

gives $k_{\psi} = 2.85 \text{ s}^{-1}$ ($2.7 \times 10^{-2} \text{ s}^{-1}$ in the absence of vesicles). In these cases, we believe that the catalyzed cleavage reactions are still too slow to effectively compete with substrate or reagent (OH^-) permeations, so that site equilibria, if established, are "drained" by slow, probably exovesicular, cleavage reactions.

Experimental Section

Materials. Di-*n*-hexadecyldimethylammonium bromide, **2**, was prepared by the reaction of *n*-hexadecyl bromide with *N*-*n*-hexadecyl-*N,N*-dimethylamine³³ and purified by repeated crystallization from ethyl acetate, mp 145–155 °C. A satisfactory microanalysis (C, H, Br) was obtained. Cetyltrimethylammonium bromide (Sigma) was purified by the method of Perrin et al.,³⁴ mp 227–235 °C (lit.³⁴ mp 227–235 °C dec). *N,N,N*-Trimethyl-*N*-(*p*-mercaptobenzyl)ammonium bromide (protonated form of **4**) was prepared by the procedure of Moss and Dix.⁸ Thiophenol, **3** (Aldrich, >99%), was used without further purification. Also used as received were cholesterol (Sigma, >99%), sodium dithionite (J. T. Baker, purified), sodium sulfite, (Fisher, ACS certified), 5,5'-dithiobis(2-nitrobenzoic acid), **1** (Aldrich), and 18-crown-6 (Aldrich). Solvents were of ACS reagent grade quality and were dried before use. Buffer solutions were prepared from N_2 -purged "Steam-Distilled" water (distilled, U.S.P.,

(33) Okahata, Y.; Ando, R.; Kunitake, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3647. Ueoka, R.; Matsumoto, Y. *J. Org. Chem.* **1984**, *49*, 3774.

(34) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: New York, 1966; p 106.

Electrified Water Co., East Orange, NJ).

Methods. UV spectra were obtained on a Cary Model 17D spectrophotometer. pH measurements were made with a Radiometer Type PHM 25 pH meter. Cmc determinations employed a Fisher "Tensiomat" and were determined from the "break points" of observed surface tension vs. log [surfactant]. Vesicular solutions were prepared by sonication with a Braun Sonic Model 1510 probe-type sonicator; the conditions appear in Results. The vesicle solutions were filtered through 0.8- μm Millipore "Millex-PF" filters before use.

Kinetic Studies. Slower reactions were followed with use of a Gilford Model 250 spectrophotometer equipped with a Gilford Model 6051 recorder. Faster reactions were monitored with the stopped-flow or multixing units described in Results. All reactions were carried out at 25.0 ± 0.2 °C, except as noted. Rate constants were obtained from computer-generated correlations of $\log(A_{\infty} - A_t)$ vs. time. Conditions, errors, monitoring wavelengths, and other details appear in Results, cf., especially, Tables I and II.

Acknowledgment. We are grateful to the U.S. Army Research Office and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. R.P.S. thanks the Graduate School of Rutgers University and the J. L. R. Morgan Fund for fellowships.

Registry No. **1**, 69-78-3; **2**, 70755-47-4; **3**, 108-98-5; **4**, 98541-71-0; **5**, 77874-90-9; sodium dithionite, 7775-14-6; sodium sulfite, 7757-83-7; CTAB, 57-09-0.

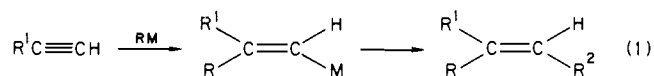
Carbometalation Reaction of Alkynes with Organoalane-Zirconocene Derivatives as a Route to Stereo- and Regiodefined Trisubstituted Alkenes¹

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Contribution from the Department of Chemistry, Syracuse University, Syracuse, New York 13210, and Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received April 22, 1985

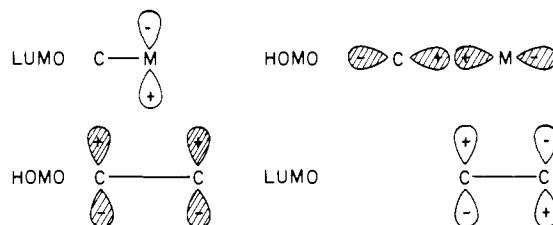
Abstract: The reaction of alkynes with a methylalane, such as Me_3Al , and a zirconocene derivative, such as Cl_2ZrCp_2 , provides a convenient and selective route to (*E*)-2-methyl-1-alkenylalanes in high yields. The reaction is catalytic in Zr. The stereoselectivity is generally >98%, and the regioselectivity observed with terminal alkynes is typically ca. 95%. Although the reaction of alkynes with trialkylalanes containing β -hydrogens and Cl_2ZrCp_2 is complicated by competitive hydrometalation and diminished (70–80%) regioselectivity, the hydrometalation reaction can be avoided by using chlorodialkylalanes and Cl_2ZrCp_2 . The Zr-catalyzed carboalumination reaction of typical alkynes, such as phenylacetylene and 1-octyne, most likely involves direct Al–C bond addition assisted by Zr.

Controlled carbometalation of alkynes as shown in eq 1 provides a conceptually attractive route to trisubstituted alkenes. Con-



sideration of the frontier orbitals of alkynes and organometals (RM) suggests that the key requirement for concerted carbometalation, which is expected to involve cis addition of the R–M bond to the $\text{C}\equiv\text{C}$ bond, is the presence or the ready availability of a low-lying metal orbital (Scheme I) and that this requirement is essentially the same as that for concerted hydrometalation. In reality, however, the greater steric requirements of the M–C bond

Scheme I



relative to the corresponding M–H bond are expected to limit the scope of carbometalation. Thus, for example, whereas hydroboration³ is facile and general, simple alkylboranes, such as BEt_3 , do not readily add to alkenes and alkynes.⁴ Similarly, the scope

(1) Controlled Carbometalation. 20. Part 19: Miller, J. A.; Negishi, E. *Tetrahedron Lett.* **1984**, *25*, 5863. Some preliminary results of the work have been communicated: (a) Van Horn, D. E.; Negishi, E. *J. Am. Chem. Soc.* **1978**, *100*, 2252. (b) Yoshida, T.; Negishi, E. *Ibid.* **1981**, *103*, 4985.

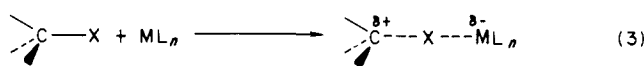
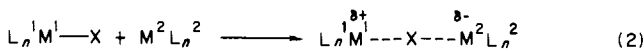
(2) Address correspondence to this author at Department of Chemistry, Purdue University, W. Lafayette, Indiana 47907.

(3) Brown, H. C. "Hydroboration"; Benjamin: New York, 1962.

of the reaction of alkynes with organoalanes⁵ has been much more limited than the corresponding hydroalumination.⁵ In fact, the reaction of terminal alkynes with organoalanes generally involves alkyne proton abstraction rather than carbometalation.⁵ Abstraction of alkynyl protons is a general problem with electro-positive metals, such as alkali metals, magnesium, and other group 2 metals. On the other hand, the metal-alkyl bond containing group 14 metals, such as Si, Ge, and Sn, appears to be relatively unreactive toward alkynes presumably due to (i) the absence of low-lying empty metal orbitals and (ii) the relatively large steric requirements.

Many organotransition metals are capable of undergoing carbometalation.⁶ At the outset of our investigation, however, examples of controlled single-stage carbometalation of alkynes (eq 1) were very scarce.⁷ Carbocupration^{6a,8} was essentially the only such reaction that featured high yields, reasonably wide scope, and high regio- and stereoselectivity. However, the difficulty in the use of methylcopper reagents seriously limited its synthetic utility, especially in the synthesis of methyl-substituted alkenes of terpenoid origin. This and other limitations, such as the thermal instability of organocoppers and undesirable variations of regio- and stereochemistry due to proximal heterofunctionalities, prompted us to seek new types of controlled carbometalation reactions of alkynes.

In the Ziegler-Natta olefin polymerization⁹ bimetallic reagents, such as Al-Ti systems, are used to induce a series of carbometalation reactions of alkenes, and it has been suggested that transition metals, such as Ti, provide active sites. However, it was also tempting to speculate that, in such bimetallic systems, one metal might activate the other toward alkenes and alkynes via three-center two-electron bonding (eq 2), which would be closely analogous to the mode of carbon activation in the Friedel-Crafts reaction¹⁰ (eq 3). We have found that Me₃Al-Cl₂TiCp₂



(Cp = η⁵-C₅H₅) reacts smoothly with diphenylacetylene to give a product which produces (*Z*)-1,2-diphenylpropene in 84% yield

(4) Allylboration of activated alkynes is known (Mikhailov, B. M. *Organomet. Chem. Rev. A* 1972, 8, 1).

(5) Mole, T.; Jeffery, E. A. "Organoaluminum Compounds"; Elsevier: Amsterdam, 1972.

(6) (a) For a review of controlled carbometalation, see: Normant, J. F.; Alexakis, A. *Synthesis* 1981, 841. (b) See also: Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980.

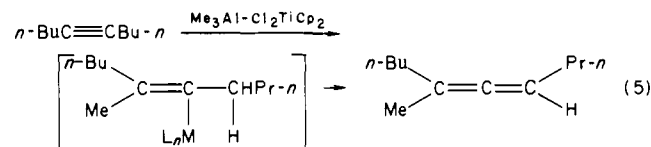
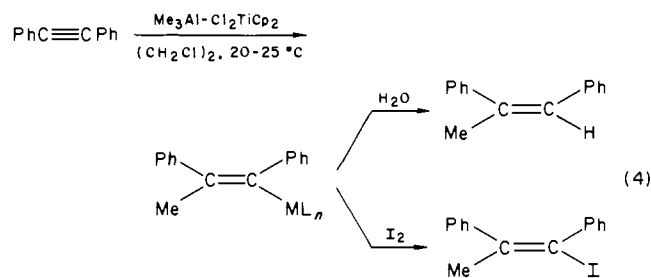
(7) Aside from various allylmatalation reactions and carbometalation reactions of propargyl alcohols,⁶ the following single-stage carbometalation reactions of alkynes were known. (a) For an intramolecular cyclization reaction of alkyneyllithiums, see: Ward, H. R. *J. Am. Chem. Soc.* 1967, 89, 5517. (b) For a related Grignard reaction, see: Richey, H. G., Jr.; Rothman, A. M. *Tetrahedron Lett.* 1968, 1457. (c) For a related organocopper reaction, see: Crandall, J. K.; Battioni, P.; Wehlac, J. T.; Bindra, R. *J. Am. Chem. Soc.* 1975, 97, 7171. (d) For carboalumination of internal alkynes, see: Eisch, J. J.; Kaska, W. C. *Ibid.* 1966, 88, 2976. See also references cited in ref 6. (e) For carbotitanation of alkynols, see: Coleman, R. A.; O'Doherty, C. M.; Tweedy, H. E.; Harris, T. V.; Thompson, D. W. *J. Organomet. Chem.* 1976, 107, C15. (f) For a photochemical reaction of Cp₂TiMe₂ with diphenylacetylene, see: Boon, W. H.; Rausch, M. D. *J. Chem. Soc., Chem. Commun.* 1977, 397. (g) For a carborhodation reaction of diphenylacetylene see: Michman, M.; Balog, M. *J. Organomet. Chem.* 1971, 31, 395. (h) For an addition reaction of MeMgBr-Cl₂Ni(PPh₃)₂ with internal alkynes, see: Dubouin, J.-G.; Jousseume, B. *Ibid.* 1972, 44, C1.

