

Multiple Mechanistic Pathways for Zirconium-Catalyzed Carboalumination of Alkynes. Requirements for Cyclic Carbometalation Processes Involving C–H Activation

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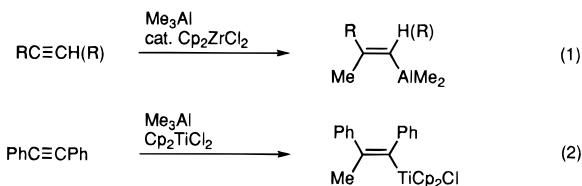
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Abstract: The reactions of internal and terminal alkynes with organoalanes containing Et, *n*-Pr, and *i*-Bu groups in the presence of Cp₂ZrCl₂ and MeZrCp₂Cl were investigated with the goal of clarifying mechanistic details of some representative cases. Three fundamentally different processes, *i.e.*, (i) C–M bond addition without C–H activation in the alkyl group, (ii) cyclic C–M bond addition via C–H activation, and (iii) hydrometalation, have been observed, and the courses of these reactions significantly depend on (i) the nature and number of alkyl groups in organoalanes, (ii) their amounts, and (iii) solvents. The reaction of alkynes with Et₃Al in the presence of 0.1 equiv of Cp₂ZrCl₂ in nonpolar solvents, *e.g.*, hexanes, proceeds via C–H activation to give the corresponding aluminacyclopentenes. Investigation of the reaction of 5-decyne with 1–3 equiv of Et₃Al and 1 equiv of Cp₂ZrCl₂, which gave mono-, di-, or trideuterated (*Z*)-5-ethyl-5-decene as shown in Scheme 10, together with the previously reported structural study on the reaction of Et₃Al with Cp₂ZrCl₂ leading to the formation of well-characterized bimetallic species **9**, **10**, and **11** (Scheme 11), supports a catalytic cycle involving bimetallic species **10** and **18** (Scheme 15). In summary, this process requires a zirconocene derivative containing one Zr-bound Et group which is linked to Et₃Al (but not to Et₂AlCl) through a Cl bridge, *i.e.*, **18**, to produce **10** via β C–H activation. In sharp contrast, the reaction of Et₂-AlCl–Cp₂ZrCl₂ as well as of (*n*-Pr)₂AlCl–Cp₂ZrCl₂ does not involve any C–H activation processes. It proceeds well in chlorinated hydrocarbon solvents, *e.g.*, (CH₂Cl)₂, but it is extremely sluggish in nonpolar solvents, *e.g.*, hexanes. The reaction may well involve direct C–Al bond addition to alkynes, as suggested earlier for Zr-catalyzed Me–Al bond addition to alkynes, but a few other alternatives cannot be ruled out on the basis of the currently available data. The reaction of alkynes with (*n*-Pr)₃Al–Cp₂ZrCl₂ in nonpolar solvents proceeds partially via C–H activation and partially via hydrometalation. In contrast with the C–H activation process observed with Et₃Al, that with (*n*-Pr)₃Al is totally dominated by dimerization of alkynes to give aluminacyclopentadienes rather than aluminacyclopentenes, reflecting a previously established generalization that propene can be much more readily displaced from Zr by alkynes than ethylene. Hydrometalation is the exclusive process with (*i*-Bu)₃Al–Cp₂ZrCl₂. This hydrometalation reaction, however, reveals a few interesting complications. Alkyl-substituted internal alkynes give double bond migrated products in addition to the expected hydrometalation products. With terminal alkynes the reaction produces the expected hydrometalation products and the 1,1-dimetalloalkanes in comparable yields. Various other related reactions involving other alkynes, *e.g.*, PhC≡CPh, *n*-OctC≡CH, and PhC≡CH, and other reagents, *e.g.*, Et₃Al–MeZrCp₂Cl, Et₂AlCl–MeZrCp₂Cl, and (*n*-Pr)₃Al–MeZrCp₂Cl, were also studied.

Introduction

In 1978 we reported the zirconium-catalyzed controlled single-stage carboalumination of alkynes¹ (eq 1) as well as its titanium analogue² (*e.g.*, eq 2), the latter of which has turned out to be only stoichiometric in titanium.³ We initially envisioned that the Zr-catalyzed methylalumination of alkynes might involve (i) methylation of Cp₂ZrCl₂ with Me₃Al to produce MeZrCp₂Cl and Me₂AlCl, (ii) methylzirconation of alkynes to give the corresponding alkenylzirconium derivatives,



and (iii) their transmetalation with Me₂AlCl to yield the observed alkenyldimethylalanes with regeneration of Cp₂ZrCl₂ (Scheme 1). This proposed mechanism was primarily based on a reversible Me–Cl exchange between Me₃Al and Cp₂ZrCl₂ observed by NMR spectroscopy,⁴ and the stoichiometric reaction of RC≡CAlMe₂ with MeZrCp₂Cl shown in eq 3.⁵ However, our later study has indicated that the reaction may involve direct addition of the Me–Al bond to alkynes assisted by a ZrCp₂ derivative⁴ (Scheme 2). Specifically, Me₂AlCl–Cp₂ZrCl₂ is a reasonable methylaluminating agent⁴ (eq 4), even though no

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(1) (a) Van Horn, D. E.; Negishi, E. *J. Am. Chem. Soc.* **1978**, *100*, 2252. (b) Negishi, E.; Van Horn, D. E.; Yoshida, T. *J. Am. Chem. Soc.* **1985**, *107*, 6639. (c) Negishi, E. *Pure Appl. Chem.* **1981**, *53*, 2333.

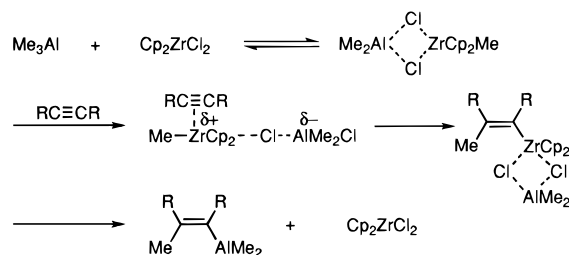
(2) Van Horn, D. E.; Valente, L. F.; Idacavage, M. J.; Negishi, E. *J. Organomet. Chem.* **1978**, *156*, C20.

(3) Unpublished results by Kondakov, D. Y. and Negishi, E.

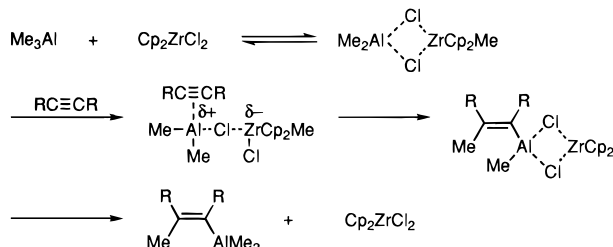
(4) Negishi, E.; Yoshida, T. *J. Am. Chem. Soc.* **1981**, *103*, 4985.

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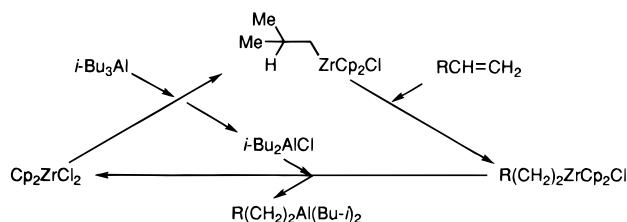
Scheme 1



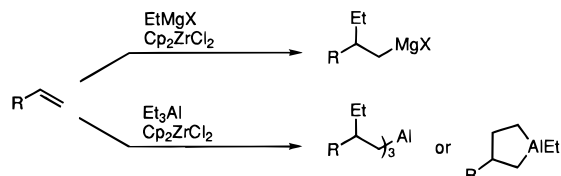
Scheme 2



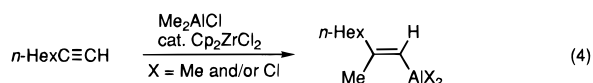
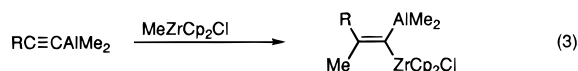
Scheme 3



Scheme 4



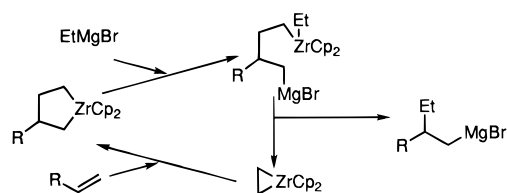
$\text{Me}-\text{Cl}$ exchange to produce MeZrCp_2Cl is detectable by NMR spectroscopy. However, rigorous exclusion of the mechanism shown in Scheme 1 cannot be made on the basis of the available data.



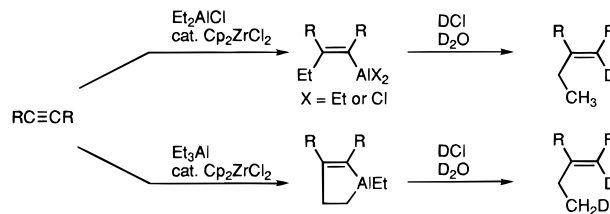
In contrast with $\text{Me}_3\text{Al}-\text{Cp}_2\text{ZrCl}_2$, $i\text{-Bu}_3\text{Al}-\text{Cp}_2\text{ZrCl}_2$ would hydroaluminate alkynes as well as alkenes, for which a transmetalation–hydrozirconation–back transmetalation mechanism shown in Scheme 3 was proposed.⁶

Our initial attempts to observe Zr-catalyzed carboalumination of alkenes did not yield the desired products in detectable yields (vide infra). Several years later, Dzhemilev⁷ reported Zr-catalyzed ethylmagnesium addition of monosubstituted alkenes (Scheme 4). Methylmagnesium derivatives did not participate in this reaction.⁸ A related reaction of Et_3Al with monosubstituted alkenes catalyzed by ZrCp_2 derivatives was also reported⁹

Scheme 5



Scheme 6



(Scheme 4). Although the authors initially reported tris(2-ethylalkyl)alanes as the products,^{9a} they later found that the reaction yielded 3-substituted aluminacyclopentanes.¹⁰ In 1991 we¹¹ clarified the mechanism of the Dzhemilev's ethylmagnesium addition reaction (Scheme 5), and our conclusion has been further supported by concurrent and subsequent related studies.¹² In summary, Zr-catalyzed reactions of organoalanes with alkenes and alkynes may proceed by (i) direct C–M bond addition without the formation of cyclic intermediates, (ii) C–M bond additions involving metallacyclic intermediates, and (iii) hydrometalation.

The contrasting reaction courses and mechanisms presented above are not solely attributable to the difference in the alkyl groups, *i.e.*, Me, Et, and *i*-Bu, since even organoalanes containing the same alkyl group can undergo two or more distinct reactions. For example, we have reported that the reaction of $\text{R}_2\text{AlCl}-\text{Cp}_2\text{ZrCl}_2$, where $\text{R} = \text{Et}$, *n*-Pr, and higher *n*-alkyls, with alkynes gives the corresponding alkylaluminated products, for which a process similar to that shown in Scheme 2 has been proposed.⁴ In 1992 Dzhemilev¹³ reported that the corresponding reaction of $\text{Et}_3\text{Al}-\text{Cp}_2\text{ZrCl}_2$ gave aluminacyclopentene derivatives. In fact, a similar enyne bicyclization reaction with $\text{Et}_3\text{Al}-\text{Cp}_2\text{ZrCl}_2$ had also been observed by us¹⁴ a few years before the Dzhemilev's publication. The dichotomous behavior shown in Scheme 6 as well as those diverse results reported earlier prompted us to systematically investigate various reactions of alkynes and alkenes with organoaluminums and zirconocene derivatives. Herein we discuss those results obtained with alkynes with emphasis on various reaction parameters governing strikingly multimechanistic aspects of these reactions. We

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(10) Dzhemilev, U. M.; Ibragimov, A. G.; Zolotarev, A. P.; Muslukhov, R. R.; Tolstikov, G. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1991**, 2570.

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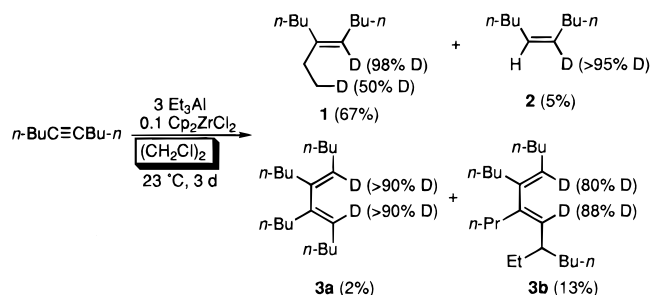
(13) Dzhemilev, U. M.; Ibragimov, A. G.; Zolotarev, A. P. *Mendeleev Commun.* **1992**, 135.

