Carbometalation Reactions of Diphenylacetylene and Other Alkynes with Methylalanes and Titanocene Derivatives

Ei-ichi Negishi,* Denis Y. Kondakov, and David E. Van Horn[†]

Department of Chemistry, Purdue University, W. Lafayette, Indiana 47907

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The reaction of PhC≡CPh with methylalanes and titanocene derivatives is multimechanistic. In cases where 1:1 mixtures of Me_3Al or Me_2AlCl with Cl_2TiCp_2 or $MeTiCp_2Cl$ are used, the reaction proceeds exclusively via methyltitanation, which needs to be promoted by a methylalane but is stoichiometric in both Ti and Al. The product of methyltitanation is ≥98% stereoisomerically pure (*E*)-1,2-diphenyl-1-propenyltitanocene chloride (**10**) complexed with methylalanes, from which **10** can be obtained as a pure substance. In cases where a 2:1 mixture of Me_3Al and Cl_2TiCp_2 is used, the course of reaction varies and is very much dependent on several reaction parameters. To observe the known formation of the Tebbe reagent (**4**) and its reaction with PhC≡CPh to give a titanacyclobutene **5**, it is necessary to premix Me_3Al and Cl_2TiCp_2 in a 2:1 ratio for a few days and run the reaction in the presence of a base, *e.g.*, DMAP. If no base is added, fast methyltitanation is observed with Me_3Al and Cl_2TiCp_2 before their conversion to **4**. Even after the formation of **4**, only slow methyltitanation of PhC≡CPh is observed in the absence of a base, presumably via formation of a $MeTiCp_2$-containing reagent from **4** and Me_2AlCl. Some other intricate aspects of the reaction are also discussed. The reaction of 5-decyne with a 1:1 mixture of Me_3Al and Cl_2TiCp_2 provides 6-methyl-4,5-decadiene in 92% yield, while the corresponding reaction of 1-octyne gives, after protonolysis, 2-methyl-1-octene only in 25% yield along with at least 3 unidentified but apparently dimeric products.

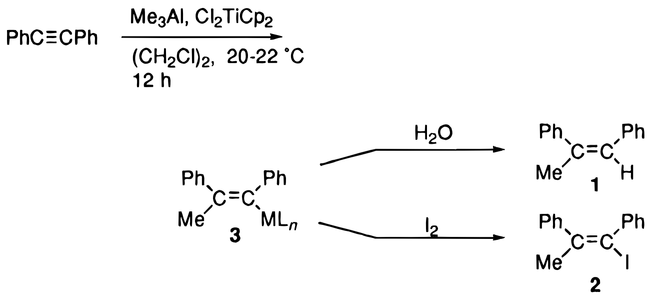
Introduction

We reported in 1978[1] that treatment of diphenylacetylene with 2 equiv each of Me_3Al and Cl_2TiCp_2 in 1,2-dichloroethane at 20−22 °C for 12 h produced, after quenching with H_2O, (*Z*)-α-methylstilbene (**1**) in 84% yield by GLC along with a minor amount (<3%) of an unidentified byproduct. Iodinolysis of the product gave (*E*)-1-iodo-1,2-diphenylpropene (**2**) (≥97% *E*) in 75% yield by GLC. These results pointed to the formation of an alkenylmetal represented by **3** (Scheme 1). However, it was not further characterized.

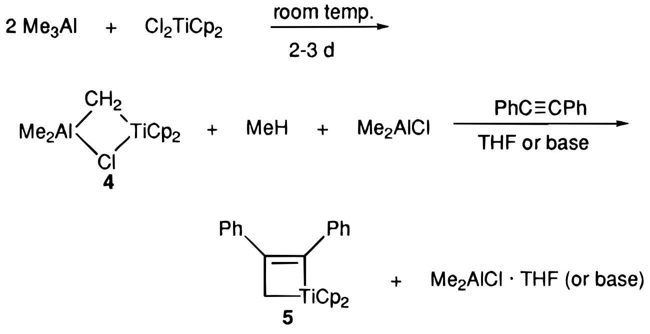
A few years later, Tebbe *et al.*[2] reported that treatment of diphenylacetylene with a reagent represented by **4**, commonly known as the Tebbe reagent[3] and preformed by mixing Cl_2TiCp_2 with 2 equiv of Me_3Al for 2−3 d at room temperature, in the presence of THF or some other base produced a titanacyclobutene **5** (Scheme 2). It should be noted here that, in the two reactions shown in Schemes 1 and 2, the three reactants, *i.e.*, Cl_2TiCp_2, Me_3Al, and PhC≡CPh, are identical, even though the products are totally different.