(8) (a) Normant, J. F.; Bourgain, M. *Tetrahedron Lett.* 1971, 2583. (b) For a recent review, see: Normant, J. F.; Alexakis, A. In "Current Trends in Organic Synthesis"; Nozaki, H. Ed.; Pergamon Press: Oxford, 1983; p 291. (c) For a later improvement of carbocupration involving methylcopper derivatives, see: Marfat, A.; McGuirk, P. R.; Helquist, P. *J. Org. Chem.* 1979, 44, 3888.

(9) (a) Boor, J. "Ziegler-Natta Catalysts and Polymerization"; Academic Press: New York, 1978. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* 1980, 18, 99.

(10) Olah, G. A., Ed. "Friedel-Crafts and Related Reactions"; Interscience: New York, 1963-1965; 4 volumes.

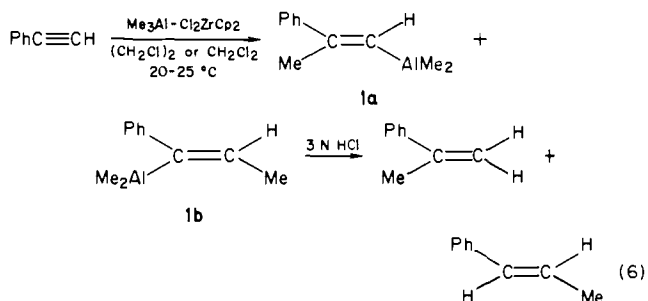
on hydrolysis and (*E*)-1-iodo-1,2-diphenylpropene in 75% yield on iodolysis¹¹ (eq 4). Unfortunately, the current scope of the reaction is very limited. Thus, alkyl-substituted internal alkynes, such as 5-decyne, directly produce allenes instead of alkenes (eq 5), and the yields of carbometalation products obtained from terminal alkynes are generally ≤30%. Since certain Al-Zr



reagent systems were known to induce the Ziegler-Natta alkene polymerization with a diminished reactivity as compared with the corresponding Al-Ti systems,¹² we thought that Al-Zr systems might be better suited for controlled single-stage carbometalation than Al-Ti systems.

Results and Discussion

The reaction of phenylacetylene (10 mmol) with a clear lemon-yellow solution of Me₃Al (20 mmol) and Cl₂ZrCp₂ (10 mmol) in 20 mL of 1,2-dichloroethane or dichloromethane at 20-25 °C under nitrogen produced within 24 h an alkenylmetal species which gave a 98% combined yield of 2-phenylpropene and (*E*)-1-phenylpropene in a 96:4 ratio (eq 6). It is noteworthy that, when



we either omitted Cl₂ZrCp₂ or used Al-free Cl(Me)ZrCp₂,¹³ no reaction occurred even after 24 h under otherwise comparable conditions, indicating that both Al and Zr are essential to the reaction. In this connection, it should also be noted that Me₂ZrCp₂ has been reported to undergo only a slow proton abstraction reaction with phenylacetylene even in refluxing toluene.¹⁴

The ¹H NMR spectrum of the reaction mixture in CH₂Cl₂ shows two distinct allylic proton signals at δ 2.35 and 1.93 in a ratio of ca. 95:5. Evaporation of CH₂Cl₂, extraction with pentane to separate Cl₂ZrCp₂, evaporation of pentane, and addition of CH₂Cl₂ to the residue gave a solution which showed the allylic proton signals at δ 2.35 and 1.93 in the same 95:5 ratio. The absence of alkenylzirconium derivatives was indicated by the absence of Cp signals in the δ 6.5-5.5 region. Taken together with the protonolysis results, the alkenylalane structures **1a** and **1b** may

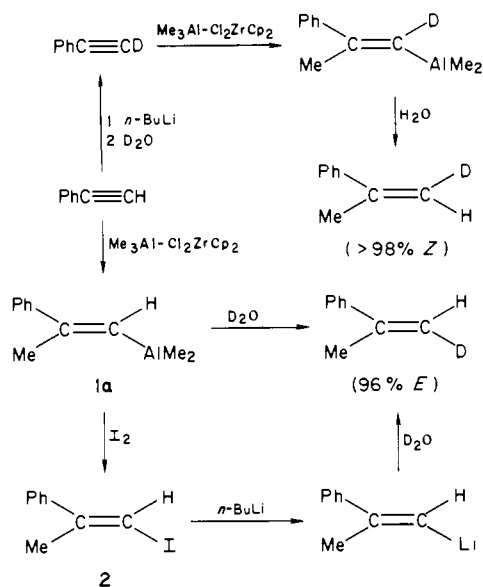
(11) Van Horn, D. E.; Valente, L. F.; Idacavage, M. J.; Negishi, E. *J. Organomet. Chem.* 1978, 156, C20.

(12) See, for example: Yazima, Y.; Yaguchi, S. *Bull. Chem. Soc. Jpn.* 1966, 39, 404.

(13) Surtees, J. R. *J. Chem. Soc., Chem. Commun.* 1965, 567.

(14) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* 1972, 34, 155.

Scheme II



be assigned to the organometallic products.¹⁵

The results presented above suggested that the reaction should be catalytic in Zr. Accordingly, we ran the reaction using 10 mol % of Cl_2ZrCp_2 under otherwise the same conditions and obtained, after protonolysis, the same product mixture in 85% yield after 48 h.

Stereochemistry. To establish the stereochemistry of the reaction, phenylacetylene was reacted with $\text{Me}_3\text{Al}-\text{Cl}_2\text{ZrCp}_2$ as described above and quenched with D_2O (100.0 atom %) to give the expected C_9 products in 98% combined yield. The ^1H NMR spectrum of a purified sample of 2-phenylpropene indicated that the area ratio of the β -proton peaks, that are trans and cis to phenyl at δ 5.0 and 5.3,¹⁶ respectively, was 0.04. Thus, 1-deuterio-2-phenylpropene was at least 96% *E*. That the stereoselectivity of the reaction is actually >98% has been shown by the formation of >98% pure (*Z*)-1-deuterio-2-phenylpropene from >99% pure 2-deuterio-1-phenylacetylene, as summarized in Scheme II. Another point of significance indicated by the above results is that the reaction is not complicated by the known proton-abstraction reactions of terminal alkynes with organozirconium¹⁴ and organoaluminum⁵ compounds. Treatment of **1** with 1 equiv of iodine in THF gave 1-iodo-2-phenylpropene (*Z*) in 73% isolated yield (83% by GLC). The stereochemistry of **2** was established by converting it to ca. 96% pure (*E*)-1-deuterio-2-phenylpropene by its treatment with *n*-BuLi and deuterolysis (Scheme II).

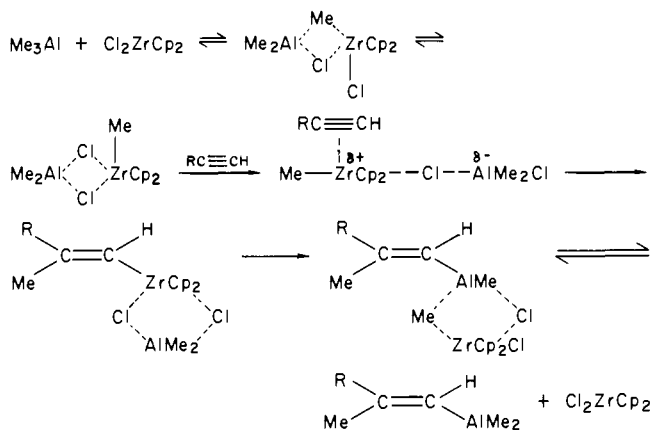
Scope. To probe the scope of the Zr-catalyzed methylaluminum reaction of alkynes with respect to the alkyne structure, several representative alkynes were treated with $\text{Me}_3\text{Al}-\text{Cl}_2\text{ZrCp}_2$, and the products were quenched with 3 N HCl and/or iodine.¹⁷ As the experimental results summarized in Table I indicate, acetylenes containing alkyl, aryl, conjugated alkenyl, and isolated alkenyl groups gave the expected carbometalation products in excellent yields, as judged by the yields of the protonolysis products. The stereoselectivity determined by ^1H and ^{13}C NMR as well as by GLC was >98%. The regioselectivity observed with the terminal alkynes was $95 \pm 1\%$. Internal alkynes, such as 5-decyne and diphenylacetylene, also participate in the carbometalation reaction. In sharp contrast with the reaction of $\text{Me}_3\text{Al}-\text{Cl}_2\text{TiCp}_2$ with 5-decyne (eq 5), the corresponding reaction of $\text{Me}_3\text{Al}-\text{Cl}_2\text{ZrCp}_2$ cleanly produced, after protonolysis, an 89% GLC yield of (*Z*)-5-methyl-5-decene uncontaminated by even a trace of an allenic product. The reaction was, however, slower

Table I. Reaction of Alkynes with Trimethylaluminum and Zirconocene Dichloride^a

alkyne	yield of protonolysis product, ^b %	yield of iodolysis product, ^c %	regio-selectivity ^d	stereo-selectivity
phenylacetylene ^e	98	73 (83)	96	>98
1-hexyne	95–100	85	95	>98
1-heptyne	95–100	83	95	>98
1-octyne	95–100	81	94	>98
2-methyl-1-buten-3-yne ^f	95	70	95	>98
2-methyl-2-hepten-6-yne ^g	95	72 (79)	95	>98
5-decyne ^h	89			97

^a Unless otherwise mentioned, the reaction was run for 3–6 h at room temperature in $(\text{CH}_2\text{Cl})_2$ or CH_2Cl_2 . ^b By GLC. ^c By isolation. The numbers in parentheses are GLC yields. ^d By analysis of protonolysis products. The regiochemical purity of iodolysis products ranged from 95 to 100%. ^e The reaction was run for 24 h. ^f The results were obtained by N. Okukado. ^g The results were obtained by A. O. King. ^h The reaction was run for 6 h at 50 °C.