(14) Observed in 1990 by Swanson, D. R. Work along this line is in progress with Choueiry, D. and Kondakov, D. Y.

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

(7) Dzhemilev, U. M.; Vostrikova, O. S.; Sultanov, R. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, 218.

Scheme 7



further focus our attention on elucidation of factors critically responsible for those C–M bond addition reactions involving C–H activation to produce metallacyclic intermediates.

Results and Discussion

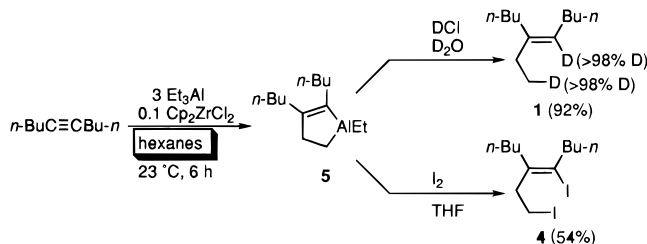
With the goal of further exploring the synthetic scope and probing mechanistic details of alkylmetalation other than methylmetalation¹ of alkynes with alkylalanes catalyzed or promoted by zirconocene derivatives, various reactions involving the following reagents were investigated: alkynes, internal alkynes (5-decyne, 3-hexyne, and diphenylethyne) and terminal alkynes (1-octyne, 1-decyne, 1-dodecyne, and phenylethyne); organoalanes,¹⁵ R_3Al and R_2AlCl , where $R = Et, n\text{-}Pr$, and $i\text{-}Bu$; zirconocene derivatives, Cp_2ZrCl_2 and $MeZrCp_2Cl$; and solvents, hexanes, benzene, CH_2Cl_2 , and $(CH_2Cl)_2$.

Trialkylalanes, *i.e.*, Et_3Al , $(n\text{-}Pr)_3Al$, and $(i\text{-}Bu)_3Al$, and Et_2AlCl , as well as Cp_2ZrCl_2 , were purchased from commercial sources. Di(*n*-propyl)aluminum chloride was prepared *in situ* by mixing $(n\text{-}Pr)_3Al$ and $AlCl_3$ in a 2:1 molar ratio, respectively, according to the literature.¹⁶ Conversion of Cp_2ZrCl_2 to $O(ZrCp_2Cl)_2$ followed by the treatment of the latter with Me_3Al according to the literature¹⁷ provided $MeZrCp_2Cl$.

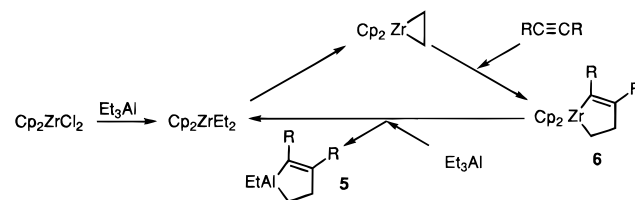
Reactions of Alkynes with Ethylalanes and Zirconocene Derivatives. (a) Results of Representative Reactions of 5-Decyne with Et_3Al in the Presence of a Catalytic Amount of Cp_2ZrCl_2 . The reaction of 5-decyne with Et_3Al (3 equiv) and 0.1 equiv of Cp_2ZrCl_2 in $(CH_2Cl)_2$ at 23 °C, following the typical conditions for the Zr-catalyzed methylalumination,¹ produced, after deuterolysis with $DCl\text{--}D_2O$, mono- and/or dideuterated **1**–**3** in the yields indicated in Scheme 7. It should be noted that the extent of D incorporation in the Et group of **1** was only 50%. The use of hexanes in place of $(CH_2Cl)_2$ not only accelerated the reaction but also led to a cleaner product. Thus, the reaction was over within 6 h at 23 °C, and the product obtained in 92% yield after deuterolysis as above was **1** in which the extents of D incorporation were >98% at both positions. Treatment of the reaction mixture provided the expected diiodinated product **4** in 54% yield. These results support the assignment of an aluminacyclopentene derivative **5** to the product, as in the previous report,¹³ although other cyclooligomeric and polymeric structures may be present (*vide infra*) (Scheme 8).

(b) Initially Proposed but Untenable Mechanism via Double Transmetalation. We initially assumed that the cycloalumination reaction shown in Scheme 8 would proceed in a manner similar to Dzheilev's Zr-catalyzed ethylmagnesiation of alkenes¹¹ (Scheme 5). On this basis, we envisioned a mechanism involving reversible double transmetalation in which

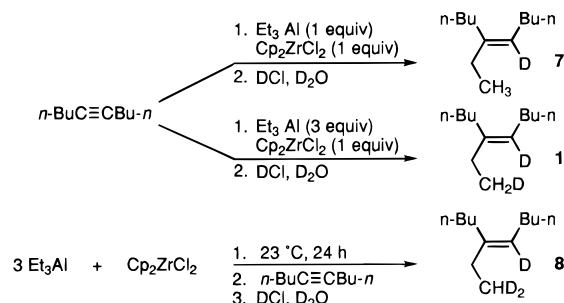
Scheme 8



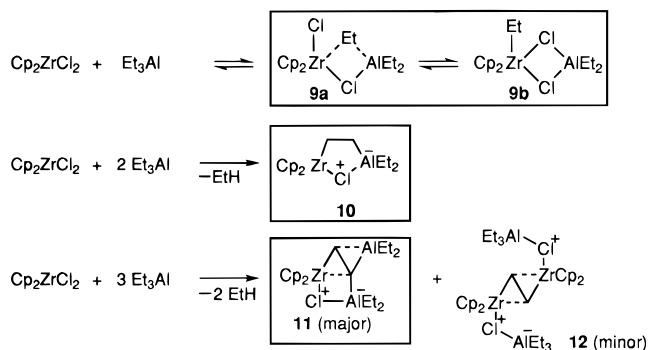
Scheme 9



Scheme 10



Scheme 11



a zirconacyclopentene **6** is generated as a crucial intermediate (Scheme 9), even though there was no spectroscopic indication for the formation of Cp_2ZrEt_2 by the reaction of Et_3Al and Cp_2ZrCl_2 in a 1:1 molar ratio. Both the formation of (ethylene)-zirconocene¹⁸ and its ring expansion to give **6**¹⁹ were known. To our surprise, however, no desired reaction was observed at a significant rate when 0.2 equiv of **6** preformed by the reaction of Cp_2ZrEt_2 with 5-decyne¹⁸ was added to a mixture of 5-decyne and Et_3Al (1.2 equiv). The results ruled out the intermediacy of **6** and hence the mechanism shown in Scheme 9.

(c) Results of Representative Reactions of 5-Decyne with Et_3Al in the Presence of the Stoichiometric Amount of Cp_2ZrCl_2 . Highly informative from the viewpoint of mechanistic clarification were the results of the reaction of 5-decyne

(15) Organoalanes generally exist as dimers. For the sake of simplicity, however, monomeric structures are used unless the use of dimeric structures is considered to be essential.

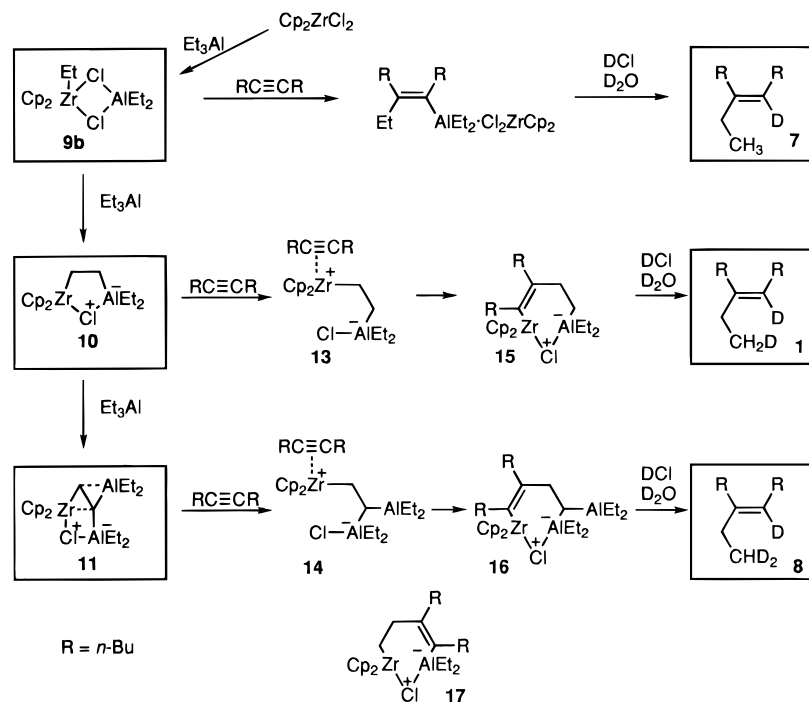
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Scheme 12



with Et_3Al (1–3 equiv) in the presence of the stoichiometric amount of Cp_2ZrCl_2 . As summarized in Scheme 10, three discrete carbometalation products, i.e., **1**, **7**, and **8**, were obtained after deuterolysis under three slightly different conditions. Specifically, **1** is the predominant product (84%), when 5-decyne, Et_3Al (3 equiv), and Cp_2ZrCl_2 (1 equiv) were mixed all at once in benzene. In sharp contrast, when only 1 equiv of Et_3Al was allowed to react with 1 equiv of Cp_2ZrCl_2 for 24 h before addition of 5-decyne, (*Z*)-5-(2',2'-dideuteroethyl)-6-deutero-5-decene (**8**) was obtained as the major product in 87% yield. Clearly, three discrete, if related, processes must take place under the indicated conditions.

(d) Previously Known Results of the Reaction of Et_3Al with Cp_2ZrCl_2 in the Absence of Alkynes. A series of detailed investigations of the reaction of Et_3Al with Cp_2ZrCl_2 using NMR spectroscopy and X-ray analysis by Sinn^{20,21} and Kaminsky²¹ has proved to be highly relevant. These workers have reported that the reaction of Cp_2ZrCl_2 with Et_3Al in C_6D_6 rapidly produces a mixture of **9a** and **9b**, which is relatively stable when only 1 equiv of Et_3Al is used. With an excess of Et_3Al , however, a C–H activation process takes place to give a relatively unstable species **10** which is subsequently converted to a more stable product **11** via the second C–H activation process along with a smaller amount of **12**. The X-ray structures of **11** and **12** have also been reported.^{21c} We have confirmed these results mainly with NMR spectroscopy.

(e) Correlation between the Stoichiometric Processes Shown in Schemes 10 and 11. Comparison of the results shown in Schemes 10 and 11 suggested to us that there must be 1:1 correspondences between the three reactions in Scheme 10 and those in Scheme 11 as shown in Scheme 12. Since the formation of **7** does not incorporate D in the Et group, it most

likely proceeds via direct ethylmetalation of 5-decyne with **9**. Judging from the extents of D incorporation, **1** and **8** must be formed via the reactions of 5-decyne with **10** and **11**, respectively. Among several possible alternatives we favor the four-centered carbозirconation process proceeding via **13** and **14**, respectively. This process should provide **15** and **16**, respectively, as the initial carbometalation products which may undergo subsequent transformations (vide infra). Similar modes of activation of C–Zr bonds via polarization by ring opening have been proposed for carbometalation of alkenes.²² Furthermore, the regiochemistry of D incorporation in **8** is compatible with the proposed carbозirconation but incompatible with carboalumination, which would produce the 1,2-dideuteroethyl-containing isomer of **8**. By analogy, we favor the proposed carbозirconation process producing **15** as the initial product over a carboalumination process which would initially give **17**. Of these three stoichiometric processes, however, only the process involving the formation of **10** and its reaction with 5-decyne to give **1** upon deuterolysis are relevant to the catalytic process, since neither **7** nor **8** was formed in the catalytic reaction shown in Scheme 8.