During the past few years, Petasis *et al.*[4] and Doxsee *et al.*[5] have independently reported that Me_2TiCp_2 reacts with PhC≡CPh to give **5** and/or the methyltitanation product **6**. Although **6** can be slowly converted to **5** upon prolonged heating,[5] it must not be an intermediate in the initial and relatively rapid formation of **5** at 75−80 °C.[4] One plausible explanation for the dichotomous behavior is that Me_2TiCp_2 undergoes α-H abstraction to give $CH_2{=}TiCp_2$ (**7**) which rapidly adds to PhC≡CPh to give **5** in competition with methyltitanation of Me_2TiCp_2 with PhC≡CPh to give **6**.[4] The slow conver-

Scheme 1



Scheme 2



[†] Work by D.E.V.H. was performed at Syracuse University.

[⊗] Abstract published in *Advance ACS Abstracts*, February 15, 1997.

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

(2) Tebbe, F. N.; Harslow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6149.

(3) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.

(4) Petasis, N. A.; Fu, D. K. *Organometallics* **1993**, *12*, 3776.

(5) Doxsee, K. M.; Juliette, J. J. J.; Mouser, J. K. M.; Zientara, K. *Organometallics* **1993**, *12*, 4682.

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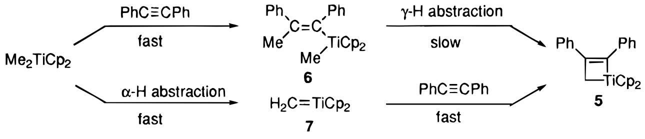
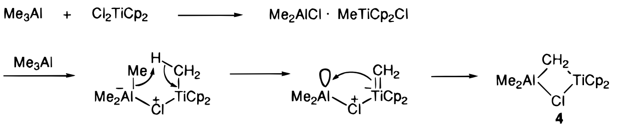
Scheme 3



Scheme 4



sion of **6** into **5** is thought to proceed via rare γ-H abstraction. Despite an apparent discrepancy between the two studies[4,5] on the ease of thermal decomposition of **6** to give **5**, the nature of the dichotomy observed in the reaction of Me_2TiCp_2 with PhC≡CPh appears to be reasonably clear (Scheme 3).

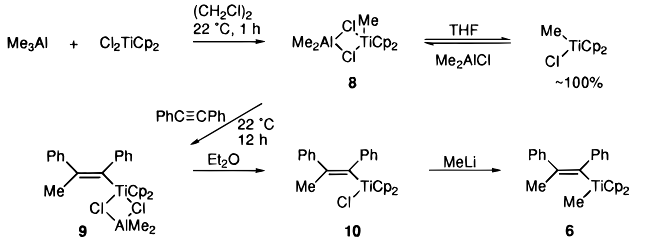
The structure of the Tebbe reagent (**4**)[3] and the mechanism of its formation from Cl_2TiCp_2 and Me_3Al[6] are both well clarified. The latter may be best represented by an α-H abstraction process shown in Scheme 4.[6] Treatment of **4** with THF or some other base is thought to generate **7** which can then add to diphenylacetylene to give **5**.[2]

Far less well established are the structure of **3** and the nature of the dichotomous relationship between the reactions shown in Schemes 1 and 2. The main goal of this study is to present results and discussion shedding some light on these aspects, thereby permitting fuller understanding of the intriguingly multifaceted methyltitanation of alkynes. This study is also intended to supplement our parallel study on the corresponding reactions of alkynes with organoalanes and zirconocene derivatives[7] which have also displayed different but related multimechanistic features.