Scheme III



than that of a terminal alkyne and was carried out at 50 °C. The Zr-catalyzed methylaluminum reaction of diphenylacetylene was unexpectedly complex. After protonolysis, the expected product, i.e., (*Z*)-1,2-diphenylpropene, was obtained only in 30% yield. Although unidentified, the major byproducts appeared to be a mixture of chlorinated 1,2-diphenylpropenes.

The reaction of 1-octyne with *n*-Pr₃Al-Cl₂ZrCp₂ in a 1:2:1 molar ratio in 1,2-dichloroethane for 1 h at 25 °C produced, after protonolysis, 2-(*n*-propyl)-1-octene (52%), (*E*)-4-undecene (13%), and 1-octene (30%). The regioselectivity of the carbometalation reaction in this case was therefore 80%, and a hydrometalation reaction competed to the extent of ca. 30%. As described later, the competitive hydrometalation reaction can be prevented by proper choice of reagents, although the regioselectivity problem has not yet been overcome. The reaction of 1-octyne with *i*-Bu₃Al-Cl₂ZrCp₂ produced, after protonolysis, 1-octene (51%) and *n*-octane (44%) without showing any sign of carbometalation. This reaction has been exploited in developing a Zr-catalyzed procedure for hydroalumination of alkenes, as described elsewhere.¹⁸

Mechanism. Since the Zr-catalyzed carbometalation reaction of alkynes requires the simultaneous presence of an organoalane and a zirconocene derivative, it must involve either Al-assisted Zr-C bond addition or Zr-assisted Al-C bond addition.¹⁹ The following set of observations and considerations initially led us to consider a mechanism involving Al-assisted Zr-C bond addition (Scheme III). (1) Addition of 2 equiv of Me_3Al to Cl_2ZrCp_2 suspended in 1,2-dichloroethane at room temperature gave a clear lemon-yellow solution. Its ^1H NMR spectrum in the same solvent taken at 30 °C exhibited only two broad signals (half-width \approx

(15) The signal at δ 1.93 was initially assigned to the allylic protons of chlorobis(cyclopentadienyl){(*E*)-2-phenyl-1-propenyl}zirconium. However, our later study clearly established the absence of any zirconium derivatives.

(16) Sadler NMR Catalog No. 9908.

(17) Negishi, E.; Van Horn, D. E.; King, A. O.; Okukado, N. *Synthesis* 1979, 501.

(18) Negishi, E.; Yoshida, T. *Tetrahedron Lett.* 1980, 21, 1501.

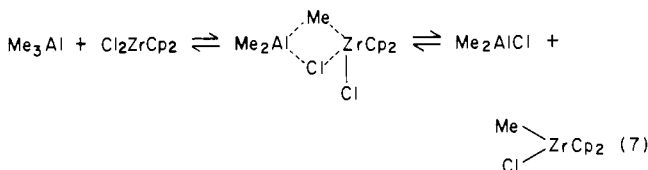
(19) In principle, Al---C---Zr bond addition, in which both Al and Zr play essentially the same roles, may also be operative. Except for the extreme and unlikely case where the two metals play the identical roles, however, this mode of reaction may be represented by the two considered here.

Table II. Reaction of 1-Heptyne with Methylalane-Zirconocene Systems^a

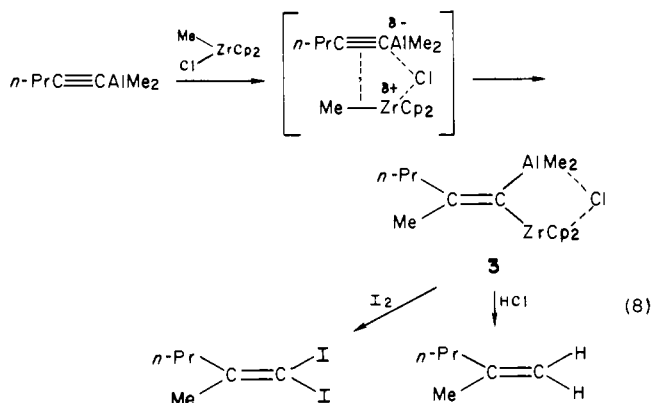
Al-Zr reagent	total protonolysis products ^b (%) formed after indicated time (h)				products obtained after iodinolysis at 24 h, %			
	1	3	6	24	$n\text{-C}_5\text{H}_{11}\text{C}(\text{Me})=\text{C}(\text{H})\text{I}$	$n\text{-C}_5\text{H}_{11}\text{C}(\text{I})=\text{C}(\text{H})\text{Me}$	$n\text{-C}_5\text{H}_{11}\text{C}(\text{Me})=\text{C}(\text{H})\text{H}$	$n\text{-C}_5\text{H}_{11}\text{C}(\text{H})=\text{C}(\text{H})\text{Me}$
Me ₃ Al-Me ₂ ZrCp ₂	24	48	70	99 ^c	93	2	2	3
Me ₃ Al-Cl(Me)ZrCp ₂	95	98			93	2	trace	3
Me ₃ Al-Cl ₂ ZrCp ₂	100				94	2	trace	3
Me ₂ AlCl-Cl ₂ ZrCp ₂	15	35	42	70 ^d	47 ^d	trace ^d	13 ^d	5 ^d
MeAlCl ₂ -Cl ₂ ZrCp ₂	0	0	0	0	0	0	0	0

^a 1-Heptyne (5 mmol) was treated with 5 mmol each of a methylalane and a zirconocene derivative at room temperature in 1,2-dichloroethane. ^b A 95:5 mixture of 2-methyl-1-heptene and (*E*)-2-octene. ^c The yields after 9 and 18 h were 85 and 98%, respectively. ^d The yield figures were taken after 48 h.

4 Hz) at δ -0.31 and 6.40. Addition of 2 equiv of THF split the high-field Me signal into three at δ 0.25, -0.73, and -0.95 and the Cp signal into two sharp signals (half-width \approx 2 Hz) at δ 6.45 and 6.22. The chemical shift and relative integration data indicated that the THF-quenched mixture consisted of Cl₂ZrCp₂, Cl(Me)ZrCp₂, Me₃Al·THF, and Me₂AlCl·THF, the Cl₂ZrCp₂/Cl(Me)ZrCp₂ ratio being ca. 1:2. No Me₂ZrCp₂ was present. Thus, under the reaction conditions Cl₂ZrCp₂ and Me₃Al undergo Me-Cl exchange, which is rapid on the NMR time scale, to produce Cl(Me)ZrCp₂ (eq 7). (2) As stated earlier, Cl-

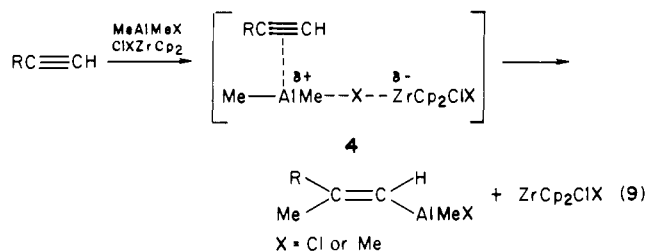


(Me)ZrCp₂ does not react with ordinary terminal alkynes, such as phenylacetylene and 1-octyne, at room temperature. On the other hand, the reaction of Cl(Me)ZrCp₂ with 1-pentynyl-dimethylalane in CH₂Cl₂ at room temperature for 3 h cleanly produced an alkenylmetal species, which has been identified as **3**.²⁰ Its protonolysis with 3 N HCl gave 2-methyl-1-pentene in 95% yield, and its iodinolysis with an excess of iodine (2.2 equiv) gave 1,1-diiodo-2-methyl-1-pentene in 92% yield. Its IR, ¹H and ¹³C NMR, and elemental analytical data are consistent with the assigned structure. We believe that the reaction represents the first example of single-stage carbozirconation of alkynes which may well proceed as shown in eq 8. (3) It has been reported that

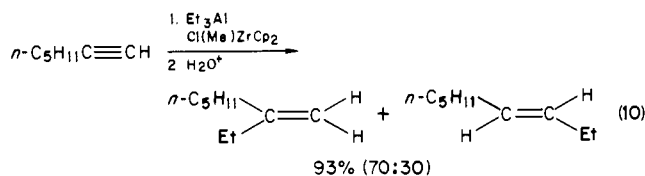


chlorobis(cyclopentadienyl)(1-alkenyl)zirconiums react with chlorodialkylalanes in CH₂Cl₂ to transfer the alkenyl group from Zr to Al.²¹ (4) We have established that the Zr-catalyzed hydroalumination reaction of alkenes mentioned earlier involves addition of Zr and H to alkenes followed by transmetalation.¹⁸ (5) Finally, the Ziegler-Natta polymerization reaction is generally thought to involve addition of carbon-transition metal bonds containing Ti or Zr.⁹ All these either strongly support or are consistent with the mechanism shown in Scheme III.

To further scrutinize the above-suggested mechanism, however, we investigated the reaction of 1-heptyne with Me₃Al-Me₂ZrCp₂, Me₃Al-Cl(Me)ZrCp₂, Me₃Al-Cl₂ZrCp₂, Me₂AlCl-Cl₂ZrCp₂, or MeAlCl₂-Cl₂ZrCp₂. The results summarized in Table II indicate that, although the MeAlCl₂-Cl₂ZrCp₂ reagent system did not give the expected carbometalation products, the other four Al-Zr reagent systems did induce the expected Zr-catalyzed carboalumination. The rates and product yields observed with Me₃Al-Cl₂ZrCp₂ and Me₃Al-Cl(Me)ZrCp₂ were very similar. We then examined by ¹H NMR those Al-Zr reagent systems that gave the expected carbometalation products. In sharp contrast with Me₃Al-Cl₂ZrCp₂, which showed two broad Cp signals at δ 6.45 and 6.25 for Cl₂ZrCp₂ and Cl(Me)ZrCp₂, respectively, at ambient temperature (ca. 35 °C), the Cp signals of Me₂AlCl-Cl₂ZrCp₂ and Me₃Al-Cl(Me)ZrCp₂ were sharp (half-width \approx 2 Hz) at δ 6.45 and 6.24, respectively, with no sign of Me-Cl exchange over the temperature range of -50 to 80 °C. Therefore, Me-Cl exchange is not required for the carboalumination reaction. Furthermore, the fact that the Me₂AlCl-Cl₂ZrCp₂ system without a methyl group bonded to Zr induced the desired carboalumination reaction cast a serious doubt upon the Al-assisted Zr-C bond addition mechanism shown in Scheme III and suggested that the reaction must involve Zr-assisted direct addition of Al-C bond to simple terminal alkynes, such as shown in eq 9.