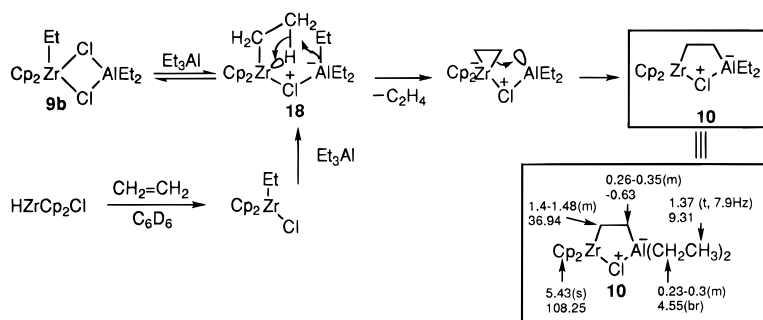
(f) Mechanistic Interpretation of the Formation of **10 via Bimetallic β C–H Activation and Its Reaction with 5-Decyne Under Stoichiometric Conditions.** The formation of **10** by the reaction of **9** with Et_3Al requires a β C–H activation process. Addition of an excess of ClAlEt_2 to **9** does not induce the desired C–H activation to produce **10**. Evidently, this process requires the second equivalent of Et_3Al . We propose that Et_3Al displaces ClAlEt_2 in an unfavorable equilibrium and that the $\text{EtZrCp}_2\text{Cl}(\text{AlEt}_2)_2$ complex **18** thus formed undergoes a bimetallic β C–H activation reaction, most probably triggered by β agostic interaction of the EtZrCp_2 moiety, to give **10**, as depicted in Scheme 13. An extra equivalent of Et_3Al rather than ClAlEt_2 is necessary probably because ClAlEt_2 forms a relatively stable complex **9b** and is hence less prone to give an open and hence activated species corresponding to **18**. Et_3Al should also be more basic and hence better able to abstract H than ClAlEt_2 . To further

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Scheme 13

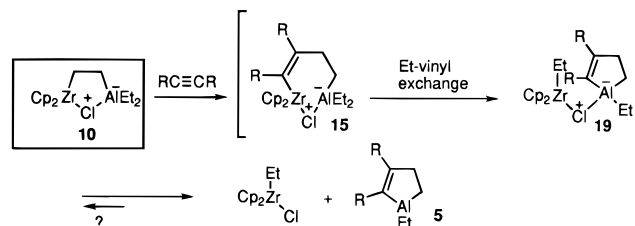


support the mechanism shown in Scheme 13, an Al-free sample of EtZrCp_2Cl was generated by hydrosilylation of ethylene with HZrCp_2Cl in C_6D_6 in 90% NMR yield and then treated with 1 equiv of Et_3Al at 23 °C. This reaction cleanly produced within 30 min an 83% yield of **10**. In contrast, the reaction of Cp_2ZrCl_2 with two or more equivalents of Et_3Al was much slower, and is complicated by side reactions. The major difference in these two reactions may be attributable to the absence of ClAlEt_2 in the former and its presence in the latter in which Et_3Al must displace *in situ* generated ClAlEt_2 .

Analysis of **10** prepared by the reaction of EtZrCp_2Cl and Et_3Al by ^1H (500 MHz) and ^{13}C (75.4 MHz) NMR spectroscopy including COSY and HETCOR techniques led to the signal assignments shown in Scheme 13. Although the ^1H NMR signals were previously reported,²⁰ there exists a significant discrepancy between the chemical shift value of δ 1.45–1.5 ppm assigned by us to a multiplet attributable to the Zr-bound CH_2 group and the previously assigned shift value of δ 0.7 ppm.²⁰ We presume that the use of a low-field frequency in the previous study must have led to an erroneous assignment. The ^{13}C NMR data have not been previously reported.

As expected, the reaction of **10** with 1 equiv of 5-decyne proceeded smoothly in C_6D_6 at 23 °C and was fast and complete in 10 min to give EtZrCp_2Cl and **5**. This reaction is much faster than either the catalytic reaction shown in Scheme 8 or the stoichiometric reaction producing **1** on deuterolysis shown in Scheme 10. Here again, the difference may be attributable to the inhibitory effect of *in situ* generated Et_2AlCl on the formation of **10** in the latter two reactions. The formation of EtZrCp_2Cl was readily indicated by the ^1H and ^{13}C NMR signals at δ 5.78 $\pm$ 0.04 and 112.60 $\pm$ 0.35, respectively, for the Cp group of EtZrCp_2Cl regardless of whether or not Et_2AlCl and/or Et_3Al were additionally present. Consequently, they did not provide accurate information about the interactions between EtZrCp_2Cl and organoalanes. These signals were also very insensitive to various solvents such as THF, provided that C_6D_6 was used as an NMR solvent. Luckily, we found that the ^{13}C NMR signal for the Zr-bound CH_2 of Et was very sensitive to the presence or absence of an additional organoalane, even though it was still insensitive to THF. Specifically, it appeared at δ 46.5 $\pm$ 0.16 in the absence of Et_2AlCl , but it shifted downfield (δ 49–54) in the presence of Et_2AlCl . Analysis of this signal also indicated that there was little, if any, interaction between EtZrCp_2Cl and the alkyne-inserted organoaluminum product, although this point should be further clarified. The organoaluminum product showed as before a relatively complex set of signals, but it was cleanly converted to **1** upon deuterolysis. We suggest that the stoichiometric reaction of 5-decyne with **10** to give EtZrCp_2Cl and **5** proceeds via **15** and **19** as shown in Scheme 14. Conversion of **15** into **19** merely requires Et–vinyl exchange, which should be kinetically facile, and **19** must prefer to exist as a mixture of EtZrCp_2Cl and **5**.

Scheme 14

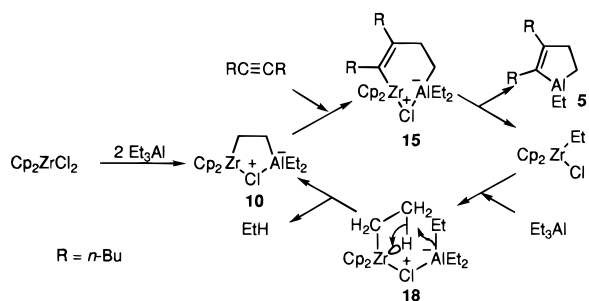


(g) Mechanism of the Catalytic Reaction of 5-Decyne with an Excess of Et_3Al in the Presence of Cp_2ZrCl_2 . The observed results and interpretations of the stoichiometric reactions shown in Schemes 13 and 14 combine to point to the mechanism shown in Scheme 15 for the Cp_2ZrCl_2 -catalyzed reaction of 5-decyne with an excess of Et_3Al . In this scheme, the catalytic process is initiated by the reaction of Cp_2ZrCl_2 with two or more equivalents of Et_3Al to produce **10** via bimetallic β C–H activation (Scheme 13). This bimetallic reagent then undergoes carbozirconation with 5-decyne to give EtZrCp_2Cl and **5**, most probably via **13**, **15**, and **19** (Schemes 12 and 14). EtZrCp_2Cl thus generated reacts with Et_3Al to regenerate **10** via **18** (Scheme 13) to complete a catalytic cycle. The crucial bimetallic β C–H activation process depicted in **18** requires (i) a coordinatively unsaturated EtZrCp_2 moiety capable of exhibiting β C–H agostic interaction, (ii) the second equivalent of Et_3Al , and (iii) one Cl atom to bind Zr and Al via a Zr–Cl–Al bond. The requirement for the second equivalent of Et_3Al or an equivalent trialkylalane has been experimentally demonstrated under both stoichiometric and catalytic conditions.

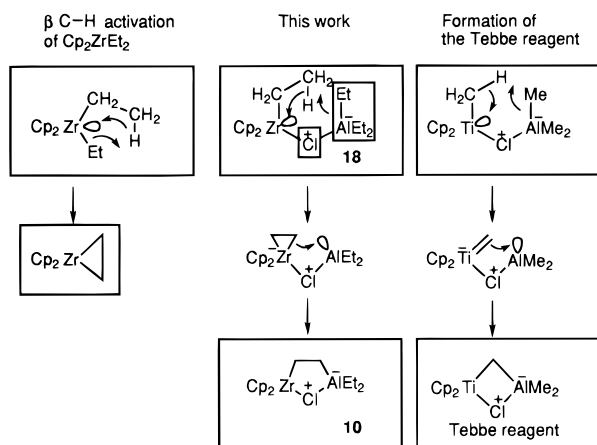
To further substantiate the need for one Cl atom, the following comparative experiments were carried out. As stated earlier, a zirconacyclopentene **6** did not induce the cyclic carboalumination of 5-decyne with Et_3Al . However, addition of Et_2AlCl to the reaction mixture did generate an active catalyst for the desired reaction. Similarly, the reaction of 5-decyne with 1 equiv of Et_3Al and 0.2 equiv of $(n\text{-Bu})_2\text{ZrCp}_2$, generated from Cp_2ZrCl_2 and 2 equiv of $n\text{-BuLi}$ ²³ in toluene and added as a source of “ ZrCp_2 ”, produced, on hydrolysis, only traces (<5%) of (*Z*)-5-ethyl-5-decene along with (*E,E*)-6,7-di(*n*-butyl)-5,7-dodecadiene formed as the major product (20%). In this reaction, all Cl atoms are sequestered in the form of LiCl. In sharp contrast, addition of 0.2 equiv of Et_2AlCl to the same reaction mixture at the beginning of the reaction followed by protonolysis led to a 73% yield of (*Z*)-5-ethyl-5-decene along with a minor amount (14%) of the conjugated diene. On deuterolysis, **1** was obtained in a comparable yield. These results indicate that alkene-zirconocenes alone do not serve as catalysts for cyclic carboalumination of alkynes with Al–Zr

(23) (a) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, 27, 2829. (b) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, 111, 3336.

Scheme 15



Scheme 16

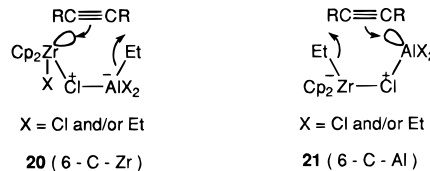


reagent systems but that introduction of Cl converts them to active catalysts. It is very likely that Et_2AlCl converts (ethyl-ene)zirconocene into **10** as shown in Scheme 13.

(h) Comparison of α and β C–H Activation Processes of Zirconocenes and Titanocenes. It is worth mentioning here that the C–H activation process depicted in **18** in Scheme 13 and the catalytic process and principle involving **10** and **18** shown in Scheme 15 represent novel modes of C–H activation and catalysis, although some related but different processes such as (i) β C–H activation of dialkylzirconocenes¹⁸ and its involvement in the Zr-catalyzed carbomagnesiation reaction^{11,21b} and (ii) α C–H activation processes involving Al and Ti compounds²⁴ are known. In this connection, it is instructive to compare some salient features of these related processes, which are summarized in Scheme 16. In contrast with the Zr-catalyzed carbomagnesiation of alkenes^{7,11,12} proceeding via monometallic C–H activation, the mode of C–H activation shown in **18** is *bimetallic*. Whereas the former requires double alkylation of zirconium, the latter proceeds via single alkyl transfer. The three crucial requirements for the Al–Zr bimetallic β C–H activation process are as discussed above. In these respects, the Al–Zr reaction might more closely resemble the formation of the Tebbe reagent²⁴ from Cp_2TiCl_2 and Me_3Al . However, this Al–Ti reaction involves α C–H activation. Furthermore, to the best of our knowledge, essentially all known reactions of the Tebbe reagents appear to be only stoichiometric. On the other hand, both of the β C–H activation processes of organozirconiums can be crucial steps in catalytic processes.

(i) Reaction of 5-Decyne with Et_2AlCl – Cp_2ZrCl_2 . Remarkable Solvent Effects. As indicated in Scheme 6, the Et_2 –

AlCl – Cp_2ZrCl_2 reagent system lacking Et_3Al is incapable of inducing cyclic carboalumination of alkynes via C–H activation. This reaction is also sensitive to the nature of solvents. Thus, treatment of 5-decyne with 1 equiv of Et_2AlCl in the presence of either 0.1 or 1 equiv of Cp_2ZrCl_2 in *hexanes* at 23 °C did not induce any reaction over at least 1 day, with ≥ 90 –95% of the starting materials remaining unchanged. In sharp contrast, the same reaction run in $(\text{CH}_2\text{Cl})_2$ at 23 °C using either 0.1 or 1 equiv of Cp_2ZrCl_2 proceeded smoothly to give, after treatment with DCl – D_2O , a 90% yield of **7**, in which the extent of D incorporation was $\geq 95\%$. Zirconocene dichloride was regenerated to the extent of $\geq 95\%$. The observed solvent effects are analogous to those observed in the methylalumination reaction with Me_3Al – Cp_2ZrCl_2 ,^{1,4} suggesting that significant bond polarization occurs in the transition state, which must be essential to the observed reaction. Examination of a 1:1 mixture of Et_2AlCl and Cp_2ZrCl_2 by NMR spectroscopy indicates that no Et transfer from Al to Zr occurs beyond the detection limit of 0.1%. It should also be noted that both stoichiometric and catalytic reactions with Et_2AlCl and Cp_2ZrCl_2 produce the same products including regenerated Cp_2ZrCl_2 most probably via the same mechanism. As in the case of the Zr-catalyzed methylalumination, we are inclined to propose direct C–Al bond addition mechanisms similar to that shown in Scheme 2 (designated as 4-C–Al).²⁵ However, other mechanisms such as that involving direct C–Zr bond addition similar to the one shown in Scheme 1 (4-C–Zr)²⁵ and even some six-centered processes represented by **20** (6-C–Zr)²⁵ and **21** (6-C–Al)²⁵ cannot be rigorously ruled out on the basis of the currently available data. Despite mechanistic ambiguities, the highly contrasting features of this reaction and its cyclic analogue as well as its synthetic value should be clearly noted.