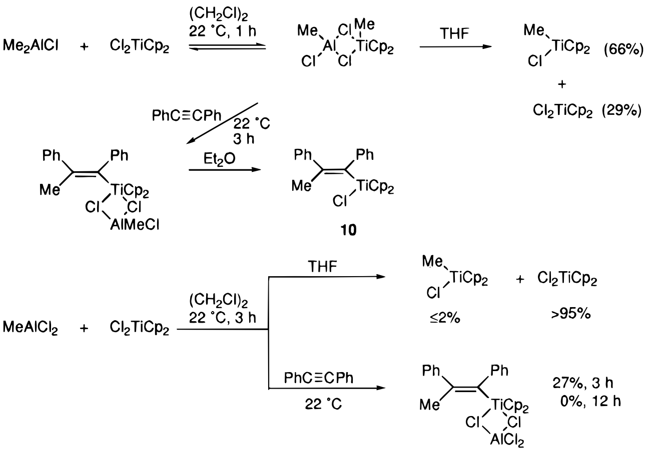
Results and Discussion

Reaction of Diphenylacetylene with 1:1 Mixtures of Methylalanes and Cl_2TiCp_2. As reported previously,[6] treatment of Cl_2TiCp_2 with 1 equiv of Me_3Al for 1 h at 22 °C gave $MeTiCp_2Cl{\cdot}AlMe_2Cl$ (**8**) exhibiting ^{13}C NMR singlets at 60.24 and 117.33 ppm for the Ti-bound Me and Cp, respectively. There was no indication for the formation of Me_2TiCp_2. Its quenching with THF provided $MeTiCp_2Cl$[8] (54.23 and 116.39 ppm for the Ti-bound Me and Cp, respectively) in quantitative yield. The reaction of Cl_2TiCp_2 with 1 equiv of Me_2AlCl also produced a methyltitanocene derivative. Although only one set of ^{13}C NMR signals were seen, quenching of the reaction mixture with THF provided a mixture of $MeTiCp_2Cl$ and Cl_2TiCp_2 in 66 and 29% yields, respectively. The formation of Me_2TiCp_2 was not detectable. Treatment of Cl_2TiCp_2 with $MeAlCl_2$ under similar conditions did not produce a detectable amount of $MeTiCp_2Cl$ (<2%). We then confirmed our previous results[1] that the reaction of diphenylacetylene with a 1:1 mixture (2 equiv each) of Me_3Al and Cl_2TiCp_2 or preformed **8** would produce, after iodinolysis, (*E*)-1-iodo-1,2-diphenylpropene (**2**) in 80% yield. Examination of the reaction mixture before quenching by NMR spectroscopy indicated the formation of titanocene derivatives **9** in 81% yield. Also detectable was $MeTiCp_2Cl{\cdot}AlMe_2Cl$ (**8**) remaining unreacted to the extent of 11%. No other Cp-containing species was detectable. After treatment of the reaction mixture with Et_2O and removal of Al-containing compounds by washing with Et_2O, an Al-free titanocene derivative was isolated and identified as **10** by NMR spectroscopy and high-resolution mass spectrometry. Its treatment with $DCl-D_2O$ gave >95% isomerically pure (*Z*)-1-deuterio-1,2-diphenylpropene (**11**) in 90% yield, the extents of D incorporation at the C-1 and C-3 positions being ≥95 and <5%, respectively. It was stable at 22 °C for at least several days. Its identity was further established by its conversion by treatment with MeLi into **6**.[4,5] There was no indication for the formation of **5**. Similarly, the reaction of diphenylacetylene with $Me_2AlCl-Cl_2TiCp_2$ for 3 h at 22 °C produced, after quenching with Et_2O, a 90% yield of **10**. We were a little surprised to find that even $MeAlCl_2-Cl_2TiCp_2$ reacted with diphenylacetylene to give a methyltitanation product in 27% yield after 3 h at 22 °C. However, this product was unstable under the reaction conditions, and it completely decomposed within 12 h. These experimental results are summarized in Schemes 5 and 6.

Scheme 5



Scheme 6



Reaction of Diphenylacetylene with 2:1 Mixtures of Me_3Al and Cl_2TiCp_2. As previously reported,[3] treatment of Cl_2TiCp_2 with 2 equiv of Me_3Al for 3 d provided the Tebbe reagent **4**. Complete consumption of Cl_2TiCp_2 was observed by NMR spectroscopy. Addition of diphenylacetylene to the Tebbe reagent in the presence of 4 equiv of 4-(dimethylamino)-