To further probe the critical question of Al-assisted Zr-C bond addition vs. Zr-assisted Al-C bond addition, we reacted 1-heptyne with a 1:1 mixture of Et₃Al and Cl(Me)ZrCp₂ and found that the reaction produced, after protonolysis, a ca. 70:30 mixture of 2-ethyl-1-heptene and *trans*-3-nonene in 93% combined yield. No more than traces, if any, of the methylmetalated products were detected (eq 10). The results are consistent with direct carboalumination but appear to be inconsistent with direct carbozirconation.



To rule out any special effect due to the difference between Me and Et, we then ran the reaction of 1-heptyne with a 1:1 mixture of Me₃Al and CD₃(Cl)ZrCp₂ prepared by the reaction of Cl₂ZrCp₂ with 2 equiv of CD₃MgI followed by treatment with 1.5 equiv of PbCl₂ in benzene for 1 h at room temperature. The product obtained in 95% GLC yield (ca. 80% by isolation) after iodination was stereochemically \geq 98% pure (*E*)-1-iodo-2-

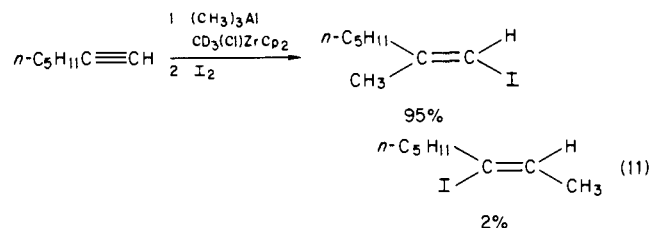
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Table III. The Effect of Solvent upon the Rate of the Reaction^a of Phenylacetylene with Me₃Al-Cl₂ZrCp₂

time, h	yield ^b of 2-phenylpropene, %		
	in benzene	in chlorobenzene	in 1,2-dichloroethane
0.5	5		44
1		19	52
2	9		65
3		24	
4	12		79
18	40	58	98

^aAll reactions were run at 30.00 ± 0.02 °C. ^bBy GLC.

methyl-1-heptene contaminated with a small amount (2%) of (Z)-3-iodo-2-octene. The extent of deuterium incorporation was <4% (eq 11).



In summary, the Zr-catalyzed carboalumination reaction of typical terminal alkynes involves Zr-assisted direct Al-C bond addition, one plausible scheme being that shown in eq 9. However, the reaction of Cl(Me)ZrCp₂ with *n*-PrC≡CAlMe₂ shown in eq 8 must be a genuine, albeit special, example of Al-assisted direct carbozirconation of alkynes. Consequently, we must now view that Al-Zr reagent systems may undergo either Zr-assisted Al-C bond addition or Al-assisted Zr-C bond addition, depending on the reaction parameters involved. This reversible relationship between two coordinatively unsaturated species containing Al and Zr suggests that the electronegativities of these two metals are comparable. The Pauling electronegativity values²² for Al and Zr are 1.5 and 1.4, respectively. More relevant, albeit only qualitative, is the fact that the reaction of Me₃Al with Cl₂ZrCp₂ to give Me₂AlCl and Cl(Me)ZrCp₂ is a reversible equilibrium process. We also note that the reaction of chlorobis(cyclopentadienyl)(1-alkenyl)zirconium with AlCl₃ or R₂AlCl involves clean transfer of the alkenyl group from Zr to Al,²¹ while the reaction of (1-alkenyl)trialkylalanes with Cl₂ZrCp₂ involves clean transfer of the alkenyl group from Al to Zr.²³ These experimental findings indicate that Al and Zr indeed possess comparable electronegativity values and suggest that polarization between these two metals via three-center two-electron bonding may occur in either direction.

Finally, the presumed significance of polarization in reactive intermediates, such as Me₂Al^{δ+}...Cl...Zr^{δ-}Cp₂MeCl, was probed by examining the effect of solvent on the rate of reaction. As the experimental data summarized in Table III indicate, the rate of the reaction of phenylacetylene with Me₃Al-Cl₂ZrCp₂ in 1,2-dichloroethane (ε = 10.37), chlorobenzene (ε = 5.61), and benzene (ε = 2.27) decreases as the dielectric constant of solvent²⁴ decreases.

One intriguing aspect of the Zr-catalyzed carboalumination of alkynes is that the reaction is a strictly controlled single-stage process. This, at first sight, was highly puzzling, since the majority of known reactions of alkenyldialkylalanes involve selective alkenyl transfer.²⁵ On this basis, one might expect that oligomerization and polymerization of alkynes involving a series of alkenyl transfer should occur preferentially. However, it is well established that both trialkylalanes and alkenyldialkylalanes exist as bridged dimers

except in strongly donating solvents⁵ and that alkenyl bridging leads to formation of more strongly bridged dimers than alkyl bridging. During the carboalumination reaction, e.g., the reaction of 1-octyne with Me₃Al and Cl₂ZrCp₂, there is an *intermolecular* competition for Cl₂ZrCp₂ and an alkyne between Me₃Al and 1-alkenyldimethylalane, both of which exist as dimers and must dissociate for their interaction with Cl₂ZrCp₂ and the alkyne. If their dissociation is a controlling factor, Me₃Al should win over the alkenylalane. On the other hand, if the competition between Me and an alkenyl group were *intramolecular*, the same factor, i.e., the greater bridging ability and hence greater transferability of the alkenyl group relative to Me, should now favor alkenyl transfer.

To test the above rationalization, (*E*)-1-octenyldiisobutylalane was generated by the reaction of 1-octyne with 1 equiv of *i*-Bu₂AlH. Its treatment with 1-octyne and Cl₂ZrCp₂ in 1,2-dichloroethane gave, after protonolysis, (*E*)-2-(*n*-hexyl)-1,3-decadiene in 25% yield,²⁶ indicating that, in the absence of competition with a trialkylalane, alkenylmetalation can indeed take place.

Development of a Modified Carboalumination Procedure. As mentioned earlier, one of the difficulties in the Zr-catalyzed carboalumination reaction with alkylalanes containing β-hydrogens was competitive hydrometalation. The results presented in the preceding sections indicate that, whereas the carbometalation reaction does not require alkyl transfer from Al to Zr, the hydrometalation reaction does.¹⁸ It was therefore reasonable to think that the undesirable hydrometalation could be avoided, if an Al-Zr system that does not undergo alkyl-Cl exchange was used. The ¹H NMR spectrum of a 1:1 mixture of *n*-Pr₃Al and Cl₂ZrCp₂, which had been shown to induce partial hydrometalation, in 1,2-dichloroethane at ambient temperature showed two Cp signals at δ 6.44 and 6.21 with comparable areas. The presence of more than one kind of *n*-Pr groups was also evident. On the other hand, the ¹H NMR spectrum of a 1:1 mixture of *n*-Pr₂AlCl and Cl₂ZrCp₂ under comparable conditions exhibited only one sharp Cp signal at δ 6.45 along with a well-defined set of a triplet (*J* = 7.5 Hz) at δ -0.05, a triplet (*J* = 7.5 Hz) at δ 0.90, and a triplet of quartet (*J* = 7.5 Hz) at δ 1.43. As expected, the reaction of 1-heptyne with *n*-Pr₂AlCl and Cl₂ZrCp₂ in a 1:1:1 ratio in 1,2-dichloroethane at room temperature produced, after protonolysis, 2-(*n*-propyl)-1-heptene and (*E*)-4-decene in 76 and 21% yields, respectively, with no indication of hydrometalation.

Conclusions

The Zr-catalyzed carboalumination reaction of alkynes with a methylalane and a zirconocene derivative, e.g., Cl₂ZrCp₂, provides a convenient and selective route to (*E*)-2-methyl-1-alkenyralanes in high yields. The stereoselectivity is generally >98%, and the regioselectivity observed with terminal alkynes is typically ca. 95%. (*E*)-2-Methyl-1-alkenyralanes have proven to be versatile intermediates for the preparation of a wide variety of trisubstituted alkenes that are potentially useful in the synthesis of terpenoids and other natural products. Thus, the Al moiety of (*E*)-2-methyl-1-alkenyralanes can be readily replaced with H,^{1a} D,^{1a} I,¹⁷ Hg,²⁷ B,²³ Zr,²³ various one-carbon groups,²⁸ such as hydroxymethyl, methoxymethyl, carboxyl, and carbethoxy, two- and multicarbon groups, such as hydroxyethyl²⁹ and γ-oxoalkyl,²³ alkyl,³⁰ homoallyl,³⁰ homobenzyl,³¹ homopropargyl,³⁰ allyl,³² benzyl,³³ aryl,³⁴ alkenyl,³⁴ alkynyl,³⁴ heteroaryl,³⁵ and acyl³⁶ groups.

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Several proximal heterofunctional groups,³⁷ such as Me₃Si,³⁸ OH, OSiMe₂Bu-*t*, SPh, Br, and I, in the propargylic and/or homopropargylic positions can be tolerated.

The reaction has been applied to the synthesis of various natural products including geraniol,²⁸ farnesol,³⁰ monocyclofarnesol³⁹ (**5**), α -farnesene³² (**6**), dendrolasin^{29b} (**7**), vitamin A⁴⁰ (**8**), moku-palide^{29b} (**9**), brassinolide⁴¹ (**10**) and other brassinosteroids,⁴² milbemycin⁴³ (**11**), and verrucarins,⁴⁴ such as verrucarins J (**12**).