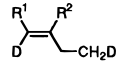
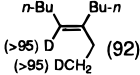
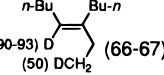
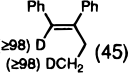
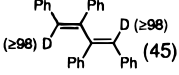
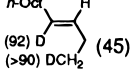
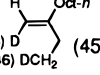
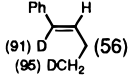
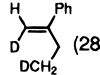
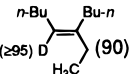
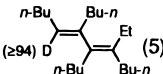
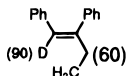
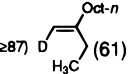
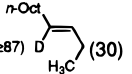


(j) Synthetic Scope of Ethylalumination of Alkynes in the Presence of Cp_2ZrCl_2 . We have also studied the stoichiometric reactions of 5-decyne with (i) Et_3Al – MeZrCp_2Cl and (ii) Et_2AlCl – MeZrCp_2Cl . The reaction of 5-decyne with 1 equiv each of Et_3Al and MeZrCp_2Cl in *hexanes* at 23 °C for 2 h provided, after deuteration, **1** in 67% yield with $\geq 90\%$ D incorporation at either position along with the dimer **3a** ($\geq 90\%$ D) obtained in 20% yield. The same reaction in $(\text{CH}_2\text{Cl})_2$ required 12–14 h at 23 °C for completion, and the products consisted of **1** (69%) and **3a** ($\leq 9\%$). These results clearly point to a C–H activation process similar to that shown in Scheme 13. We earlier used the same Et_3Al – MeZrCp_2Cl system and concluded that the exclusive incorporation of Et rather than Me was an indication of direct C–Al bond addition.⁴ This was clearly incorrect and must therefore be corrected. Interestingly, the reaction of 5-decyne with Et_2AlCl (3 equiv) and MeZrCp_2Cl (1 equiv) in $(\text{CH}_2\text{Cl})_2$ cleanly produced, after deuteration, the monodeuterated alkene **7** in 93% yield. The extent of D incorporation at the alkenyl position was $\geq 91\%$. No D incorporation in the Et group was observed. Curiously, the amount of (Z)-5-methyl-5-decene was negligible, even though a mixture of Et_2AlCl and MeZrCp_2Cl undergoes Me–Et exchange. The courses of the Zr-catalyzed ethylalumination of various alkynes including those

(24) (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733. (c) Ott, K. C.; deBoer, E. J. M.; Grubbs, R. H. *Organometallics* **1984**, *3*, 223.

(25) In this designation, the first number indicates the number of participating atoms, and C–Al and C–Zr indicate addition of C–Al and C–Zr bonds to alkynes, respectively.

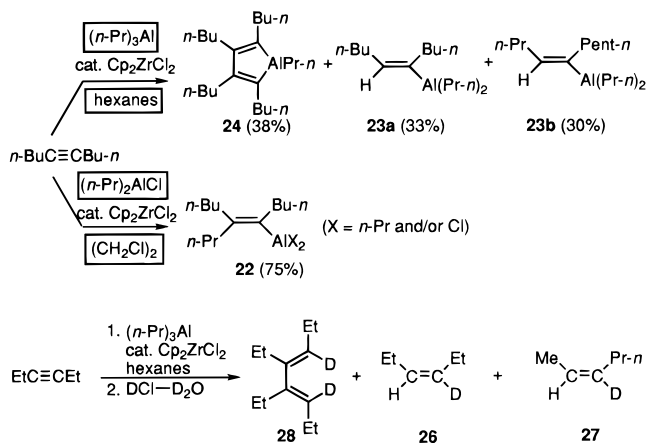
Table 1. Reaction of Alkynes with Et₃Al and Et₂AlCl in the Presence of 10 mol % of Cp₂ZrCl₂

alkyne	ethylalane (equiv)	solvent	temp. °C	time h	deuterolysis products (yield, ^a %)		
							others
<i>n</i> -BuC≡CBu- <i>n</i>	Et ₃ Al (3)	hexanes	23	6		<i>b</i>	<i>b</i>
<i>n</i> -BuC≡CBu- <i>n</i>	Et ₃ Al (3 or 6)	(CH ₂ Cl) ₂	23	72		<i>b</i>	<i>c</i>
PhC≡CPh	Et ₃ Al (3)	benzene	55	19		<i>b</i>	
<i>n</i> -OctC≡CH	Et ₃ Al (3)	benzene	23	17			<i>b</i>
PhC≡CH	Et ₃ Al (3)	hexanes	55	7			<i>b</i>
<i>n</i> -BuC≡CBu- <i>n</i>	Et ₂ AlCl (3)	(CH ₂ Cl) ₂	55	20	<i>b</i>		
PhC≡CPh	Et ₂ AlCl (3)	(CH ₂ Cl) ₂	70-75	36-40	<i>b</i>		<i>b</i>
<i>n</i> -OctC≡CH	Et ₂ AlCl (3)	(CH ₂ Cl) ₂	23	5	<i>b</i>		

^a By NMR spectroscopy or GLC. ^b Not detected or determined. ^c See Scheme 7 for information on the products.

observed with 5-decyne are summarized in Table 1. These results permit the following generalizations. First, the courses of the reactions of various other alkynes are similar to those observed with 5-decyne. Specifically, the reaction with Et₃Al involves largely the C–H activation process leading to the formation of dideuterated products via deuterolysis. On the other hand, the reaction with Et₂AlCl leads to the formation of monodeuterated products. Second, two possible regioisomers are obtained from terminal alkynes, although all of the reactions proceed without producing stereoisomers to any detectable extents. The extent of D incorporation at the C_{sp}² center is uniformly high (>90%), while that in the Me group of the Et substituent varies. With Et₂AlCl as the carbometallating agent, no D incorporation in the Et substituent is observed. In the reactions of terminal alkynes with Et₃Al, the extent of D incorporation in the Et substituent of the 1,2-disubstituted alkenes is >90%, indicating that these products are obtained via the C–H activation process. On the other hand, the extent of D incorporation in the Et substituent of the 1,1-disubstituted alkenes has been in the 40–60% range, suggesting that roughly half of these products stem from the C–H activation process. This represents a deviation from the course of the reaction of internal alkynes.

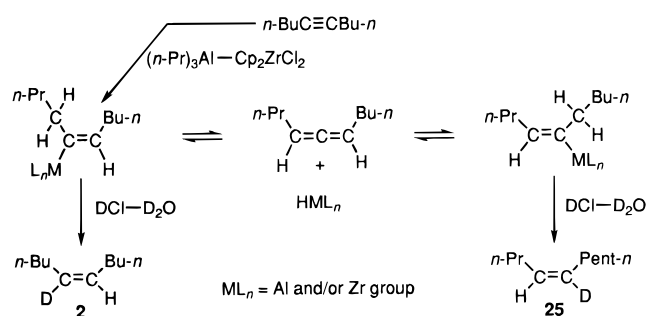
Reactions of Alkynes with *n*-Propyl- and Isobutylalanes and Zirconocene Derivatives. The reaction of 5-decyne with either (*n*-Pr)₃Al or (*n*-Pr)₂AlCl in the presence of 0.1 equiv of either Cp₂ZrCl₂ or MeZrCp₂Cl was carried out in hexanes, toluene, or (CH₂Cl)₂, and the results summarized in Table 2 indicate that the course of the reaction significantly depends on the structure of the *n*-propylalane reagent and the solvent. In addition to alkyl–metal bond addition and C–H activation

Scheme 17

processes, hydrometalation can be a dominant process with *n*-propylalanes. Specifically, the reaction of 5-decyne with (*n*-Pr)₃Al in hexanes with either Cp₂ZrCl₂ or MeZrCp₂Cl as a catalyst did not yield the expected *n*-propylmetalation product 22 in more than trace quantities, if any. The major products were a mixture of 23a and 23b (~65% combined yield) and a dimer 24 (30–40% based on 5-decyne) (Scheme 17). The hydroalumination products were stereoisomerically >98% pure. On deuterolysis of the reaction mixtures, 2, (Z)-5-deuterio-4-decene (25), and 3a were obtained. The extents of D incorporation were all ≥90–95%. Although 25 was regioisomerically pure (>98%), its regiochemistry was not readily determined on the basis of its NMR spectra. However, the corresponding reaction of 3-hexyne gave, after deuterolysis, a mixture of 26

Table 2. Reaction of 5-Decyne with (*n*-Pr)₃Al or (*n*-Pr)₂AlCl in the Presence of 10 mol % of Cp₂ZrCl₂ or MeZrCp₂Cl

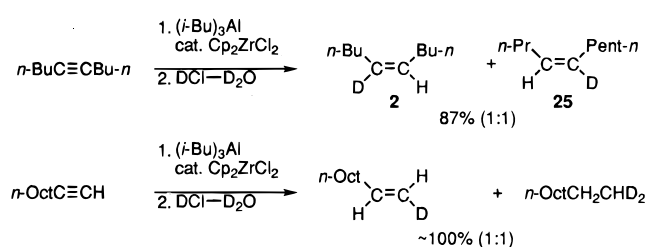
alane (equiv)	Cp ₂ Zr deriv.	solvent	temp °C	time h	product yield, ^a %				others
(<i>n</i> -Pr) ₃ Al (3)	Cp ₂ ZrCl ₂	hexanes	23	12	<2	33	30	38	<i>b</i>
(<i>n</i> -Pr) ₃ Al (3)	MeZrCp ₂ Cl	hexanes	23	24	<2	42	24	30	<i>b</i>
(<i>n</i> -Pr) ₃ Al (3)	Cp ₂ ZrCl ₂	(CH ₂ Cl) ₂	50	3	9	52	35	<3	<i>b</i>
(<i>n</i> -Pr) ₃ Al (3)	MeZrCp ₂ Cl	(CH ₂ Cl) ₂	23	48	11	63	12	7	<i>b</i>
(<i>n</i> -Pr) ₂ AlCl (3)	Cp ₂ ZrCl ₂	hexanes	23	12	<2	13	10	<2	<i>n</i> -BuC≡CBu- <i>n</i> (75)
(<i>n</i> -Pr) ₂ AlCl (3)	Cp ₂ ZrCl ₂	(CH ₂ Cl) ₂	50	12	75	≤2	<2	<2	<i>b</i>

^a By GLC or NMR spectroscopy and based on the starting alkyne. ^b Not observed.**Scheme 18**

and 27 along with 28, and the regiochemistry of 27 was unequivocally assigned by NMR spectroscopy. The formation of 25 and 27 and the regioselective D incorporation are consistent with the hydrometalation-dehydrometalation mechanism shown in Scheme 18 for the reaction of 5-decyne, which involves exclusive attachment of Zr to the central carbon atom of an allene.²⁶ Both predominant hydrometalation and alkyne dimerization are attributable to the use of (*n*-Pr)₃Al in place of Et₃Al. Evidently, *n*-PrZrCp₂Cl generated *in situ* from (*n*-Pr)₃Al and Cp₂ZrCl₂ is a more efficient hydrometalating agent than the corresponding Et derivative. It has been amply demonstrated that, whereas (ethylene)zirconocene can react with alkynes to produce zirconacyclopentenes, (1-butene)zirconocene gives predominantly or exclusively zirconacyclopentadienes.²³ (Propene)zirconocene containing a monosubstituted alkene must react more like (1-butene)zirconocene than (ethylene)zirconocene. The course of the reaction observed with (*n*-Pr)₃Al-MeZrCp₂Cl is very similar to that observed with (*n*-Pr)₃Al-Cp₂ZrCl₂. Here again, the absence of methylmetalation products remains as a puzzle to be clarified.

As expected, the reaction of 5-decyne with 3 equiv of (*n*-Pr)₂AlCl and 0.1 equiv of Cp₂ZrCl₂ in (CH₂Cl)₂ produced the *n*-propylmetalation product 22 in 75% yield, the amounts of other monomeric and oligomeric products <5% each. Examination of a 1:1 mixture of (*n*-Pr)₂AlCl and Cp₂ZrCl₂ in (CH₂Cl)₂ by NMR spectroscopy failed to reveal *n*-Pr-Cl exchange. We suggest that, as in the reactions of Me₂AlCl-Cp₂ZrCl₂⁴

(26) Attachment of metals to the central carbon atom of allenes to varying degrees has been observed in hydroboration. [For a review, see: Zaidlewicz, M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds. Pergamon Press: Oxford, 1980; Vol. 7, pp 217-218.] On the other hand, exclusive attachment of metals to the terminal carbon atoms of allenes has been observed in carbopalladation. [Ahmar, M.; Cazes, B.; Goré, J. *Tetrahedron Lett.* **1984**, 25, 4505.]

