 (entry 1).

(3-Methyl-2-butyl)$_2$BH and 4. A THF solution of (3-methyl-2-butyl)$_2$BH (1.90 mL, 0.56 M, 1.06 mmol) was added to a hexane solution of **4** (10.0 mL, 0.106 M, 1.06 mmol) at ambient temperature. After 1.5 h, the reaction was quenched by addition of acetic acid and then worked up in the usual way. GC analysis showed the presence of **16** (46%) and the absence of **4**. For a similar reaction that had been heated at the reflux temperature for 3 h, GC analysis showed the presence only of **16** (76%).

(2,3-Dimethyl-2-butyl)$_2$BH and 4. A THF solution of (2,3-dimethyl-2-butyl)$_2$BH (1.06 mL, 1.00 M, 1.06 mmol) was added to a hexane solution of **4** (10.6 mL, 1.00 M, 1.06 mmol) at ambient temperature. After 1.5 h, the reaction was quenched by addition of acetic acid and then worked up in the usual way. During workup, a white solid precipitated from the solution. GC analysis of the solution showed the presence only of **16** (46%).

Et$_3$Ga and 4. A hexane solution of **4** (1.00 mL, 0.170 M, 0.17 mmol) was added to a hexane solution of Et$_3$Ga (0.25 mL, 0.78 M, 0.20 mmol) at ambient temperature. After 1 h, the reaction was quenched. The product compositions for this reaction and for a similar reaction at 0 °C for 1 h are given in Table 3 (entries 2 and 3).

Et$_3$Ga and 7. A hexane solution of **7** (1.00 mL, 0.28 M, 0.28 mmol) was added to a hexane solution of Et$_3$Ga (0.40 mL, 0.78 M, 0.32 mmol) at 0 °C. After 1 h, the reaction was quenched. GC analysis showed the presence only of **9** (100%). The product compositions for this reaction and for a similar reaction at −60 °C for 1.5 h are given in Table 3 (entries 4 and 5).

Et$_2$Mg and 4. A hexane solution of **1** (1.00 mL, 0.20 M, 0.20 mmol) was added to a diethyl ether solution of Et$_2$Mg (0.23 mL, 0.86 M, 0.20 mmol) at ambient temperature. After 19 h, the reaction was quenched. The product compositions for this reaction and for a similar reaction that used a THF solution of Et$_2$Mg are given in Table 3 (entries 6 and 7). A product not observed in prior reactions with **4** was identified as **17**. ^{1}H NMR (360 MHz, CDCl$_3$): δ 0.01 (s, H's of cyclopropane ring), 0.89 (t, J = 7.4 Hz, CH$_3$), 1.39 (q, J = 7.4 Hz, C*H*$_2$CH$_3$), 1.44−1.62 (c, (CH$_2$)$_5$). EIMS: *m*/*z* (rel intensity) 166 (4), 137 (16), 86 (63), 84 (100), 49 (20), 47 (27), 28 (65). EIHRMS: *m*/*z* 166.1729 (M$^+$ calcd for C$_{12}$H$_{22}$ 166.1721).

Et$_2$Mg and 7. A hexane solution of **7** (1.00 mL, 0.28 M, 0.28 mmol) was added to a diethyl ether solution of Et$_2$Mg (0.32 mL, 0.86 M, 0.28 mmol) at ambient temperature. After 19 h, the reaction was quenched. The product composition for this reaction is given in Table 3 (entry 8).

Et$_2$Zn and 4. A hexane solution of **1** (1.00 mL, 0.17 M, 0.17 mmol) was added to a hexane solution of Et$_2$Zn (0.12 mL, 1.6 M, 0.19 mmol) at ambient temperature. After 10 h the reaction was quenched. The product compositions for this reaction and for a similar reaction at −25 °C for 44 h are given in Table 3 (entries 9 and 10). Another preparation was the same except that diethyl ether (0.2 mL) was added to the hexane solution of **4** before it was added to the Et$_2$Zn solution and the reaction time was 20 h. The product composition for this reaction is given in Table 3 (entry 11).