Although the reaction of alkynes with trialkylalanes containing β -hydrogens and Cl₂ZrCp₂ is complicated by (i) competitive hydrometalation and (ii) diminished (70–80%) regioselectivity, the hydrometalation reaction can be avoided by using chlorodi-alkylalanes and Cl₂ZrCp₂. More recent results indicate that allylaluminum and benzylaluminum can also be promoted by Cl₂ZrCp₂.¹

The Zr-catalyzed carboalumination reaction of typical alkynes, such as phenylacetylene and 1-octyne, most likely involves direct Al–C bond addition assisted by Zr. The greater stability of the alkenyl-bridged carbometalation products relative to trialkylalane reagents is thought to make the former much less reactive than the latter. This, in turn, is believed to be responsible for the strictly controlled single-stage nature of the reaction.

Experimental Section

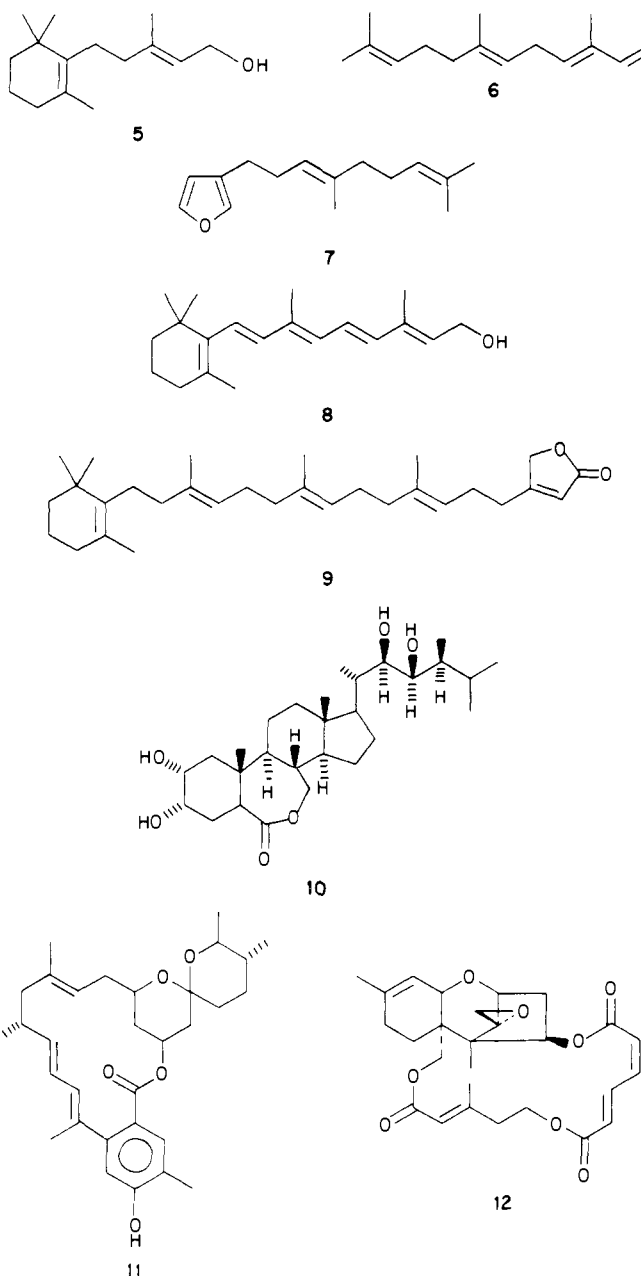
General. All organometallic reactions were run under an inert atmosphere of nitrogen. Unless otherwise stated, chemicals were used as received. Tetrahydrofuran (THF) was dried with sodium and benzophenone and distilled as needed. In some experiments, 1,2-dichloroethane, methylene chloride, benzene, and hexane were dried by distillation from P₂O₅. Trimethylalane, triethylalane, and triisobutylalane were obtained in metal cylinders from Ethyl Corp. Tri(*n*-propyl)alane was obtained from Alfa Chemical Co. Gas-liquid chromatographic analyses (GLC) were performed on SE-30 columns with appropriate linear and saturated hydrocarbons as internal standards. The GLC response factor of a compound against an internal standard was measured and used to calculate its amount in a reaction mixture.

The Reaction of Alkynes with Trimethylalane and Zirconocene Dichloride. The following procedures for the conversion of phenylacetylene into 2-phenylpropene and (*E*)-1-iodo-2-phenylpropene are representative of the preparation of 2-methyl-1-alkenes and (*E*)-1-iodo-2-methyl-1-alkenes via carbometalation, respectively.

(a) **2-Phenylpropene.** To a suspension of Cl₂ZrCp₂ (2.92 g, 10 mmol) in 1,2-dichloroethane (25 mL) was added Me₃Al (1.44 g, 1.92 mL, 20 mmol) (pyrophoric!) under nitrogen at room temperature. All Cl₂ZrCp₂ dissolved within 10–15 min to give a lemon-yellow solution. To this was added 1.02 g (1.11 mL, 10 mmol) of phenylacetylene at room temperature. After being stirred for 24 h, the reaction mixture was quenched by adding 2 mL of water followed by 25 mL of petroleum ether (30–60 °C). The organic layer was separated by filtration, and the filter cake was thoroughly extracted with ether (4 × 10 mL). The combined organic layers were dried over MgSO₄ and distilled to give 1.00 g (85%) of a 96:4 mixture of 2-phenylpropene and (*E*)-1-phenylpropene. In another run, the reaction mixture was analyzed by GLC (SE-30) after addition of a hydrocarbon internal standard and quenching as above. The combined yield of the two compounds by GLC was 98%. The two products were identified by GLC coinjection with commercially available authentic samples.

(b) **(*E*)-1-Iodo-2-phenylpropene.** To the reaction mixture obtained above was added 3.04 g (12 mmol) of iodine dissolved in 15 mL of THF

Chart I



at 0 °C. After the iodine color faded, the reaction mixture was quenched with water-ether. The organic layer was separated, washed with aqueous Na₂S₂O₃, dried over MgSO₄, filtered, and distilled to give 1.79 g (73%, 83% by GLC) of (*E*)-1-iodo-2-phenylpropene: bp 72.5 °C (0.55 run); IR (neat) 3020 (m), 1585 (m), 1485 (m), 1430 (s), 1365 (m), 1285 (m), 1195 (s), 1025 (m), 793 (m), 745 (s), 692 (s) cm⁻¹; ¹H NMR (CDCl₃, Me₄Si) δ 2.27 (d, *J* = 1.5 Hz, 3 H), 6.45–6.6 (q, *J* = 1.5 Hz, 1 H), 7.30 (s, 5 H); stereoisomer purity >98%; regioisomeric purity \geq 97%. Anal. Calcd for C₉H₉I: C, 44.29; H, 3.72. Found: 44.22; H, 3.87.

(c) **(*E*)-1-Iodo-2-methyl-1-hexene.** The carbometalation reaction was carried out for 3 h as described above. Examination of the protonolysis product by GLC indicated the formation of 2-methyl-1-hexene and 2-heptene in 95–100% combined yield in a 95:5 ratio. Iodolysis according to the representative procedure gave the title compound in 85% yield (GLC). The ratio of the two regioisomeric products was 97:3. The product isolated by distillation yielded the following data: bp 42–43 °C (1.3 mmHg); n_D²⁰ 1.5104; ¹H NMR (CCl₄, Me₄Si) δ 0.90 (t, *J* = 6 Hz, 3 H), 1.1–1.6 (m, 4 H), 1.85 (s, 3 H), 2.21 (t, *J* = 7 Hz, 2 H), 5.84 (m, 1 H).

(*E*)-1-Iodo-2-methyl-1-hexene (5 mmol) was treated at –60 °C with *n*-BuLi (6 mmol) in THF. The reaction mixture was warmed to room temperature over 1–2 h and quenched with aqueous NH₄Cl. The organic layer was washed with aqueous NaHCO₃, dried over MgSO₄, and distilled to give stereochemically >98% pure (*E*)-5-methyl-5-decene: ¹H NMR (CDCl₃, Me₄Si) δ 0.7–1.1 (m, 6 H), 1.1–1.5 (m, 8 H), 1.60 (s,

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3 H), 1.8–2.3 (m, 4 H), 5.10 (t, $J = 7$ Hz, 1 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.11, 15.88, 22.62, 27.89, 30.58, 32.46, 39.75, 124.81, 135.06.

(d) **(E)-1-Iodo-2-methyl-1-heptene**. This compound was prepared in the same manner as that for the preparation of (E)-1-iodo-2-methyl-1-hexene: yield 83% (GLC); stereoisomeric purity by ^{13}C NMR >98%; regioisomeric purity 98%; $n_{\text{D}}^{25.5}$ 1.5063; ^1H NMR (CCl_4 , Me_4Si) δ 0.87 (t, $J = 6$ Hz, 3 H), 1.1–1.6 (m, 6 H), 1.80 (s, 3 H), 2.20 (t, $J = 7$ Hz, 2 H), 5.84 (m, 1 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.01, 22.45, 23.79, 27.42, 31.24, 39.55, 74.51, 147.74.

(e) **2-Methyl-1-octene**. The reaction of 1-octyne with $\text{Me}_3\text{Al}-\text{Cl}_2\text{ZrCp}_2$ was carried out for 3 h at room temperature following the representative procedure. After the mixture was quenched with water, a 94:6 mixture of 2-methyl-1-octene and (E)-2-nonene was obtained in 95–100% yield (GLC): ^1H NMR (CCl_4 , Me_4Si) δ 0.60–2.20 (m, 13 H), 1.63–1.77 (br s, 3 H), 4.50–4.77 (br s, 2 H), 5.20–5.47 (m, 2 H).

(f) **(E)-1-Iodo-2-methyl-1-octene**. This compound was prepared in the same manner as that for the preparation of (E)-1-iodo-2-methyl-1-hexene: yield by isolation 81%; bp 52–54 °C (0.2 mmHg); 3060 (w), 1617 (w), 1460 (m), 1375 (m), 1270 (m), 1140 (m), 765 (m), 665 (m) cm^{-1} ; ^1H NMR (CDCl_3 , Me_4Si) δ 0.90 (t, $J = 6$ Hz, 3 H), 1.1–1.7 (m, 8 H), 1.84 (s, 3 H), 2.22 (t, $J = 7$ Hz, 2 H), 5.88 (br s, 1 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.97, 22.48, 23.74, 27.64, 28.66, 31.53, 39.52, 74.29, 147.96. Anal. Calcd for $\text{C}_9\text{H}_{17}\text{I}$: C, 42.87; H, 6.80. Found: C, 43.24; H, 6.99.