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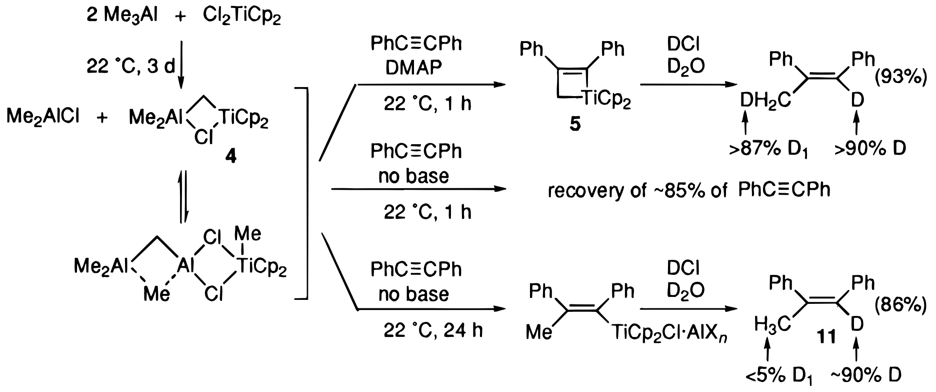
(6) Ott, K. C.; deBoer, E. J. M.; Grubbs, R. H. *Organometallics* **1984**, *3*, 223. See also: Clauss, K.; Bestian, H. *Justus Liebigs Ann. Chem.* **1962**, *654*, 8.

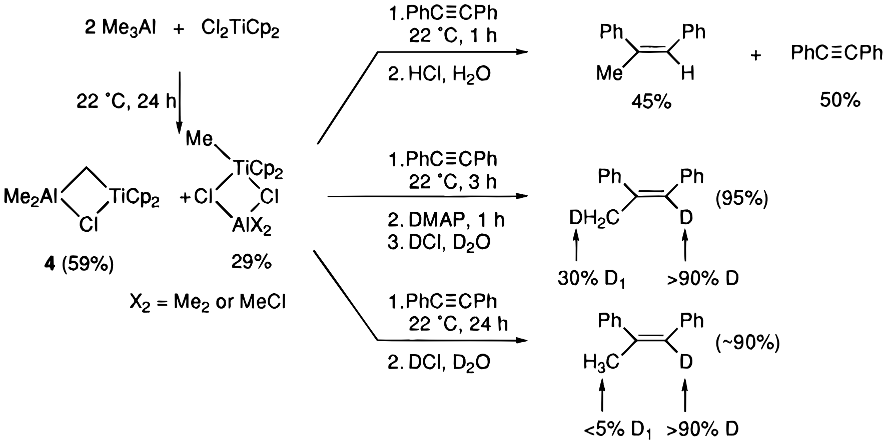
(7) (a) Van Horn, D. E.; Negishi, E. *J. Am. Chem. Soc.* **1978**, *100*, 2252. (b) Negishi, E. *Pure Appl. Chem.* **1981**, *53*, 2333. (c) Yoshida, T.; Negishi, E. *J. Am. Chem. Soc.* **1981**, *103*, 1276. (d) Negishi, E.; Yoshida, T. *J. Am. Chem. Soc.* **1981**, *103*, 4985. (e) Negishi, E.; Van Horn, D. E.; Yoshida, T. *J. Am. Chem. Soc.* **1985**, *107*, 6639.

(8) (a) Long, W. P. *J. Am. Chem. Soc.* **1959**, *81*, 5312. (b) Beachell, H. C.; Butler, S. A. *Inorg. Chem.* **1965**, *4*, 1133.

Scheme 7



Scheme 8



pyridine (DMAP) at 22 °C for 1 h led to smooth formation of **5**[5] which, upon treatment with DCl−D_2O, gave (*Z*)-1,3-dideuterio-1,2-diphenylpropene in 93% yield. The extents of D incorporation at the C-1 and C-3 positions were >90 and >87%, respectively. In the absence of DMAP or any other added base, however, a totally different and very slow reaction took place under otherwise the same conditions. After 24 h at 22 °C, the product obtained in 86% yield after deuterolysis was **11**. Addition of DMAP to the reaction mixture after 24 h did not change the outcome of deuterolysis. Although D incorporation at the C-1 position was about 90%, that at the C-3 position was only <5%. It is likely that Me_2AlCl formed as a byproduct reacts with **4** to generate an equilibrium quantity of a methyltitanocene derivative which may tentatively be represented as $MeTiCp_2Cl·Me(Cl)AlCH_2AlMe_2$ and reacts with diphenylacetylene to undergo methyltitanation. The formation of $MeTiCp_2Cl·Me(Cl)AlCH_2AlMe_2$ may occur via substitution of the Me_2AlCH_2 group in **4** with Me. Similar reactions producing polymethyl(methylene)aluminum derivatives have been previously reported by other workers.[9] These results are summarized in Scheme 7.