Et$_2$Zn and 7. A hexane solution of **7** (1.00 mL, 0.28 M, 0.28 mmol) was added to a hexane solution of Et$_2$Zn (0.20 mL, 1.6 M, 0.32 mmol) at ambient temperature. After 46 h, the reaction was quenched. The product compositions for this reaction and for a similar reaction for 4 h are given in Table 3 (entries 12 and 13).

(Methallyl)$_2$Zn and 4. A hexane solution of **4** (7.0 mL, 0.13 M, 0.91 mmol) was added to a hexane solution of (methallyl)$_2$Zn (6.3 mL, 0.16 M, 0.99 mmol) at ambient temperature. After 20 h, the reaction was quenched. GC analysis showed the presence only of **18a** (81%). ^{1}H NMR (360 MHz, CDCl$_3$): δ 0.06 (d of d, J = 4.7 and 8.4 Hz, cyclopropane ring H cis to methallyl), 0.41 (d of d, J = 4.1 and 8.4 Hz, cyclopropane ring H trans to methallyl), 0.62 (m, cyclopropane ring H gem to methallyl), 0.91−1.56 (c, (CH$_2$)$_5$), 1.77 (s, CH$_3$), 1.93 (d of d, J = 6.8 and 15.7 Hz, C*H*HC═), 2.13 (d of d, J = 7.4 and 15.7 Hz, CH*H*C═), 4.72 (s, ═C*H*H), 4.78 (s, ═CH*H*). EIMS: *m*/*z* (rel intensity) 164 (11), 149 (11), 121 (12), 119 (36), 117 (34), 109 (44), 108 (26), 96 (14), 95 (12), 93 (14), 83 (11), 82 (38), 81 (55), 80 (13), 79 (21), 77 (10), 69 (13), 68 (24), 67 (100), 55 (42), 54 (12), 53 (16), 43 (13), 41 (53), 40 (10), 39 (25), 32 (16). EIHRMS: *m*/*z* 164.1559 (M$^+$ calcd for C$_{12}$H$_{20}$ 164.1565).

(Methallyl)$_2$Zn and 7. A hexane solution of **7** (0.56 mL, 1.31 M, 0.73 mmol) was added to a hexane solution of (methallyl)$_2$Zn (6.0 mL, 0.16 M, 0.96 mmol) at ambient temperature. After 20 h, the reaction was quenched. GC analysis showed the presence only of **18b** (98%). ^{1}H NMR (360 MHz, CDCl$_3$): δ 0.14 (d, J = 7.9 Hz, C*H*H of cyclopropane ring), 0.16 (d, J = 7.6 Hz, CH*H* of cyclopropane ring), 0.87 (t, J = 7.4 Hz, C*H*$_3$CH$_2$), 1.23−1.69 (c, C*H*$_2$CH$_3$ and (CH$_2$)$_5$), 1.73 (s, CH$_3$C═), 2.00−2.23 (c, CH$_2$C═), 4.74 (s, ═C*H*H), 4.77 (s, ═CH*H*). EIMS: *m*/*z* (rel intensity) 192 (3), 163 (27), 137 (15), 121 (29), 119 (92), 117 (93), 96 (11), 95 (28), 84 (13), 82 (21), 81 (37), 69 (13), 67 (16), 55 (17), 47 (18), 41 (18), 36 (14), 35 (12), 28 (100). EIHRMS: *m*/*z* 192.1893 (M$^+$ calcd for C$_{14}$H$_{24}$ 192.1878).