(g) **(E)-1-Iodo-2,3-dimethyl-1,3-butadiene**. This compound was prepared in 70% yield according to the representative procedure: bp 56 °C (25 mmHg); $n_{\text{D}}^{25.5}$ 1.5684; ^1H NMR (CCl_4 , Me_4Si) δ 1.95 (s, 3 H), 2.06 (s, 3 H), 4.9–5.15 (m, 2 H), 6.41 (s, 1 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 20.84, 22.18, 81.46, 113.82, 142.29, 146.34.

(h) **(E)-1-Iodo-2,6-dimethyl-1,5-heptadiene**. This compound was prepared in 72% yield (79% by GLC) according to the representative procedure: bp 54–55 °C (0.55 mmHg); ^1H NMR (CCl_4 , Me_4Si) δ 1.60 (s, 3 H), 1.67 (s, 3 H), 1.80 (s, 3 H), 2.0–2.4 (m, 4 H), 4.8–5.2 (m, 1 H), 5.80 (s, 1 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 17.68, 23.92, 25.68, 26.41, 39.50, 74.88, 123.09, 132.08, 147.46. Anal. Calcd for $\text{C}_9\text{H}_{17}\text{I}$: C, 43.22; H, 6.04. Found: C, 43.50; H, 6.09. The stereoselectivity was >98%. Examination by GLC of the protonolysis product indicated that the yield of the protonolysis product was 95% and that the regioselectivity was 95%.

(i) **(Z)-5-Methyl-5-decene**. This compound was prepared from 5-decyne in a manner similar to the representative example, except that the reaction mixture was heated for 6 h at 50 °C. After protonolysis a 97:3 mixture of (Z)- and (E)-5-methyl-5-decenes was obtained in 89% yield by GLC: (^{188}D) 1.4350; IR (neat) 2970 (w), 2830 (s), 1455 (s), 1370 (m), 835 (m) cm^{-1} ; ^1H NMR (CCl_4 , Me_4Si) δ 0.47–2.40 (m, 18 H), 1.60–1.70 (s, 3 H), 4.83–5.27 (br t, $J = 7$ Hz, 1 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.14, 22.68, 22.94, 23.47, 27.76, 30.63, 31.76, 32.66, 125.51, 135.33. The stereoselectivity of 97% was determined by the intensity ratio of peaks at 125.51 and 124.80 ppm. No allenic product¹¹ was detected.

(j) **(Z)-1,2-Diphenylpropene**. Diphenylacetylene was treated with $\text{Me}_3\text{Al}-\text{Cl}_2\text{ZrCp}_2$ for 48 h at 50 °C. After hydrolysis, GLC examination indicated the presence of the title compound¹¹ in 30% yield along with a mixture of unidentified byproducts having longer GLC retention times (SE-30).

Reaction of Phenylacetylene with Chloro(methyl)bis(cyclopentadienyl)zirconium. Chloro(methyl)bis(cyclopentadienyl)zirconium was prepared according to the procedure of Surtees.¹³ Phenylacetylene (5 mmol) was mixed with $\text{Cl}(\text{Me})\text{ZrCp}_2$ (5 mmol) in 1,2-dichloroethane at room temperature. No consumption of phenylacetylene was observed within 24 h at this temperature.

Reaction of Phenylacetylene with Trimethylalane in the Presence of a Catalytic Amount of Zirconocene Dichloride. This reaction was carried out in a manner similar to that described above for the preparation of 2-phenylpropene except that only 10 mol % of Cl_2ZrCp_2 was used. The yields of the protonolysis product at 24 and 48 h were 60 and 85%, respectively, by GLC.

(E)-1-Deuterio-2-phenylpropene. The reaction of phenylacetylene with $\text{Me}_3\text{Al}-\text{Cl}_2\text{ZrCp}_2$ was carried out as described earlier for the preparation of 2-phenylpropene. Quenching the reaction mixture with D_2O (100.0 atom %) produced the title compound in 98% yield by GLC. The product was isolated according to the representative procedure: ^1H NMR (CCl_4 , Me_4Si) δ 2.10 (s, 3 H), 5.27 (s, 1 H), 7.0–7.5 (m, 5 H). In addition to these signals, a finely split multiplet centered at δ 5.00, which corresponds to the terminal vinyl proton trans to phenyl,¹⁶ was also present. The integration ratio of the peaks at δ 5.27 and 5.00 was 96:4.

(Z)-1-Deuterio-2-phenylpropene. 2-Deuterio-1-phenylacetylene was prepared by treatment of phenylacetylene with *n*-BuLi followed by addition of D_2O (100.0 atom %). The isotopic purity of the compounds was estimated to be >99% by ^1H NMR. Its reaction with $\text{Me}_3\text{Al}-\text{Cl}_2\text{ZrCp}_2$ and product isolation were carried out according to the representative

procedure. The ^1H NMR spectrum of the product showed a finely split multiplet centered at δ 5.00 in addition to the methyl and phenyl proton signals at 2.10 and 7.0–7.5, respectively. The signal at δ 5.27 was <2% of that at δ 5.00. Therefore, the stereoisomeric purity of the compound was >98%.

Conversion of (E)-1-Iodo-2-phenylpropene into (E)-1-Deuterio-2-phenylpropene. (E)-1-Iodo-2-phenylpropene was treated with 1.5 equiv of *n*-BuLi in ether for 30 min at 60 °C and quenched at this temperature with an excess of D_2O . The ^1H NMR spectrum of the product was virtually identical with that of an authentic sample obtained above. The stereochemical purity was 96%.

Examination by ^1H NMR of (E)-(2-Phenyl-1-propenyl)dimethylalane. The reaction of phenylacetylene with $\text{Me}_3\text{Al}-\text{Cl}_2\text{ZrCp}_2$ was carried out in a manner similar to that for the representative case except that CH_2Cl_2 was used as solvent. The solvent and the residual Me_3Al were evaporated at 50 °C (<1 mmHg). The cooled residue was extracted with pentane, and the pentane was evaporated in vacuo. The residue was dissolved in CH_2Cl_2 and examined by ^1H NMR. There was no signal assignable to Cl_2ZrCp_2 . No zirconium compound appeared to be present. Two signals at δ 2.35 and 1.93 showed an integration ratio of 95:5. Since protonolysis of this mixture gave 2-phenylpropene and (E)-1-phenylpropene in a 95:5 ratio, the two signals mentioned above were assigned to the allylic protons of the title compound and its regioisomer.

Reaction of 1-Octyne with Tri(*n*-propyl)alane and Zirconocene Dichloride. To a suspension of 2.92 g (10 mmol) of Cl_2ZrCp_2 in 25 mL of 1,2-dichloroethane was added 3.81 mL (20 mmol) of *n*- Pr_3Al at 0 °C under nitrogen. After all Cl_2ZrCp_2 had dissolved (10 min), 1.50 mL (10 mmol) of 1-octyne was added at 0 °C. The reaction mixture was stirred at room temperature for 1 h and quenched with 2 mL of water. Examination by GLC indicated that the mixture contained 2-(*n*-propyl)-1-octene (52%), (E)-4-undecene (13%), and 1-octene (30%) which were formed in yields indicated in parentheses. After working up the mixture as described for the preparation of 2-phenylpropene, distillation gave an 80:20 mixture of 2-(*n*-propyl)-1-octene and (E)-4-undecene identified spectroscopically as a mixture: IR (neat) 3050 (w), 2900 (s), 1635 (w), 1450 (m), 1370 (w), 888 (s) cm^{-1} ; ^1H NMR (CDCl_3 , Me_4Si) δ 0.89 (t, $J = 7$ Hz, 6 H), 1.1–1.7 (m, 8 H), 1.99 (t, $J = 7$ Hz, 4 H), 4.69 (t, $J = 1$ Hz, 1.6 H), 5.2–5.5 (m, 0.4 H). The integration ratio of two peaks at δ 4.69 and 5.2–5.5 was 80:20, indicating that the product consisted of an 80:20 mixture of 2-(*n*-propyl)-1-octene and (E)-4-undecene.

Reaction of 1-Octyne with Triisobutylalane and Zirconocene Dichloride. Triisobutylalane (1.26 mL, 5 mmol) was added to a suspension of Cl_2ZrCp_2 (0.73 g, 2.5 mmol) in 4 mL of benzene at 0 °C. To a resultant yellow solution was added 0.37 mL (2.5 mmol) of 1-octyne at 0 °C. After 20 min, the reaction mixture was quenched with 3 N HCl. Examination by GLC indicated the formation of 1-octene and *n*-octane in 51 and 44% yields, respectively, with no more than a trace of 1-octyne remaining unreacted.

Preparation of 3 by the Reaction of 1-Pentynylidimethylalane with Chloro(methyl)bis(cyclopentadienyl)zirconium. 1-Pentynylidimethylalane was prepared by successive treatment of 1-pentyne with *n*-BuLi in hexane and Me_2AlCl in benzene, the latter of which was generated in situ by mixing Me_3Al and AlCl_3 in a 2:1 ratio in benzene. To 0.73 g (2.68 mmol) of $\text{Cl}(\text{Me})\text{ZrCp}_2$ in 3 mL of CH_2Cl_2 was added 0.33 g (2.68 mmol) of 1-pentynylidimethylalane in 3 mL of CH_2Cl_2 at room temperature for 3 h. The reaction mixture containing 3 was used for the following three experiments.

(a) **2-Methyl-1-pentene.** The reaction mixture prepared as described above was quenched with 3 N HCl. After the mixture was washed with aqueous NaHCO_3 , analysis by GLC indicated that 2-methyl-1-pentene, identified by coinjection with an authentic sample, was formed in 95% yield.

(b) **1,1-Diiodo-2-methyl-1-pentene.** The preparation of 3 was carried out on a 5 mmol scale as above. To this was added 2.79 g (11 mmol) of iodine in 5 mL of THF at –78 °C. The reaction mixture was warmed to room temperature and successively treated with water and pentane. The organic layer was treated with 3 N HCl and washed successively with aqueous solutions of NaHCO_3 and $\text{Na}_2\text{S}_2\text{O}_3$ and then with water. After the solution was dried over MgSO_4 , distillation provided the title compound in 60% yield. Its GLC yield was 92%. The compound exhibited the following data: IR (neat) 3000 (s), 1590 (w), 1450 (s), 1185 (m), 1095 (m), 750 (s), 735 (m), 725 (m) cm^{-1} ; ^1H NMR (CDCl_3 , Me_4Si) δ 0.93 (t, $J = 7$ Hz, 3 H), 1.15–1.65 (m, 2 H), 1.95 (s, 3 H), 2.31 (t, $J = 7$ Hz, 2 H).