Scheme 19

and Et₂AlCl-Cp₂ZrCl₂, this reaction may involve direct C-Al bond addition assisted by Zr either via 4-C-Al or the 6-C-Zr process. In accord with the other cases, the reaction was very sluggish in nonpolar solvents, such as hexanes.

The reaction of PhC≡CPh, *n*-OctC≡CH, and PhC≡CH with 3 equiv of (*n*-Pr)₃Al and 0.1 equiv of Cp₂ZrCl₂ in hexanes or toluene gave, after protonolysis, a 3:2 mixture of (*E*)- and (*Z*)-stilbene in 68% yield along with (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene (24% based on PhC≡CPh). The reaction of *n*-OctC≡CH and PhC≡CH gave, after protonolysis, the corresponding alkenes in 61 and 53% yields, respectively, along with minor amounts of the doubly hydrometalated products.

In view of our recent report on the hydrozirconation of alkynes with *i*-BuZrCp₂Cl generated *in situ* from *t*-BuMgCl and Cp₂ZrCl₂ in ether,²⁷ similar results might be expected from (*i*-Bu)₃Al-Cp₂ZrCl₂. Indeed, the reaction of 5-decyne and 1-decyne with 3 equiv of (*i*-Bu)₃Al and 0.1 equiv of Cp₂ZrCl₂ was totally dominated by hydrometalation with no indication of carbometalation with a couple of notable but expected deviations from the course of the corresponding reaction with *t*-BuMgCl-Cp₂ZrCl₂. Thus, the reaction of 5-decyne gave, after deuterolysis, an essentially 1:1 mixture of 2 and 25 in 87% overall yield, while that of 1-decyne produced an essentially 1:1 mixture of (*E*)-1-deuterio-1-decene and 1,1-dideuteriododecane in quantitative combined yield (Scheme 19).

Conclusions

Various aspects of the reactions of internal and terminal alkynes with organoalanes containing Et, *n*-Pr, and *i*-Bu groups

(27) Swanson, D. R.; Nguyen, T.; Noda, Y.; Negishi, E. J. *Org. Chem.* **1991**, 56, 2590.

(28) An authentic sample of 2-ethyl-1-decene was prepared by the Wittig methylenation of 3-undecanone. For the Wittig methylenation of alkenes, see: Wittig, G.; Schoellkopf, U. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. 5, p 751.

(29) Zweifel, G.; Steele, R. B. *J. Am. Chem. Soc.* **1967**, 89, 5085.

in the presence of Cp_2ZrCl_2 and MeZrCp_2Cl were elucidated. Some of the noteworthy conclusions are as follows.

1. These reactions may involve one or more of at least three fundamentally different processes, *i.e.*, (i) C–M bond addition without involving C–H activation, (ii) C–H activation, and (iii) the hydrometalation, and the courses of these reactions significantly depend on (i) the nature and number of alkyl groups in organoalanes, (ii) their amounts, and (iii) solvents.

2. Exclusive or nearly exclusive carbometalation without involving C–H activation is observed with Et_2AlCl or $(n\text{-Pr})_2\text{AlCl}$ in the presence of 0.1 equiv of Cp_2ZrCl_2 in polar solvents, *e.g.*, $(\text{CH}_2\text{Cl})_2$. We tentatively suggest that these reactions involve direct carboalumination via either 4-C–Al or 6-C–Zr process, but others via 4-C–Zr and 6-C–Al processes cannot be rigorously ruled out.

3. Exclusive or nearly exclusive C–H activation is observed with Et_3Al and 0.1 equiv of Cp_2ZrCl_2 in nonpolar solvents, *e.g.*, hexanes. A catalytic cycle involving bimetallic species **10** and **18** shown in Scheme 15 accommodates the observed results. Generation of **10**, which acts as an active carbometalating agent, requires **18**, which contains (i) a coordinatively unsaturated alkylzirconocene moiety containing the β C–H bond, (ii) one Cl atom, and (iii) Et_3Al .

4. Exclusive hydrometalation is observed with $(i\text{-Bu})_3\text{Al}$ – Cp_2ZrCl_2 . This process, however, is complicated by double bond migration observed with alkyl-substituted internal alkynes and double hydrometalation observed with terminal alkynes.

5. Some reactions involve more than one process. For example, the reaction with $(n\text{-Pr})_3\text{Al}$ and Cp_2ZrCl_2 involves simultaneously hydrometalation and C–H activation.

Although capricious and initially unpredictable, the results herein presented as well as those reported earlier together with the mechanistic interpretations discussed above help provide a reasonable overview of the reactions of alkynes with organoalanes and zirconocene derivatives, which may be used even in a predictable manner. Perhaps most significantly, a novel bimetallic mode of β C–H activation and a catalytic principle involving such a C–H activation have been unravelled. This study should provide a foundation on which to further develop additional catalytic reactions.

Experimental Section

General. Manipulations involving organometallics were carried out under an atmosphere of N_2 or Ar. Hexanes, 1,2-dichloroethane, benzene, and toluene were distilled from CaH_2 ; tetrahydrofuran from sodium benzophenone ketyl; and HMPA from triphenylmethyl lithium. Di(*n*-propyl)aluminum chloride was prepared *in situ* by mixing $(n\text{-Pr})_3\text{Al}$ and AlCl_3 in a 2:1 molar ratio.¹⁶ Chloro(methyl)zirconocene was prepared by conversion of Cp_2ZrCl_2 to $\text{O}(\text{ZrCp}_2\text{Cl})_2$ followed by the treatment of the latter with Me_3Al .¹⁷ The other starting materials were purchased from commercial sources and used as received. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini-200, Varian VXR-500, GE QE-300, and JEOL EX-270 FT NMR spectrometers.

Reaction of 5-Decyne with Et_3Al in the Presence of a Catalytic Amount of Cp_2ZrCl_2 in 1,2-Dichloroethane. The reaction of 5-decyne (0.36 mL, 2 mmol) with Et_3Al (0.82 mL, 6 mmol) and Cp_2ZrCl_2 (59 mg, 0.2 mmol) in $(\text{CH}_2\text{Cl})_2$ (4 mL) for 72 h at 23 °C gave, after protonolysis, (Z)-5-ethyl-5-decene in 67% yield along with (Z)-5-decene (5%), (*E,E*)-6,7-di(*n*-butyl)-5,7-dodecadiene¹⁹ (2% based on 5-decyne), and (*E,E*)-6-(*n*-butyl)-9-ethyl-7-(*n*-propyl)-5,7-tridecadiene (13% based on 5-decyne): ^1H NMR (CDCl_3 , Me_4Si) δ 0.7–1.0 (m, 12 H), 0.98 (t, $J = 7$ Hz, 3 H), 1.05–1.5 (m, 16 H), 1.8–2.15 (m, 8 H), 2.75–2.9 (m, 1 H), 4.93 (d, $J = 10$ Hz, 1 H), 5.09 (t, $J = 7$ Hz, 1 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.06, 14.06 (3 C), 14.28, 20.79, 22.47, 23.12, 23.21, 27.51, 29.29, 29.59, 30.15, 30.73, 31.87, 32.45, 37.28, 44.26, 124.10, 127.78, 140.45, 142.76. Deuterolysis gave a 1:1 mixture of (Z)-5-deuterio-6-ethyl-5-decene and (Z)-5-deuterio-6-(2-deuterioethyl)-5-

decene along with **2** (>95% D), **3a** (>90% D), and (*E,E*)-6-(*n*-butyl)-5,8-dideuterio-9-ethyl-7-(*n*-propyl)-5,7-tridecadiene (**3b**): ^1H NMR (CDCl_3 , Me_4Si) δ 0.75–1.05 (m, 15 H), 1.05–1.55 (m, 16 H), 1.85–2.15 (m, 8 H), 2.75–2.9 (m, 1 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.06, 14.06 (3 C), 14.28, 20.81, 22.49, 23.14, 23.22, 27.43, 29.30, 29.54, 30.16, 30.75, 31.88, 32.45, 37.29, 44.14, 123.76 (t, $J = 23$ Hz), 127.45 (t, $J = 23$ Hz), 140.35, 142.69; $\geq 80\%$ D at C-5 and $\geq 88\%$ D at C-8 by ^{13}C NMR.

Reaction of Various Alkynes with Et_3Al in the Presence of a Catalytic Amount of Cp_2ZrCl_2 in Hexanes or Benzene. (a) 5-Decyne. Representative Procedure. A mixture of Cp_2ZrCl_2 (0.059 g, 0.2 mmol) and 5-decyne (0.36 mL, 2 mmol) in hexanes (4 mL) cooled to 0 °C was treated with Et_3Al (0.82 mL, 6 mmol) and warmed to 23 °C. After 6 h, analysis of a protonolyzed aliquot by GLC indicated that the reaction was complete. **(i) Protonolysis.** The reaction mixture was cooled to 0 °C and quenched with 3 N HCl and THF (5 mL), extracted with pentane, washed with NaHCO_3 and H_2O , dried over MgSO_4 , and concentrated. Analysis of the product by NMR spectroscopy indicated the formation of (Z)-5-ethyl-5-decene in >95% yield (GLC). After Kugelrohr distillation (oven temperature = 50 °C at 5 mmHg), 0.284 g (85%) of (Z)-5-ethyl-5-decene¹⁹ was obtained: $\geq 97\%$ Z; ^1H NMR (CDCl_3 , Me_4Si) δ 0.8–0.95 (m, 6 H), 0.98 (t, $J = 7$ Hz, 3 H), 1.2–1.5 (m, 8 H), 1.9–2.15 (m, 6 H), 5.09 (t, $J = 7$ Hz, 1 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 12.97, 14.06 (2 C), 22.54, 22.97, 27.48, 29.67, 29.99, 30.91, 32.56, 123.55, 140.99. **(ii) Deuterolysis.** In another run, the reaction mixture was quenched at 0 °C with DCl (20 wt % in D_2O , 5 mL) and THF (5 mL) and stirred for 2–3 h at 23 °C. In this case, (Z)-5-deuterio-6-(2-deuterioethyl)-5-decene was obtained in 92% yield (GLC): ^1H NMR (CDCl_3 , Me_4Si) δ 0.8–1.05 (m, 8 H), 1.2–1.45 (m, 8 H), 1.9–2.1 (m, 6 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 12.65 (5, $J = 19$ Hz), 14.05 (2 C), 22.52, 22.94, 27.35, 29.49, 29.97, 30.88, 32.51, 123.14 (t, $J = 23$ Hz), 140.90; $\geq 98\%$ D at the Me of the ethyl group and $\geq 98\%$ D at C-5. **(iii) Iodinolysis.** In the third run (1 mmol scale), the reaction mixture was quenched with a solution of I_2 (3.1 g, 12.2 mmol) in THF (13 mL) at 0 °C and stirred at 23 °C for 8–10 h. After workup, purification by column chromatography afforded 0.21 g (54%, 69% by NMR) of (*E*)-5-iodo-6-(2-iodoethyl)-5-decene: ^1H NMR (CDCl_3 , Me_4Si) δ 0.91 (t, $J = 7$ Hz, 3 H), 0.92 (t, $J = 7$ Hz, 3 H), 1.25–1.45 (m, 6 H), 1.45–1.6 (m, 2 H), 2.19 (t, $J = 7.5$ Hz, 2 H), 2.49 (t, $J = 7.5$ Hz, 2 H), 2.79 (t, $J = 9.5$ Hz, 2 H), 3.15 (t, $J = 9.5$ Hz, 2 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 1.46, 13.89, 14.00, 21.60, 22.58, 30.93, 31.56, 31.83, 41.00, 46.86, 107.78, 143.06.