Et$_2$Cd and 4. A hexane solution of **4** (1.00 mL, 0.170 M, 0.17 mmol) was added to a hexane solution[37] of Et$_2$Cd (0.50 mL, 0.55 M, 0.28 mmol) at ambient temperature. After 70 h, the reaction was quenched. The product composition for this reaction is given in Table 3 (entry 14). The GC analysis showed the presence of an unidentified product whose GC peak was just before (and overlapping) the peak produced by **6**. Mass spectra suggested that it was an isomer of **6**, and on that basis its yield was 7%. EIMS: *m*/*z* (rel intensity) 246 (18), 217 (68), 163 (33), 146 (12), 145 (70), 122 (39), 121 (100), 108 (14), 109 (29), 95 (38), 94 (11), 93 (38), 91 (19), 82 (15), 81 (49), 79 (38), 64 (13), 62 (47), 55 (17).

Et$_2$Cd and 7. A hexane solution of **7** (1.00 mL, 0.28 M, 0.28 mmol) was added to a hexane solution[37] of Et$_2$Cd (0.70 mL, 0.58 M, 0.41 mmol) at ambient temperature. After 70 h, the reaction was quenched. The product composition for this reaction is given in Table 3 (entry 15).

Et$_2$Hg and 4. A hexane solution of **4** (2.00 mL, 0.34 M, 0.68 mmol) was added to a hexane solution of Et$_2$Hg (2.00 mL, 0.34 M, 0.68 mmol) at ambient temperature. After 96 h, the reaction was quenched. The product composition for this reaction is given in Table 3 (entry 16).

EtLi and 4. A hexane solution of **4** (1.00 mL, 0.20 M, 0.20 mmol) was added to a benzene solution of EtLi (0.24 mL, 0.93 M, 0.22 mmol) at ambient temperature. After 1 h, the reaction was quenched. The product composition for this reaction is given in Table 3 (entry 17).

EtLi and 7. A hexane solution of **7** (1.00 mL, 0.28 M, 0.28 mmol) was added to a benzene solution of EtLi (0.33 mL, 0.93 M, 0.31 mmol) at ambient temperature. After 1 h, the reaction was quenched. The product composition for this reaction is given in Table 3 (entry 18). When a similar reaction was quenched with D$_2$O, GC/MS analysis indicated that ca. 12% of the recovered **7** was monodeuterated.

Et$_4$Sn and 1. A hexane solution of Et$_4$Sn (1.74 mL, 0.70 M, 1.22 mmol) was added to a hexane solution of **4** (4.50 mL, 0.26 M, 1.17 mmol) in a Pyrex tube. The tube was sealed and then heated at 70 °C. After 96 h, the reaction was quenched. The product composition for this reaction is given in Table 3 (entry 19).

---

(37) The Et$_2$Cd solution contained a small amount of diethyl ether.

***t*-Bu$_2$Mg and 7.** In a typical reaction, a hexane solution of **7** (5.4 mL, 0.28 M, 1.5 mmol) was added to a diethyl ether solution of *t*-Bu$_2$Mg (5.0 mL, 0.31 M, 1.6 mmol) in a Pyrex tube. The tube was sealed and then heated at 35−70 °C. After 66 h, the reaction was quenched. GC analysis showed the presence only of **7** (86%). Other reactions at room temperature for as long as 115 h also furnished no detectable amounts of products. The **7** isolated from a reaction that was quenched with D_2O after 21 h had no excess D.