(c) **Direct Identification of 3.** Evaporation of the volatile compounds off the reaction mixture containing 3 provided orange yellow crystals which were washed with a small amount of hexane. The compound yielded the following data: IR (CH_2Cl_2) 3060 (m), 2950 (s), 2300 (m), 1560 (m), 1450 (s), 1260 (s), 1030 (s), 900 (s), 800 (s) cm^{-1} ; ^1H NMR (C_6H_6 , Me_4Si) δ –0.31 (s, 6 H), 0.90 (t, $J = 7$ Hz, 3 H), 1.10–1.60 (m,

Table IV. Variable-Temperature ^1H NMR Spectra of $\text{Me}_3\text{Al}-\text{Cl}_2\text{ZrCp}_2$

temp, °C	relative integration, ^a % (half-width, ^b Hz)		Me signals			
	Cp ^c of Cl_2ZrCp_2	Cp ^d of $\text{Cl}(\text{Me})\text{ZrCp}_2$	chem shift, ppm	rel integration, ^a % (half-width, Hz)	chem shift, ppm	rel integration, ^a % (half-width, Hz)
35		98 ^e (7)	-0.42	99 (6)		
0	78 (3)	21 (6)	-0.46	93 (4)	0.24	7 (14)
-30	76 (2)	24 (3)	-0.47	94 (4)	0.25	6 (6)
-50	77 (2)	22 (2)	-0.43	94 (7)	0.32	6 (2)

^a Relative to the Cp protons of Cl_2ZrCp_2 initially introduced. ^b The half-width of benzene is 2 Hz. ^c δ 6.46. ^d δ 6.25. ^e With a shoulder of the Cp signal due to $\text{Cl}(\text{Me})\text{ZrCp}_2$.

Table V. Variable-Temperature ^1H NMR Spectra of $\text{Me}_3\text{Al}-\text{Me}_2\text{ZrCp}_2$

temp, °C	Cp of Me_2ZrCp_2		Me signals					
	chem shift, ppm	rel integration, ^a % (half-width, ^b Hz)	chem shift, ppm	rel integration, ^a % (half-width, ^b Hz)	chem shift, ppm	rel integration, ^a % (half-width, ^b Hz)	chem shift, ppm	rel integration, ^a % (half-width, ^b Hz)
80	6.09	97 (2)	-0.73	20 (2)	-0.35	73 (2)		
35	6.00	97 (2)	-0.97	20 (2)	-0.57	83 (3)		
0	6.00	98 (2)	-0.96	17 (2)	-0.58	41 (2)	-0.48	44 (2)
-30	6.02	98 (2)	-0.91	19 (2)	-0.53	40 (2)	-0.42	40 (4)
-50	6.02	100 (2)	-0.91	22 (2)	-0.54	41 (2)	-0.44	40 (20)

^a Relative to the Cp or Me protons of Me_2ZrCp_2 and Me_3Al initially introduced. ^b The half-width of benzene is 2 Hz.

2 H), 1.42 (s, 3 H), 2.04 (t, $J = 7$ Hz, 2 H), 5.68 (s, 10 H); ^{13}C NMR (C_6D_6 , Me_2Si) δ -0.32, -0.43, 14.10, 22.45, 28.12, 44.39, 106.92, 109.57, 153.09. Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{AlClZr}$: C, 54.59; H, 6.62. Found: C, 53.98; H, 6.37.

Examination by ^1H NMR of the Reaction of Methylalanes with Zirconocene Derivatives. A 1:1 mixture of an organoalane and a zirconocene derivative dissolved in 1,2-dichloroethane (ca. 2.5 M) was examined by ^1H NMR with benzene as an internal standard.

(a) $\text{Me}_3\text{Al}-\text{Cl}_2\text{ZrCp}_2$. The two reagents were mixed at room temperature. Examination by variable-temperature ^1H NMR provided the data summarized in Table IV. There was no sign of the formation of Me_2ZrCp_2 .

In a separate experiment, Me_3Al and Cl_2ZrCp_2 were mixed in a 2:1 molar ratio in 1,2-dichloroethane: ^1H NMR ($\text{ClCH}_2\text{CH}_2\text{Cl}$) δ -0.31 (br s, 18 H), 6.40 (br s, 10 H). This mixture was treated with THF (1 equiv relative to Me_3Al): ^1H NMR ($\text{ClCH}_2\text{CH}_2\text{Cl}$, THF) δ -0.95, -0.73, and +0.25 (sharp s, 18 H), 6.22 and 6.45 (sharp s, 10 H). The relative integration ratio of the three high-field signals was approximately 12:4:2, and that of the two Cp signals shown above was approximately 2:1.

(b) $\text{Me}_3\text{Al}-\text{Me}_2\text{ZrCp}_2$. The preparation of Me_2ZrCp_2 was performed as reported in the literature.¹⁴ Variable-temperature ^1H NMR spectra of $\text{Me}_3\text{Al}-\text{Me}_2\text{ZrCp}_2$ are summarized in Table V.

(c) $\text{Me}_3\text{Al}-\text{Cl}(\text{Me})\text{ZrCp}_2$. Variable-temperature ^1H NMR spectra of $\text{Me}_3\text{Al}-\text{Cl}(\text{Me})\text{ZrCp}_2$ were taken over the range of -50 to 80 °C. The only Cp signal at δ 6.20-6.24 remained sharp with a half-width of 2 Hz. A peak assignable to the Me group of $\text{Cl}(\text{Me})\text{ZrCp}_2$ also remained sharp (half-width 2 Hz) over the range of -50 to 35 °C, although its chemical shift drifted from δ 0.21 at -50 °C to δ 0.33 at 35 °C. Above 35 °C this signal gradually broadened to 12 Hz (half-width) at 80 °C. Two other relatively sharp peaks (half-width 2-3 Hz) appeared at δ -0.55 (-50 °C) to -0.35 (80 °C) and -0.91 (-50 °C) to -0.69 (80 °C) with an integration ratio of 2:1 to 3:1.

(d) $\text{Me}_2\text{AlCl}-\text{Cl}_2\text{ZrCp}_2$. The ^1H NMR spectrum of $\text{Me}_2\text{AlCl}-\text{Cl}_2\text{ZrCp}_2$ in 1,2-dichloroethane at ambient temperature exhibited two sharp peaks (half-width 2 Hz) at δ -0.38 and 6.46. No other peaks were discernible.

Reaction of 1-Heptyne with Methylalane-Zirconocene Derivative Reagent Systems. 1-Heptyne (5 mmol) was treated at room temperature (22-25 °C) with an Al-Zr reagent system consisting of 5 mmol each of a methylalane and a zirconocene derivative in 1,2-dichloroethane. The progress of the reaction was monitored by GLC analysis of the protonolysis and iodolysis products. The results are summarized in Table II. The 1-heptyne- $\text{Me}_3\text{Al}-\text{Cl}(\text{Me})\text{ZrCp}_2$ reaction mixture was also monitored by ^1H NMR. The Cp signal at δ 6.20 remained unchanged with respect to chemical shift, integration, and line shape (half-width) throughout the reaction.

Reaction of 1-Heptyne with Triethylalane and Chloro(methyl)bis(cyclopentadienyl)zirconium in a 1:1:1 Molar Ratio. Triethylalane (0.34 mL, 2.5 mmol) was added to 0.33 mL (2.5 mmol) of 1-heptyne and 0.68 g (2.5 mmol) of $\text{Cl}(\text{Me})\text{ZrCp}_2$ in 10 mL of 1,2-dichloroethane at room temperature. After 1 and 3 h, aliquots were quenched with 3 N HCl and analyzed by GLC, which indicated that 70:30 mixtures of 2-ethyl-1-

heptene and (*E*)-3-nonene were obtained in 81 and 93% yields, respectively. No more than traces, if any, of 2-methyl-1-heptene and its regioisomer were present. The same reaction was run on a 20-mmol scale. After the reaction mixture was worked up with a 3 N HCl, aqueous NaHCO_3 , and water, drying over MgSO_4 and distillation provided a 70:30 mixture of 2-ethyl-1-heptene and (*E*)-3-nonene: yield 1.64 g (65%); bp 70-27 °C (50 mmHg); ^1H NMR (CDCl_3 , Me_2Si) δ 0.90 and 1.01 (t, $J = 7$ Hz, 6 H), 1.2-1.6 (m, 6 H), 1.8-2.2 (m, 4 H), 4.70 (s, 1.4 H), and 5.3-5.5 (m, 0.6 H).

Reaction of 1-Heptyne with Trimethylalane and Chloro(trideuterio-methyl)bis(cyclopentadienyl)zirconium. (a) **Preparation of $(\text{CD}_3)_2\text{ZrCp}_2$.** The preparation of CD_3MgI was performed by treating CD_3I (4.35 g, 30 mmol) with 0.8 g of Mg (33 mmol) in 20 mL of ether at room temperature. The reaction of Cl_2ZrCp_2 (2.92 g, 10 mmol) suspended in 30 mL of ether with 15.2 mL (20 mmol) of 1.32 M of CD_3MgI in ether at room temperature for 1 h, followed by separation, extraction with hexane, and evaporation of the solvents, provided a white crystalline product. This was treated with benzene-hexane (1:5) at -20 °C, and the solid residue was filtered off. After evaporation of the solvents, $(\text{CD}_3)_2\text{ZrCp}_2$ was obtained in 90% yield (2.31 g): ^1H NMR (C_6H_6 , $\text{ClCH}_2\text{CH}_2\text{Cl}$) δ 5.73 (s, 10 H).

(b) **Preparation of $\text{Cl}(\text{CD}_3)_2\text{ZrCp}_2$.** To $(\text{CD}_3)_2\text{ZrCp}_2$ (231 g, 9 mmol) in 30 mL of benzene was added to 3.75 g (13.5 mmol) of PbCl_2 at room temperature. After 1 h, the reaction mixture was filtered through a sintered glass filter, and the filtrate was evaporated under reduced pressure to give the title compound in 80% yield (1.98 g): ^1H NMR (CDCl_3 , Me_2Si) δ 6.23 (s, 10 H); ^{13}C NMR (CDCl_3 , Me_2Si) δ 112.54.