(b) Diphenylacetylene. The corresponding reaction of diphenylacetylene required heating for 75 h at 55 °C for completion. **(i) Protonolysis.** After quenching the mixture as above, examination of the crude product by NMR spectroscopy indicated the formation of (Z)-1,2-diphenyl-1-butene³⁰ in 16% NMR yield (using CH_2Br_2 as an internal standard) and (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene^{23b} in 69% NMR yield (based on diphenylacetylene). **(ii) Deuterolysis.** Deuterolysis provided a 2:1 mixture of (Z)-1,4-dideuterio-1,2-diphenyl-1-butene and (*E,E*)-1,4-dideuterio-1,2,3,4-tetraphenyl-1,3-butadiene which yielded the following spectral data. **(Z)-1,4-Dideuterio-1,2-diphenyl-1-butene:** $\geq 98\%$ D at C-1 and C-4; ^1H NMR (CDCl_3 , Me_4Si) δ 1.0–1.1 (m, 2 H), 2.49 (t, $J = 7$ Hz, 2 H), 6.7–7.45 (m, 10 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 12.59 (t, $J = 19$ Hz), 33.37, 124.67 (t, $J = 23$ Hz), 125.98, 126.75, 127.73, 128.45 (2 C), 128.90, 137.41, 141.44, 144.77. **(E,E)-1,4-Dideuterio-1,2,3,4-tetraphenyl-1,3-butadiene:** $\geq 98\%$ D at C-1 and C-4; ^1H NMR (CDCl_3 , Me_4Si) δ 6.7–7.45 (m, 20 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 126.56, 127.29, 127.73, 128.76, 129.40, 130.29, 131.21 (t, $J = 23$ Hz), 137.07, 139.66, 145.39. The use of benzene as a solvent instead of hexanes led to a considerable acceleration of the carboalumination reaction, which was complete in 19 h at 55 °C. After deuterolysis, the two products mentioned above were obtained as a 1:1 mixture in 90% combined yield. Deuterium incorporation was $\geq 98\%$ at all deuterated carbons.

(c) 1-Decyne. This reaction was complete in 17 h at 23 °C in benzene. **(i) Protonolysis.** Quenching the mixture with 3 N HCl and THF provided, after the usual workup, a 90% yield (GLC) of a 1:1 mixture of 2-ethyl-1-decene²⁸ [^1H NMR (CDCl_3 , Me_4Si) δ 0.8–0.95

(30) Takahashi, T.; Xi, Z.; Rousset, C. J.; Suzuki, N. *Chem. Lett.* **1993**, 1001.

(m, 3 H), 1.02 (t, $J = 7$ Hz, 3 H), 1.2–1.5 (m, 12 H), 1.95–2.1 (m, 4 H), 4.68 (s, 2 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 12.37, 14.10, 22.77, 27.96, 28.77, 29.43, 29.57, 29.66, 32.02, 36.36, 107.33, 151.65] and (E)-3-dodecene²⁹ [^1H NMR (CDCl_3 , Me_4Si) δ 0.8–0.95 (m, 3 H), 0.96 (t, $J = 7$ Hz, 3 H), 1.2–1.4 (m, 12 H), 1.9–2.1 (m, 4 H), 5.3–5.5 (m, 2 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.99, 14.08, 22.77, 25.67, 29.31, 29.43, 29.62, 29.77, 32.02, 32.67, 129.37, 131.83]. (ii) **Deuterolysis.** Quenching the reaction mixture with DCl (20 wt % in D_2O , 5 mL) and THF (5 mL) provided a 1:1 mixture of (E)-1-deuterio-2-(2-deuterioethyl)-1-decene and (E)-1,4-dideuterio-3-dodecene. (E)-1-Deuterio-2-(2-deuterioethyl)-1-decene: 96% D at C-1; 46% D at the Me of the ethyl group; ^{13}C NMR (CDCl_3 , Me_4Si) δ 12.07 (t, $J = 20$ Hz), 14.11, 22.81, 28.00, 28.67 (signal of the fraction deuterated at the Me of the ethyl group), 28.75 (signal of the fraction protonated at the Me of the ethyl group), 29.48, 29.61, 29.70, 32.06, 36.37, 107.10 (t, $J = 23.5$ Hz), 151.50. (E)-1,4-Dideuterio-3-dodecene: >90% D at C-4; 92% D at C-1; ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.72 (t, $J = 19$ Hz), 14.11, 22.81, 25.57, 29.36, 29.48, 29.67, 29.80, 32.06, 32.60, 129.05 (t, $J = 23$ Hz), 131.75.

(d) **Phenylacetylene.** This reaction was complete after 7 h at 55 °C in hexanes. (i) **Protonolysis.** After protonolysis with 3 N HCl, examination of the product by NMR spectroscopy indicated the formation of (E)-1-phenyl-1-butene³⁰ [^1H NMR (CDCl_3 , Me_4Si) δ 1.08 (t, $J = 7$ Hz, 3 H), 2.22 (qd, $J = 7$ and 7 Hz, 2 H), 6.25 (dt, $J = 16$ and 6 Hz, 1 H), 6.37 (d, $J = 16$ Hz, 1 H), 7.1–7.5 (m, 5 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.63, 26.05, 125.88, 126.71, 128.43, 128.78, 132.57, 137.91] and 2-phenyl-1-butene³⁰ [^1H NMR (CDCl_3 , Me_4Si) 1.10 (t, $J = 7$ Hz, 3 H), 2.50 (q, $J = 7$ Hz, 2 H), 5.05 (s, 1 H), 5.27 (s, 1 H), 7.1–7.5 (m, 5 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 12.92, 28.04, 110.90, 125.98, 127.22, 128.19, 141.51, 150.01] in a 2:1 ratio in 84% combined NMR yield (using CH_2Br_2 as an internal standard). (ii) **Deuterolysis.** In another run, the reaction mixture was quenched with DCl/ D_2O at –78 °C. Examination of the product by NMR spectroscopy indicated the formation of a 2:1 mixture of (E)-1,4-dideuterio-1-phenyl-1-butene and 1,4-dideuterio-2-phenyl-1-butene. Analysis of their ^1H and ^{13}C NMR spectra indicated that the extents of D incorporation at C-1 were 91 and 92% and those at C-4 were 42% for the 1-phenyl isomer and 95% for the 2-phenyl isomer.

Reaction of 5-Decyne with Et_3Al in the Presence of 1 Equiv of Cp_2ZrCl_2 . (a) (Z)-5-(Ethyl-2'- d_1)-5-decene-6- d_1 (1). **Representative Procedure.** In a dry round-bottomed flask equipped with a stirring bar, a septum inlet, and a mercury bubbler were placed Cp_2ZrCl_2 (877 mg, 3 mmol) and 15 mL of benzene. To this suspension were added Et_3Al (1.25 mL, 9 mmol) and 5-decyne (0.54 mL, 3 mmol), and the reaction mixture was stirred at 23 °C for 2 h. NMR examination of the reaction mixture after quenching with THF (0.2 mL) indicated the formation of $\text{Cp}_2\text{Zr}(\text{Et})\text{Cl}$ in 60% yield, as judged from NMR signals of Cp (^1H NMR δ 5.80 (s); ^{13}C NMR δ 112.53) and $\text{CH}_2\text{-Zr}$ (^{13}C NMR δ 47.12). After deuterolysis with 4% DCl, the reaction mixture was extracted with Et_2O , washed with water, dried over MgSO_4 , filtered, and concentrated. Analysis of the product by GLC and NMR spectroscopy indicated the formation of the title compound in 84% yield (>95% D at C-6; 90% D at C-2').

(b) (Z)-5-Ethyl-5-decene-6- d_1 (7). This reaction was performed as described above using 0.42 mL (3 mmol) of Et_3Al . It was complete in 7 h. Analysis of the deuterolysis product by GLC and NMR spectroscopy indicated the formation of 7 in 65% yield ($\geq 80\%$ D at C-6; 18% D at C-2').

(c) (Z)-5-(Ethyl-2'- d_2)-5-decene-6- d_1 (8). To the suspension of Cp_2ZrCl_2 (988 mg, 3 mmol) in 15 mL of benzene was added Et_3Al (1.25 mL, 9 mmol), and the reaction mixture was stirred at 23 °C for 24 h. To the resultant mixture was added 5-decyne (0.43 mL, 2.4 mmol). the reaction mixture was stirred for 15 min, quenched with 4% DCl, extracted with Et_2O , washed with water, dried over MgSO_4 , filtered, and concentrated. Analysis of the product by GLC and NMR spectroscopy indicated the formation of 8 in 87% yield (>95% D at C-6; 83% CHD_2 and 17% CH_2D at C-2').

NMR Examination of the Reaction of 5-Decyne with Et_3Al in the Presence of 1 Equiv of Cp_2ZrCl_2 . The reaction of 5-decyne with 3 equiv of Et_3Al in the presence of 1 equiv of Cp_2ZrCl_2 was carried out as described above on 1 mmol scale. An aliquot was withdrawn and periodically examined by NMR spectroscopy. The amounts of

$\text{EtZrCp}_2\text{Cl-Et}_{3-n}\text{AlCl}_n$ at various times along with those of 10 indicated in parentheses are as follows: 91% (<5%) at 5 min, 81% (<5%) at 1 h, 75% (<5%) at 2 h, 55% (20%) at 3 h, 37% (26%) at 4 h, and <5% (17%) at 14 h. The signals for $\text{EtZrCp}_2\text{Cl-Et}_{3-n}\text{AlCl}_n$ are as follows: ^1H NMR for Cp δ 5.75; ^{13}C NMR for Cp δ 112.95; ^{13}C NMR for $\text{CH}_2\text{-Zr}$ δ 53.76.

NMR Examination of the Reaction of Cp_2ZrCl_2 with 1 Equiv of Et_3Al . To the suspension of Cp_2ZrCl_2 (292 mg, 1 mmol) in 5 mL of C_6D_6 was added Et_3Al (0.143 mL, 1 mmol). Examination of the reaction mixture by NMR spectroscopy revealed that the reaction was complete in 20 min and that $\text{EtZrCp}_2\text{Cl-Et}_2\text{AlCl}$ was formed in about 75% yield: ^1H NMR (Cp) δ 5.80; ^{13}C NMR (Cp) δ 112.45; ^{13}C NMR ($\text{CH}_2\text{-Zr}$) δ 49.20. No detectable changes were seen over 24 h at ambient temperatures. After quenching with THF (0.05 mL) NMR spectroscopy indicated that 25% of Cp_2ZrCl_2 remained unreacted, with the rest having been converted to EtZrCp_2Cl (72%); ^1H NMR (CDCl_3 , Me_4Si) δ 1.05 (q, $J = 7.3$ Hz, 2 H), 1.35 (t, $J = 7.3$ Hz, 3 H), 5.70 (s, 10 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 18.52, 46.67, 112.52.

Preparation of EtZrCp_2Cl . In a dry round-bottomed flask equipped with a stirring bar, a septum inlet, and a mercury bubbler under argon were placed HzrCp_2Cl (1.0 g, 3.88 mmol) and 16 mL of C_6D_6 . Argon was replaced with ethylene and the suspension was rapidly stirred until all solid material dissolved (3 h). NMR examination of the reaction mixture indicated that EtZrCp_2Cl (0.27 M in C_6D_6) was formed in 90% yield. ^1H NMR (C_6D_6 , Me_4Si) δ 1.12 (q, $J = 7.5$ Hz, 2 H), 1.43 (5, $J = 7.5$ Hz, 3 H), 5.82 (s, 10 H); ^{13}C NMR (C_6D_6 , Me_4Si) δ 18.38, 46.53, 112.34.

Reaction of EtZrCp_2Cl with EtAlCl_2 . In a dry NMR tube under argon was placed a solution of EtZrCp_2Cl in C_6D_6 (1.0 mL, 0.27 M, 0.27 mmol). To this solution at 5 °C was added EtAlCl_2 (0.034 mL, 0.27 mmol). Immediate precipitation of Cl_2ZrCp_2 was observed. After treatment with THF (0.05 mL) NMR analysis indicated that <0.5% of EtZrCp_2Cl remained unreacted, with the rest being converted to Cl_2ZrCp_2 .

Reaction of EtZrCp_2Cl with Et_2AlCl . In a dry NMR tube under argon was placed a solution of EtZrCp_2Cl in C_6D_6 (1.0 mL, 0.27 M, 0.27 mmol). To this solution at 5 °C was added Et_2AlCl (0.034 mL, 0.27 mmol). NMR examination of the reaction mixture revealed that the reaction was complete in 5 min. After treatment with THF (0.05 mL) NMR analysis indicated that 80% of EtZrCp_2Cl remained unreacted, with the rest being converted to Cl_2ZrCp_2 (16%).

Reaction of EtZrCp_2Cl with Et_3Al . In a dry NMR tube under argon was placed a solution of EtZrCp_2Cl in C_6D_6 (1.0 mL, 0.27 M, 0.27 mmol). To this solution at 5 °C was added Et_3Al (0.037 mL, 0.27 mmol), and the reaction mixture was kept at 23 °C for 0.5 h. NMR examination of the reaction mixture indicated that 10 was formed in 83% yield: ^1H NMR (C_6D_6 , Me_4Si) δ 0.23–0.3 (m, 4 H), 0.26–0.35 (m, 2 H), 1.37 (t, $J = 7.9$ Hz, 6 H), 1.4–1.48 (m, 2 H), 5.43 (s, 10 H); ^{13}C NMR (C_6D_6 , Me_4Si) δ –0.63, 4.55 (br, 2 C), 9.31 (2 C), 36.94, 108.25 (10 C).