***t*-Bu$_2$Mg and 23.** A diethyl ether solution of **23** (2.0 mL, 1.24 M, 2.5 mmol) was added to a diethyl ether solution of *t*-Bu$_2$Mg (4.0 mL, 0.63 M, 2.5 mmol) in a Pyrex tube. The tube was sealed and then heated at 60 °C. After 66 h, the reaction was quenched. GC analysis showed the presence of two products. The first product was identified as **25** (17%). ^{1}H NMR ($CDCl_3$): δ 0.92 (s, $(CH_3)_3C$), 1.02 (t, $J = 7.4$ Hz, $\mathrm{C}H_3\mathrm{CH_2}$), 1.95 (s, $\mathrm{C}H_2\mathrm{C(CH_3)_3}$), 2.06 (br q, $J = 7.4$ Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 4.68 (m, $=\mathrm{C}H\mathrm{H}$), 4.84 (d of d, $J = 1.6$ and 3.6 Hz, $=\mathrm{CH}H$). EIHRMS: *m*/*z* 126.1411 (M^+ calcd for C_9H_{18} 126.1408). The second product was identified as **24** (15%). ^{1}H NMR ($CDCl_3$): δ −0.05 to +0.08 (c, 1 H of cyclopropane ring), 0.26−0.39 (c, 2 H's of cyclopropane ring), 0.43−0.59 (1 H of cyclopropane ring), 0.82 (s, $(CH_3)_3C$), 0.93 (t, $J = 5.8$ Hz, $\mathrm{C}H_3\mathrm{CH_2}$), 0.98−1.43 (c, $\mathrm{C}H_2\mathrm{CH_3}$). EIHRMS: *m*/*z* 126.1402 (M^+ calcd for C_9H_{18} 126.1408). The NMR spectrum was identical with that of a compound synthesized by a Simmons−Smith reaction with *trans*-2,2-dimethyl-3-hexene.

***t*-Bu$_2$Zn and 4.** A hexane solution of **4** (6.0 mL, 0.17 M, 1.02 mmol) was added to a diethyl solution of *t*-Bu$_2$Zn (6.0 mL, 0.18 M, 1.08 mmol) at ambient temperature. After 52 h, the reaction was quenched. GC analysis showed the presence of **4** (16%) and three other compounds. The second compound was identified as **20a** (19%). ^{1}H NMR (360 MHz, $CDCl_3$): δ 1.13 (d, $J = 7.0$ Hz, $\mathrm{C}H_3\mathrm{CH}$), 1.20 (t, $J = 7.0$ Hz, $\mathrm{C}H_3\mathrm{CH_2}$), 1.41−1.63 (c, $\mathrm{CH_2(C}H_2\mathrm{)_3}$-$\mathrm{CH_2}$, 2.07−2.15 (c, $\mathrm{C}H\mathrm{HCH}=$ and 2 $\mathrm{CH_2C}H_2\mathrm{C}=$), 2.28 (m, $\mathrm{CH}H\mathrm{CH}=$), 3.39 (m, CHO), 3.50 (q, $J = 7.0$ Hz, $\mathrm{C}H\mathrm{HCO}$), 3.51 (q, $J = 7.0$ Hz, $\mathrm{CH}H\mathrm{CO}$), 5.09 (overlapping d of d (appearance of triplet), $J = 7.5$ Hz, $=\mathrm{CH}$). EIMS: *m*/*z* (rel intensity) 183 (0.5), 182 (5), 136 (26), 109 (12), 107 (16), 95 (18), 94 (12), 93 (19), 91 (15), 86 (16), 81 (32), 79 (44), 77 (22), 74 (30), 73 (98), 67 (74), 65 (13), 55 (35), 53 (21), 45 (100), 43 (24), 41 (47), 39 (35). EIHRMS: *m*/*z* 182.1670 (M^+ calcd for $C_{12}H_{22}O$ 182.1671). The third compound was identified as **19** (60%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.16−0.20 (c, 2 H's of cyclopropane ring), 0.44 (d of d, $J = 6.5$ and 8.9 Hz, 1 H of cyclopropane ring), 0.99 (s, $(CH_3)_3C$), 1.23−1.69 (c, 2 $(CH_2)_5$), 5.00 (d, $J = 16.5$ Hz, $\mathrm{C}H\mathrm{{=}CH}$), 5.25 d, $J = 16.5$ Hz, $\mathrm{CH{=}C}H$). EIHRMS: *m*/*z* 274.2675 (M^+ calcd for $C_{20}H_{34}$ 274.2660). The first compound was not identified. Its GC peak had 50% of the area of the peak due to **20a**. ^{1}H NMR (200 MHz, $CDCl_3$) [rel absorption areas in brackets]: δ 0.89 (s [21]); 1.03 (s [8]); 1.07 (s [7]), 1.26 and 1.28 (s and s [86]), 1.40−1.58 (c [41]), 2.06−2.08 (c [7]). EIMS: *m*/*z* (rel intensity) 167 (2), 166 (16), 110 (100), 109 (52), 95 (22), 93 (11), 82 (21), 81 (73), 79 (22), 77 (11), 69 (18), 67 (12), 66 (98), 57 (87), 55 (22), 53 (13), 41 (54), 39 (22).