(c) **Reaction of 1-Heptyne with Me_3Al and $\text{Cl}(\text{CD}_3)_2\text{ZrCp}_2$.** To a mixture of 0.86 mL (6.6 mmol) of 1-heptyne and $\text{Cl}(\text{CD}_3)_2\text{ZrCp}_2$ (6.6 mmol by ^1H NMR determination) in 26 mL of 1,2-dichloroethane was added 0.63 mL of Me_3Al at room temperature, and the reaction mixture was monitored at 1, 4, and 6 h by GLC. After 6 h, the mixture was quenched with 3.69 g (14.5 mmol) of iodine in 15 mL of ether at -10 °C. The organic layer and the pentane extract were combined, washed with 3 N HCl (100 mL), aqueous NaHCO_3 (100 mL), and water (2 \times 100 mL), dried over MgSO_4 , and distilled to give 1.25 g (80%) of a 98:2 mixture of (*E*)-1-iodo-2-methyl-1-heptene and 3-iodo-2-octene: IR (neat) 3055 (w), 2950 (s), 2920 (s), 2850 (s), 1612 (w), 1460 (s), 1370 (s), 1270 (s), 1135 (s), 760 (m), 660 (m) cm^{-1} ; ^1H NMR (CDCl_3 , Me_2Si) δ 0.87 (t, $J = 7$ Hz, 3 H), 1.1-1.6 (m, 6 H), 1.81 (s, 3 H), 2.20 (t, $J = 7$ Hz, 2 H), 5.84 (m, 1 H); ^{13}C NMR (CDCl_3 , Me_2Si) δ 14.00, 22.47, 23.79, 27.45, 31.27, 39.60, 74.45, 147.81.

The reaction of 1-heptyne with Me_3Al and $\text{Cl}(\text{CH}_3)_2\text{ZrCp}_2$ was run under the same reaction conditions as above. The IR as well as ^1H and ^{13}C NMR spectra of the two samples were virtually indistinguishable. However, comparison of the integrations of the allyl protons of the Me group and of the vinyl proton of the two samples indicated that the 2-Me group of the sample obtained by the 1-heptyne- $\text{Me}_3\text{Al}-\text{Cl}(\text{CD}_3)_2\text{ZrCp}_2$ reaction was of 96% isotopic purity.

Comparison of 1,2-Dichloroethane, Chlorobenzene, and Benzene in the Reaction of Phenylacetylene with Trimethylalane and Dichlorobis(cyclopentadienyl)zirconium. To a suspension of 0.585 g (2 mmol) of Cl_2ZrCp_2

in 10.0 mL of a solvent was added 0.384 mL (4 mmol) of Me_3Al . The reaction vessel is partially immersed in a constant-temperature bath ($30.00 \pm 0.02^\circ\text{C}$). After 5 h, phenylacetylene (0.222 mL, 2 mmol) was added. Aliquots were analyzed by GLC after quenching with 3 N HCl. The results were summarized in Table III.

Reaction of 1-Octyne with (*E*)-1-Octenyldiisobutylalane and Zirconocene Dichloride.²⁶ 1-Octyne (0.55 g, 5 mmol) in 5 mL of hexane was treated with 0.92 mL (5 mmol) of *i*- Bu_2AlH for 4 h at 50°C .²⁵ Hexane was evaporated under reduced pressure. To the residue were sequentially added 5 mL of 1,2-dichloroethane, 0.55 g (5 mmol) of 1-octyne, and Cl_2ZrCp_2 (1.46 g, 5 mmol). After 12 h at room temperature, the reaction mixture was worked up as described earlier for the representative case. Distillation provided 278 mg (25%) of crude (*E*)-2-(*n*-hexyl)-1,3-decadiene: IR (neat) 3090 (w), 3020 (m), 2900 (s), 1770 (w), 1640 (w), 1605 (m), 1450 (s), 1375 (m), 960 (s), 875 (s), 720 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , Me_4Si) δ 0.87 (t, 6 Hz, 6 H), 1.1-1.65 (m, 16 H), 1.8-2.3 (m, 4 H), 4.83 (s, 2 H), 5.65 (dt, $J = 16$ and 7 Hz, 1 H), 6.05 (d, 16 Hz, 1 H).

$^1\text{H NMR}$ Examination of Tri(*n*-propyl)alane and Zirconocene Dichloride. Tri(*n*-propyl)alane (0.474 mL, 2.5 mmol) and 0.73 g (2.5 mmol) of Cl_2ZrCp_2 were mixed in 10 mL of 1,2-dichloroethane at room temperature and examined 1 h later by $^1\text{H NMR}$, which showed the following signals: $^1\text{H NMR}$ ($\text{ClCH}_2\text{CH}_2\text{Cl}$, C_6H_6) δ 0.13 (t, $J = 7.5$ Hz, 6 H), 0.7-1.1 and 1.2-1.7 (m, 15 H), 6.21 (s, 5.2 H), 6.44 (s, 4.5 H). The integration ratio of the two peaks at δ 6.21 and 6.44 indicates that $\text{Cl}(\textit{n}\text{-Pr})\text{ZrCp}_2$ and Cl_2ZrCp_2 were present in a ratio of 54:46. The $^1\text{H NMR}$ spectra of *n*- Pr_3Al and *n*- Pr_2AlCl in 1,2-dichloroethane are as follows: $^1\text{H NMR}$ of *n*- Pr_3Al ($\text{ClCH}_2\text{CH}_2\text{Cl}$, Me_4Si) δ 0.13 (t, $J = 7.5$ Hz, 6 H), 0.90 (t, $J = 7.5$ Hz, 9 H), 1.2-1.7 (m, 6 H); $^1\text{H NMR}$ of

n- Pr_2AlCl ($\text{ClCH}_2\text{CH}_2\text{Cl}$, Me_4Si) δ 0.25 (t, $J = 7.5$ Hz, 4 H), 0.92 (t, $J = 7.5$ Hz), 6 H), 1.2-1.7 (m, 4 H).

$^1\text{H NMR}$ Examination of Di(*n*-propyl)chloroalane and Zirconocene Dichloride. Di(*n*-propyl)chloroalane was generated by mixing 2 mmol of *n*- Pr_3Al and 1 mmol of AlCl_3 in 1,2-dichloroethane (3 mL). This solution was then added to 0.876 g (3.0 mmol) of Cl_2ZrCp_2 in 5 mL of 1,2-dichloroethane at room temperature. The following $^1\text{H NMR}$ spectrum did not show any change with time: $^1\text{H NMR}$ ($\text{ClCH}_2\text{CH}_2\text{Cl}$, Me_4Si) δ -0.05 (t, $J = 7.5$ Hz, 4 H), 0.90 (t, $J = 7.5$ Hz, 6 H), 1.43 (tq, $J = 7.5$ Hz, 4 H), 6.45 (s, 10 H). No other Cp signal was discernible.

Reaction of 1-Heptyne with Di(*n*-propyl)chloroalane and Zirconocene Dichloride. To a mixture of 0.262 mL (2.0 mmol) of 1-heptyne and 0.584 g (2.0 mmol) of Cl_2ZrCp_2 in 8 mL of 1,2-dichloroethane was added at room temperature *n*- Pr_2AlCl generated from 0.252 mL (1.33 mmol) of *n*- Pr_3Al and 0.089 g (0.67 mmol) of AlCl_3 in 2 mL of 1,2-dichloroethane. The progress of reaction was monitored by GLC examination of protonolyzed aliquots. The combined yields of 2-(*n*-propyl)-1-heptene and 4-decene were 36, 64, 76, and 97% after 1, 3, 6, and 20 h, respectively. The molar ratio of the two products at 20 h was 76:21. No more than a trace, if any, of 1-heptene was present.

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A New Approach to Polypropionates: Routes to Subunits of Monensin and Tirandamycin

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Abstract: Reactions of (*E,Z*)-1-methoxy-3-(trialkylsilyloxy)-1,3-pentadiene with various aldehydes under Lewis acid catalysis afford silyloxydihydropyrans. In a few relatively simple operations these products are converted to the title systems, thereby providing the basis for a straightforward and stereoselective route to polypropionates.

Background

It seemed possible that systems of type **1** might be useful for the synthesis of "polypropionates"¹ such as **2**. For such a plan to become a broadly applicable reality, several desiderata must be attained. First, the capacity to assemble the dihydropyran ring (**1**) in an efficient way with various substitution patterns is necessary.² Furthermore, a variety of options should be available for exercising stereochemical control in the fashioning of the pyranoid system and throughout the subsequent buildup of functionality as the cycle is being readied for disconnection. Finally, efficient methodology will be necessary for opening of the ring.

Before describing our results in realizing these goals, it is well to place the concept implied above in the broader context of strategies for the synthesis of acyclic arrays bearing stereogenic centers.³ The classical approach focused on algorithms, wherein

the stereochemically determinative steps were carried out in cyclic systems.⁴ It was thought that the rigidity of the ring structure conferred a predictability of behavior which was exploitable for achieving stereochemical control. More recently, significant progress has been realized in attaining high margins of topographic and facial selectivity in acyclic settings.⁵ As a consequence of

(3) For an excellent review of this area see: Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1. In this review Professor Masamune identifies a new strategy, that of reagent control as opposed to the more traditional approach of induction via prior substrate dissymmetry.

(4) A modern classic which is illustrative of the ring disconnection approach is the Woodward synthesis of erythromycin. This synthesis is critically analyzed in ref 3.

(5) (a) For the use of the Sharpless epoxidation in the solution of this type of problem see: Nagaoka, H.; Kishi, Y. *Tetrahedron* **1981**, *37*, 3873. (b) For approaches involving aldol strategies see: Masamune, S.; Imperiali, B.; Garvey, D. S. *J. Am. Chem. Soc.* **1982**, *104*, 5528. Heathcock, C. H. *Science (Washington D.C.)* **1981**, *214*, 395. Evans, D. A.; Nelson, J. V.; Taber, T. R. *Top. Stereochem.* **1982**, *13*, 1. Heathcock, C. H. In "Comprehensive Carbanion Chemistry"; Durst, T., Bunzel, E., Eds., Elsevier: Amsterdam, 1983; Vol. II. (c) For approaches involving acyclic hydroborations see: Kishi, Y. *Pure Appl. Chem.* **1981**, *53*, 1163. Still, W. C.; Barrish, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 2487. Evans, D. A.; Bartroli, J. *Tetrahedron Lett.* **1982**, 807.

(1) We use this term broadly to imply systems containing poly(2-alkyl-1,3-diols) or closely related systems. Such units are present in many macrolides and ionophores.

(2) Danishefsky, S.; Kerwin, J. F., Jr.; Kobayashi, S. *J. Am. Chem. Soc.* **1982**, *104*, 358.