Reaction of 10 with 5-Decyne. Solution of 10 (0.225 mmol) in C_6D_6 prepared as described above was treated with 5-decyne (31 mg, 0.225 mmol) in an NMR tube, and the reaction mixture was kept at 23 °C for 10 min. NMR examination of the reaction mixture indicated that EtZrCp_2Cl was formed in 90% yield based on the integration of the ^1H NMR Cp signal at 5.83 ppm. After deuterolysis with 4% DCl, the reaction mixture was extracted with Et_2O , washed with water, dried over MgSO_4 , filtered, and concentrated. Analysis by GLC and NMR spectroscopy indicated the formation of (Z)-5-(ethyl-2'- d_1)-5-decene-6- d_1 in 95% yield (>95% D at C-6; >98% D at C-2').

NMR Examination of the Reaction of 2,3-Di(*n*-butyl)-1,1-bis(cyclopentadienyl)-1-zirconia-2-cyclopentene with Et_2AlCl . In a dry round-bottomed flask equipped with a stirring bar, a septum inlet, and a mercury bubbler were placed Cp_2ZrCl_2 (292 mg, 1 mmol) and 5 mL of C_6D_6 under an atmosphere of ethylene. To this suspension was added dropwise at 5 °C *n*-BuLi (2 M in cyclohexane, 1 mL, 2 mmol). After stirring for 1 h at 23 °C under an atmosphere of ethylene, 5-decyne (0.18 mL, 1 mmol) was added, and ethylene was replaced with argon. NMR examination after 1 h indicated the formation of 6 in 90% yield, as judged from the NMR signals of Cp: ^1H NMR δ 5.9 (s); ^{13}C NMR δ 110.63. Treatment of the reaction mixture with Et_2AlCl (0.13 mL, 1 mmol) afforded EtZrCp_2Cl in 65% yield, as judged from the NMR

signals of Cp (^1H NMR δ 5.75 (s); ^{13}C NMR δ 112.47) and $\text{CH}_2\text{-Zr}$ (^{13}C NMR δ 46.58).

Reaction of 5-Decyne with Et_3Al in the Presence of a Catalytic Amount of $\text{Cp}_2\text{Zr}(\text{n-Bu})_2$. In a dry round-bottomed flask equipped with a stirring bar, a septum inlet, and a mercury bubbler were placed Cp_2ZrCl_2 (58 mg, 0.2 mmol) and 5 mL of toluene. This suspension at -78°C was treated with $n\text{-BuLi}$ (2.5 M in hexanes, 0.16 mL, 0.4 mmol). The resultant clear yellow solution was slowly warmed to 0°C and treated with Et_3Al (0.14 mL, 1 mmol) and 5-decyne (0.18 mL, 1 mmol). After 24 h at 23°C the reaction mixture was quenched with 4% HCl, extracted with Et_2O , washed with water, dried over MgSO_4 , filtered, and concentrated. Analysis by GLC indicated the formation of (Z)-5-ethyl-5-decene in <5% yield.

Reaction of 5-Decyne with Et_3Al in the Presence of Catalytic Amounts of $\text{Cp}_2\text{Zr}(\text{n-Bu})_2$ and Et_2AlCl . In a dry round-bottomed flask equipped with a stirring bar, a septum inlet, and a mercury bubbler were placed Cp_2ZrCl_2 (58 mg, 0.2 mmol) and 5 mL of toluene. This suspension at -78°C was treated with $n\text{-BuLi}$ (2.5 M in hexanes, 0.16 mL, 0.4 mmol). The resultant clear yellow solution was slowly warmed to 0°C and treated with Et_3Al (0.14 mL, 1 mmol), 5-decyne (0.18 mL, 1 mmol), and Et_2AlCl (0.025 mL, 0.2 mmol). After 1 h at 23°C the reaction mixture was quenched with 4% DCl, extracted with Et_2O , washed with water, dried over MgSO_4 , filtered, and concentrated. Analysis by GLC and NMR spectroscopy indicated the formation of (Z)-5-(2'-dideuterioethyl)-6-deuterio-5-decene in 73% yield (>90% D at C-6; >98% D at C-2').

Reaction of 5-Decyne with Et_3Al in the Presence of Catalytic Amounts of Zirconocene Derivatives. (a) Use of 0.2 equiv of **6**. No reaction of 5-decyne with Et_3Al (1.2 equiv) was observed in the presence of **6** (0.2 equiv) prepared by the reaction of Et_2ZrCp_2 and 5-decyne. However, addition of Et_2AlCl (0.2 equiv) to the mixture did induce the expected reaction to give, after deuterolysis, a 40% yield of **1**.

(b) Use of 0.1 equiv of a Mixture of **6** and Et_2AlCl . The reaction of 5-decyne with Et_3Al (1.2 equiv) was carried out in hexanes in the presence of 0.1 equiv each of **6** and Et_2AlCl . After deuterolysis, **1** was produced in 85% yield.

Reaction of 5-Decyne with Et_2AlCl in Hexanes in the Presence of Cp_2ZrCl_2 . Addition of Et_2AlCl (1 equiv) to a mixture of 5-decyne in the presence of either 0.1 or 1 equiv of Cp_2ZrCl_2 in hexanes did not induce any reaction over at least 1 day at 23°C , with $\geq 90\text{--}95\%$ of the starting materials remaining unreacted.

Reaction of Various Alkynes with Et_2AlCl in $(\text{CH}_2\text{Cl})_2$ in the Presence of the Stoichiometric or a Catalytic Amount of Cp_2ZrCl_2 .

(a) **Reaction of 5-Decyne Using the Stoichiometric Amount of Cp_2ZrCl_2 .** A solution of Cp_2ZrCl_2 (0.586 g, 2 mmol) and 5-decyne (0.36 mL, 2 mmol) in $(\text{CH}_2\text{Cl})_2$ (4 mL) was treated at 0°C with Et_2AlCl (0.75 mL, 6 mmol), and the mixture was warmed to 23°C . After 20 h, analysis by GLC of a protonolyzed aliquot using nonane as an internal standard indicated that the reaction was essentially complete and that (Z)-5-ethyl-5-decene was formed in 90% yield along with 4–5% of (E,E)-6,7-di(*n*-butyl)-5-ethyl-5,7-dodecadiene (based on 5-decyne). An aliquot (0.6 mL) was transferred into a 5-mm NMR tube containing C_6D_6 (0.2 mL). THF (0.6 mL) was added to dissolve all insoluble materials. Examination of this mixture by ^1H NMR using mesitylene as an internal standard indicated that Cp_2ZrCl_2 was recovered to the extent of $\geq 95\%$ yield. (i) **Deuterolysis.** The reaction mixture was cooled to 0°C and quenched with THF (2 mL) and D_2O (2 mL). After stirring for 12 h at 23°C , the reaction mixture was extracted with pentane, washed with NaHCO_3 and H_2O , dried over MgSO_4 , filtered, and concentrated. Filtration through silica gel (pentane) followed by concentration provided 0.24 g (71%) of (Z)-5-deuterio-6-ethyl-5-decene: ^1H NMR (CDCl_3 , Me_4Si) δ 0.8–0.95 (m, 6 H), 0.98 (t, $J = 7$ Hz, 3 H), 1.2–1.45 (m, 8 H), 1.9–2.15 (m, 6 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 12.94, 14.05 (2 C), 22.53, 22.96, 27.37, 29.59, 29.97, 30.90, 32.52, 123.17 (t, $J = 23$ Hz), 140.89; $\geq 95\%$ D incorporation by ^{13}C NMR. (ii) **Iodinolysis.** In another run, the mixture was treated with a solution of I_2 (3.05 g, 12 mmol) in THF (10 mL) at 0°C and warmed to 23°C for 12 h. The mixture was then quenched with 3 N HCl, extracted with Et_2O , washed with $\text{Na}_2\text{S}_2\text{O}_3$, NaHCO_3 , and H_2O , and dried over MgSO_4 . Filtration through silica gel (pentane) followed by concentration provided 0.49 g (84%) of (E)-6-ethyl-5-iodo-

5-decene: ^1H NMR (CDCl_3 , Me_4Si) δ 0.8–0.95 (m, 6 H), 0.97 (t, $J = 7$ Hz, 3 H), 1.2–1.55 (m, 8 H), 2.17 (t, $J = 7.5$ Hz, 2 H), 2.23 (q, $J = 7$ Hz, 2 H), 2.49 (t, $J = 7.5$ Hz, 2 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 12.07, 13.91, 14.03, 21.64, 22.71, 30.78, 30.92, 32.02, 35.72, 40.88, 104.14, 145.00.

(b) **Reaction of 5-Decyne Using a Catalytic Amount of Cp_2ZrCl_2 .** This reaction was carried out similarly using 0.059 g (0.2 mmol) of Cp_2ZrCl_2 . After 20 h at 55°C , GLC analysis of a protonolyzed aliquot indicated the formation of (Z)-5-ethyl-5-decene in >90% yield along with 8–10% of (E,E)-6,7-di(*n*-butyl)-5-ethyl-5,7-dodecadiene (based on 5-decyne). (i) **Protonolysis.** The reaction mixture was cooled to 0°C and quenched with THF (5 mL) and 3 N HCl. After the usual workup, Kugelrohr distillation (oven temperature = 50°C at 5 mmHg) provided two products. After filtration (silica gel–pentane), (Z)-5-ethyl-5-decene was obtained in 70% yield (0.235 g). Also obtained was (E,E)-6,7-di(*n*-butyl)-5-ethyl-5,7-dodecadiene isolated in 4% yield (0.022 g): ^1H NMR (CDCl_3 , Me_4Si) δ 0.8–1.0 (m, 15 H), 1.15–2.05 (m, 18 H), 1.9–2.1 (m, 8 H), 4.97 (t, $J = 7$ Hz, 1 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.05 (3 C), 14.12 (2 C), 22.43, 22.73, 23.08, 23.16, 25.68, 27.43, 29.43, 29.54, 29.87, 30.36, 30.98, 31.27, 32.31, 127.32, 135.70, 137.67, 139.93. (ii) **Deuterolysis.** In another run, the reaction mixture was quenched with THF (5 mL) and DCl (20 wt % in D_2O , 5 mL) at 0°C . After stirring for 5 h at 23°C , the usual extractive workup (pentane) afforded (Z)-5-deuterio-6-ethyl-5-decene and (E,E)-6,7-di(*n*-butyl)-5-deuterio-8-ethyl-5,7-dodecadiene. After separation by Kugelrohr distillation and filtration through silica gel (pentane) (Z)-5-deuterio-6-ethyl-5-decene was obtained in 72% isolated yield (0.242 g) ($\geq 95\%$ D by ^{13}C NMR). (E,E)-6,7-Di(*n*-butyl)-5-deuterio-8-ethyl-5,7-dodecadiene was also obtained in 6% yield (0.039 g): ^1H NMR (CDCl_3 , Me_4Si) δ 0.8–1.0 (m, 15 H), 1.1–1.45 (m, 18 H), 1.9–2.1 (m, 8 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.06 (3 C), 14.13 (2 C), 22.44, 22.74, 23.09, 23.18, 25.69, 27.33, 29.39, 29.55, 29.86, 30.37, 30.98, 31.28, 32.30, 126.95 (t, $J = 23$ Hz), 135.69, 137.64, 139.81; $\geq 94\%$ D by ^{13}C NMR.

(c) **Reaction of Diphenylacetylene Using a Catalytic Amount of Cp_2ZrCl_2 .** This reaction was complete after 36–40 h at $70\text{--}75^\circ\text{C}$ and gave, after hydrolysis, (Z)-1,2-diphenyl-1-butene³⁰ in 60% NMR yield (using CH_2Br_2 as an internal standard): ^1H NMR (CDCl_3 , Me_4Si) δ 1.06 (t, $J = 7$ Hz, 3 H), 2.50 (q, $J = 7$ Hz, 2 H), 6.42 (s, 1 H), 6.7–7.45 (m, 10 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 12.88, 33.47, 125.00, 125.94, 126.72, 127.70, 128.38, 128.43, 128.89, 137.43, 141.37, 144.81.

(d) **Reaction of 1-Decyne Using a Catalytic Amount of Cp_2ZrCl_2 .** This reaction was complete after 5 h at 23°C . (i) **Protonolysis.** Protonolysis afforded a 3:1 mixture of 2-ethyl-1-decene and (E)-3-dodecene in 91% yield (GLC). (ii) **Deuterolysis.** Quenching the reaction mixture with THF and DCl (20 wt % in D_2O , 5 mL) provided after workup a 3:1 mixture of (E)-1-deuterio-2-ethyl-1-decene and (E)-4-deuterio-3-dodecene. (E)-1-Deuterio-2-ethyl-1-decene: $\geq 87\%$ D by ^{13}C NMR; ^{13}C NMR (CDCl_3 , Me_4Si) δ 12.35, 14.10, 22.80, 27.99, 28.74, 29.46, 29.60, 29.69, 32.05, 36.35, 107.08 (t, $J = 23$ Hz), 151.53. (E)-4-Deuterio-3-dodecene: $\geq 87\%$ D by ^{13}C NMR; ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.00, 14.10, 22.80, 25.65, 29.34, 29.52, 29.66, 29.78, 32.05, 32.59, 129.06 (t, $J = 23$ Hz), 131.75.