***t*-Bu$_2$Zn and 7.** A diethyl ether solution of **7** (9.0 mL, 0.076 M, 0.68 mmol) was added to a diethyl solution of *t*-Bu$_2$Zn (4.0 mL, 0.18 M, 0.72 mmol) at ambient temperature. After 20 h, the reaction was quenched. GC analysis showed the presence of **7** (7%) and three other compounds. The first compound was identified as **21** (36%). ^{1}H NMR ($CDCl_3$): δ 0.98 (t, $J = 7.5$ Hz, $\mathrm{C}H_3\mathrm{CH_2}$), 1.08 (s, $(CH_3)_3C$), 1.56−1.71 (c, $(CH_2)_5CH$), 2.14 (q, $J = 7.5$ Hz, $\mathrm{C}H_2$-$\mathrm{CH_3}$), 5.07 (s, $\mathrm{CH}=$). EIHRMS: *m*/*z* 194.2035 (M^+ calcd for $C_{14}H_{26}$ 194.2034). The second compound was identified as **22** (45%). ^{1}H NMR ($CDCl_3$): δ 0.89 (s, $(CH_3)_3C$), 0.91 (t, $J = 7.5$ Hz, $\mathrm{C}H_3$-$\mathrm{CH_2}$), 1.51−1.65 (c, $\mathrm{CH_2(C}H_2\mathrm{)_3CH_2}$), 1.97 (s, $\mathrm{C}H_2\mathrm{C(CH_3)_3}$), 2.06 (q, $J = 7.5$ Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 2.08−2.23 (c, $\mathrm{C}H_2\mathrm{(CH_2)_3C}H_2$). EIHRMS: *m*/*z* 194.2023 (M^+ calcd for $C_{14}H_{26}$ 194.2034). The third compound was identified as **20b** (8%). ^{1}H NMR (360 MHz, $CDCl_3$): δ 0.94 (t, $J = 7.5$ Hz, $\mathrm{C}H_3\mathrm{CH_2C}$), 1.12 (d, $J = 6.2$ Hz, $\mathrm{C}H_3\mathrm{CH}$), 1.19 (t, $J = 7.0$ Hz, $\mathrm{C}H_3\mathrm{CH_2O}$), 1.29−1.59 (c, $\mathrm{CH_2(C}H_2\mathrm{)_3}$-$\mathrm{CH_2}$), 2.05 (q, $J = 7.5$ Hz, $\mathrm{CH_3C}H_2\mathrm{C}=$), 2.06−2.18 (c, $\mathrm{C}H_2$-$\mathrm{(CH_2)_3C}H_2$ and $=\mathrm{CC}H\mathrm{HCH}$), 2.34 (d of d, $J = 5.6$ and 13.3 Hz, $=\mathrm{CCH}H\mathrm{CH}$), 3.42−3.55 (c, $\mathrm{CHOCH_2}$). EIHRMS: *m*/*z* 210.1986 (M^+ calcd for $C_{14}H_{26}O$ 210.1984).

Acknowledgment. We thank the National Science Foundation for supporting this research, Barry Kubala for preliminary work, Ronald Prough for assistance with some preparations, and Professor John Lowe for useful discussions.

Supporting Information Available: Text giving reactions of **4** and **7** with other organometallic compounds, preparations of cyclopropene and organometallic reactants and of **14** and **15**, details of GC analyses and sample collections. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060766T