NMR Examination of Et_2AlCl and Cp_2ZrCl_2 . A solution of Cp_2ZrCl_2 (0.146 g, 0.5 mmol) and Et_2AlCl (0.065 mL, 0.52 mmol) in CD_2Cl_2 (1.5 mL) was examined by ^1H and ^{13}C NMR spectroscopies over a period of 24 h. Examination after 10 min, 4 h, and 24 h using mesitylene as an internal standard indicated that Cp_2ZrCl_2 and Et_2AlCl were remaining unreacted to the extents of >95%. The extent of the formation of EtZrCp_2Cl was below the detection limit of 0.1%.

Reaction of 5-Decyne with Et_3Al in the Presence of the Stoichiometric Amount of MeZrCp_2Cl . (a) **In Hexanes.** A solution of MeZrCp_2Cl ¹⁷ (0.157 g, 0.58 mmol) and 5-decyne (104 μL , 0.58 mmol) in hexanes (2 mL) was treated at 0°C with Et_3Al (0.08 mL, 0.59 mmol) and stirred for 2 h at 23°C . After deuterolysis, analysis of the product by GLC and NMR spectroscopy indicated the formation of (Z)-5-deuterio-6-(2-deuterioethyl)-5-decene (**1**) in 67% yield ($\geq 90\%$ D at C-5 and $\geq 92\%$ D at Me of the ethyl group), along with a 20% yield (based on 5-decyne) of (E,E)-6,7-di(*n*-butyl)-5,8-dideuterio-5,7-dodecadiene ($\geq 90\%$ D at C-5 and C-8).

(b) **In 1,2-Dichloroethane.** The corresponding reaction run in 1,2-dichloroethane required 12–24 h at 23°C for completion and produced, after deuterolysis, **1** in 69% yield (81% D at C-5; 85% D at Me of the

ethyl group). The formation of two dimeric products ($\leq 9\%$ combined yield based on 5-decyne) was detected by GLC.

Reaction of 5-Decyne with Et_2AlCl in the Presence of the Stoichiometric Amount of MeZrCp_2Cl . The reaction of 5-decyne with 3 equiv of Et_2AlCl and 1 equiv of MeZrCp_2Cl in $(\text{CH}_2\text{Cl})_2$ was carried out similarly. After deuterolysis, (Z)-5-ethyl-6-deuterio-5-decene (7) was produced in 93% yield ($\geq 91\%$ D at C-6). The extent of formation of (Z)-5-methyl-5-decene was $< 2\%$.

Reaction of Various Alkynes with $(n\text{-Pr})_3\text{Al}$ in the Presence of a Catalytic Amount of Cp_2ZrCl_2 . **(a) 5-Decyne. Representative Procedure.** To a solution of Cp_2ZrCl_2 (0.029 g, 0.1 mmol) and 5-decyne (0.14 g, 1 mmol) in hexanes (2 mL) was added $(n\text{-Pr})_3\text{Al}$ (0.47 g, 3 mmol), at 0 °C, and the resulting mixture was stirred at 23 °C for 12 h. **(i) Protonolysis.** The mixture was quenched with 3 N HCl. After the usual extractive workup, examination by GLC and ^{13}C NMR spectroscopy indicated the formation of (Z)-5-decene (0.33 mmol), (Z)-4-decene (0.30 mmol), and (5E,7E)-6,7-di(*n*-butyl)-5,7-dodecadiene (0.19 mmol). The identity of these products was established by GLC coinjection of their authentic samples. **(ii) Deuterolysis.** Quenching the reaction mixture with $\text{DCl}/\text{D}_2\text{O}$ led to the formation of (Z)-5-deuterio-5-decene (93% D), (Z)-5-deuterio-4-decene (93% D), and (5E,7E)-6,7-di(*n*-butyl)-5,8-dideuterio-5,7-dodecadiene (97% D). **(Z)-5-Deuterio-5-decene:** ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.12, 22.48, 27.00, 32.12, 129.53 ($^1J_{\text{CD}}$ = 23 Hz), 129.76. **(Z)-5-Deuterio-4-decene:** ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.85, 14.12, 22.73, 23.03, 27.21, 29.39, 29.59, 31.68, 129.53, 129.76 ($^1J_{\text{CD}}$ = 23 Hz). **(5E,7E)-6,7-Di(*n*-butyl)-5,8-dideuterio-5,7-dodecadiene:** ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.05, 22.61, 22.90, 27.79, 27.93, 31.30, 32.43, 125.63 ($^1J_{\text{CD}}$ = 23 Hz), 141.21.

(b) 3-Hexyne. This reaction was run similarly at 50 °C for 3 h. After deuterolysis, a roughly 1:1 mixture of (Z)-3-deuterio-3-hexene and (Z)-3-deuterio-2-hexene was obtained. The extents of D incorporation were $> 90\%$. More critically, no D incorporation was observed at C-2 of (Z)-3-deuterio-2-hexene. An authentic sample of (Z)-2-hexene obtained from a commercial source exhibited ^{13}C NMR signals at 123.86 and 130.69 ppm for the alkenyl carbons.

(c) Diphenylacetylene. The corresponding reaction of diphenylacetylene was carried out in toluene at 100 °C for 6 h. After protonolysis of the reaction mixture, examination of the product by GLC and NMR spectroscopy indicated the formation of (Z)-stilbene (0.27 mmol), (E)-stilbene (0.41 mmol), and (1E,3E)-1,2,3,4-tetraphenyl-1,3-butadiene^{23b} (0.12 mmol).

(d) 1-Decyne. The corresponding reaction of 1-decyne in hexanes was complete in 6 h at 23 °C, and it gave, after hydrolysis, 1-decene (61%) and *n*-decane (15%). Deuterolysis led to the formation of (E)-1-deuterio-1-decene: 98% D at C-1; ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.15, 22.78, 29.06, 29.27, 29.41, 29.59, 32.00, 33.88, 113.85 ($^1J_{\text{CD}}$ = 24 Hz), 139.11.

(e) Phenylacetylene. This reaction gave, after hydrolysis, styrene in 53% yield.

Reaction of 5-Decyne with $(n\text{-Pr})_3\text{Al}$ in 1,2-Dichloroethane. The reaction of 5-decyne (1 mmol) with Et_3Al (3 mmol) and a catalytic amount of Cp_2ZrCl_2 (0.1 mmol) in $(\text{CH}_2\text{Cl})_2$ run at 50 °C for 3 h gave, after hydrolysis, (Z)-5-decene (0.52 mmol), (Z)-4-decene (0.35 mmol), and (Z)-5-(*n*-propyl)-5-decene (0.09 mmol).

Reaction of 5-Decyne with $(n\text{-Pr})_3\text{Al}$ in the Presence of a Catalytic or the Stoichiometric Amount of MeZrCp_2Cl . **(a) Use of a Catalytic Amount of MeZrCp_2Cl in Hexanes.** A solution of MeZrCp_2Cl ¹⁷ (0.028 g, 0.1 mmol) and 5-decyne (0.14 g, 1 mmol) in hexanes (2 mL) was treated at 0 °C with $(n\text{-Pr})_3\text{Al}$ (0.47 g, 3 mmol), and the reaction mixture was stirred at 23 °C for 24 h. Protonolysis led to the formation

of (Z)-5-decene (0.42 mmol), (Z)-4-decene (0.24 mmol), and (5E,7E)-6,7-di(*n*-butyl)-5,7-dodecadiene (0.15 mmol).

(b) Use of a Catalytic Amount of MeZrCp_2Cl in 1,2-Dichloroethane. The corresponding reaction (1 mmol scale) run in $(\text{CH}_2\text{Cl})_2$ was complete after 48 h at 23 °C and gave, after hydrolysis, (Z)-5-decene (0.63 mmol), (Z)-4-decene (0.12 mmol), (Z)-5-(*n*-propyl)-5-decene (0.11 mmol), and (5E,7E)-di(*n*-butyl)-5,7-dodecadiene (0.033 mmol).

(c) Use of the Stoichiometric Amount of MeZrCp_2Cl in Hexanes. The corresponding reaction in hexanes using 1 equiv of MeZrCp_2Cl gave, after 1 h at 23 °C and hydrolysis, (Z)-5-decene (0.31 mmol), (Z)-4-decene (0.27 mmol), and (5E,7E)-6,7-di(*n*-butyl)-5,7-dodecadiene (0.20 mmol).

(d) Use of the Stoichiometric Amount of MeZrCp_2Cl in 1,2-Dichloroethane. The corresponding reaction in $(\text{CH}_2\text{Cl})_2$ using 1 equiv of MeZrCp_2Cl at 23 °C for 1 h produced, after hydrolysis, (Z)-5-decene (0.24 mmol), (Z)-4-decene (0.21 mmol), (Z)-5-(*n*-propyl)-5-decene (0.08 mmol), and (5E,7E)-6,7-di(*n*-butyl)-5,7-dodecadiene (0.15 mmol).

Reaction of 5-Decyne with $(n\text{-Pr})_2\text{AlCl}$ in the Presence of a Catalytic Amount of Cp_2ZrCl_2 . **(a) In $(\text{CH}_2\text{Cl})_2$.** A solution of Cp_2ZrCl_2 (0.029 g, 0.1 mmol) and 5-decyne (0.14 g, 1 mmol) in $(\text{CH}_2\text{Cl})_2$ (1 mL) was treated at 0 °C with $(n\text{-Pr})_2\text{AlCl}$ (3 mmol), generated by mixing $(n\text{-Pr})_3\text{Al}$ (0.31 g, 2 mmol) with dry AlCl_3 (0.13 g, 1 mmol) in $(\text{CH}_2\text{Cl})_2$ (1 mL). The reaction mixture was heated at 50 °C for 12 h.

(i) Protonolysis. In one run the reaction mixture was quenched with 3 N HCl, extracted with pentane, washed with NaHCO_3 , and dried over MgSO_4 . Examination of the product by GLC and NMR spectroscopy indicated the formation of a 75% yield of (Z)-5-(*n*-propyl)-5-decene: ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.93, 14.11, 21.41, 22.51, 22.98, 27.48, 29.79, 30.88, 32.52, 39.22, 124.94, 139.28. **(ii) Deuterolysis.** Deuterolysis of the reaction mixture with DCl (20 wt % in D_2O) led to the formation of (Z)-5-(*n*-propyl)-6-deuterio-5-decene: 88% D at C-6; ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.92, 14.10, 21.36, 22.48, 22.94, 27.34, 29.74, 30.83, 32.46, 39.11, 124.51 ($^1J_{\text{CD}}$ = 23 Hz), 139.17. Minor quantities of other products were also detected.

(b) In Hexanes. The same reaction run in hexanes was examined after 12 h at 23 °C by GLC and NMR spectroscopy. 5-Decyne was remaining unreacted to the extent of 75%. (Z)-5-Decene and (Z)-4-decene were formed in 13 and 10% yield, respectively.

^1H NMR Examination of $(n\text{-Pr})_2\text{AlCl}$ and Cp_2ZrCl_2 . To a solution of Cp_2ZrCl_2 (0.29 g, 1 mmol) in $(\text{CH}_2\text{Cl})_2$ (5 mL) was added $(n\text{-Pr})_2\text{AlCl}$ (3 M in $(\text{CH}_2\text{Cl})_2$, 0.33 mL, 1 mmol). After heating to 80 °C for 6 h, 99% of Cp_2ZrCl_2 (δ 6.37 ppm) remained unreacted without a sign for the formation of any other ZrCp_2 derivative.

Reaction of Alkynes with $(i\text{-Bu})_3\text{Al}$ and a Catalytic Amount of Cp_2ZrCl_2 . **(a) 5-Decyne.** To Cp_2ZrCl_2 (0.029 g, 0.1 mmol) and 5-decyne (3 mmol) in hexanes (2 mL) was added $(i\text{-Bu})_3\text{Al}$ (0.59 g, 3 mmol) at 0 °C. After stirring for 12 h at 23 °C, deuterolysis provided a 1:1 mixture of (Z)-5-deuterio-5-decene and (Z)-5-deuterio-4-decene in 87% combined yield.

(b) 1-Decyne. This reaction was run for 1 h at 23 °C. After deuterolysis, a 1:1 mixture of (E)-1-deuterio-1-decene and 1,1-dideuteriododecane was obtained in essentially quantitative yield.

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