To further clarify the relationship between our methyltitanation reaction and Tebbe's reaction which produced **5** via **4**,[2] Me_3Al and Cl_2TiCp_2 were mixed in a 2:1 ratio, and diphenylacetylene was added to this mixture within several minutes at 22 °C. Protonolysis after 24 h afforded a 90:10 mixture of the *Z* and *E* isomers of 1,2-diphenylpropene in 95% combined yield. After 5 d at 22 °C the *Z*-to-*E* ratio decreased to 81:19 even though the combined yield remained essentially the same at 91%. An essentially 1:1 mixture of the *E* and *Z* isomers was obtained in 82% yield by heating the reaction mixture at 75 °C for 24 h. Deuterolysis with DCl−D_2O after 5 d incorporated D only at the C-1 position, the D incorporation at the C-3 center being <5%. Significantly, there was no indication for the formation of **5** under these conditions.

The foregoing results suggested to us that it should be possible to observe simultaneously both the straightforward methyltitanation reaction[1] and the cyclic process producing **5**[2] in one reaction mixture. Indeed, when a 2:1 mixture of Me_3Al and Cl_2TiCp_2 was stirred at 22 °C for 24 h in C_6D_6, its analysis by NMR spectroscopy indicated the formation of **4** and $MeTiCp_2Cl$ complexed with methylalanes in 59 and 29% yields, respectively. Addition of diphenylacetylene followed, 3 h later, by DMAP at 22 °C produced, after deuterolysis, a roughly 70:30 mixture of (*Z*)-1-monodeuterio- and (*Z*)-1,3-dideuterio-1,2-diphenylpropenes in 95% combined yield. The overall D incorporation at the C-1 position was >90%. Here again, omission of DMAP led only to the straightforward methyltitanation reaction which produced within 1 h at 22 °C (*Z*)-1,2-diphenylpropene in 45% yield, after protonolysis, with 50% of diphenylacetylene remaining unreacted. When this reaction was continued for 24 h, the only alkene product obtained in 90% yield after deuterolysis was (*Z*)-1-monodeuterio-1,2-diphenylpropene (Scheme 8).

It now is very clear that there are at least three critical factors for observing the formation of **5** via **4**,

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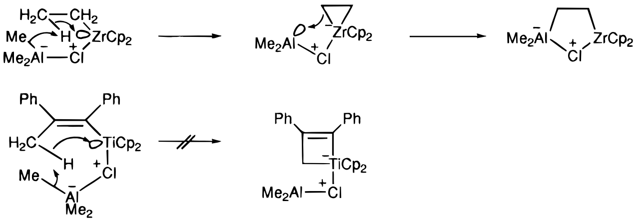
[9] Sinn, H.; Hinck, H.; Bandermann, F.; Grützmacher, H. F. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 217.

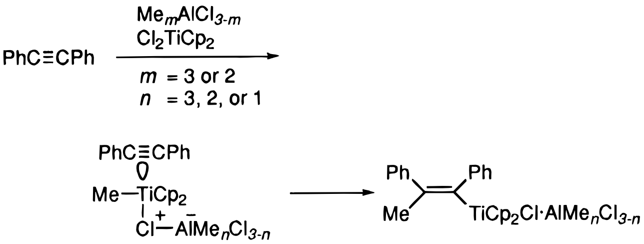
Scheme 9



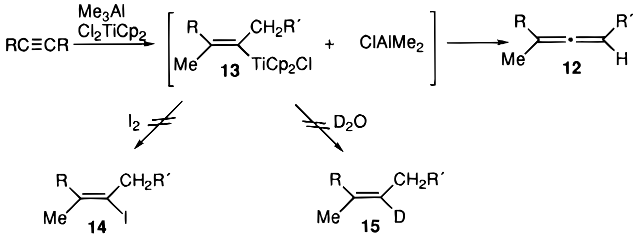
i.e., (i) an excess of Me_3Al relative to Cl_2TiCp_2, (ii) deferment of addition of diphenylacetylene to allow completion of the formation of **4**, and (iii) use of a base, such as DMAP, to induce the formation of **7** as an active cyclization reagent. Unless all of these requirements are satisfied, the straightforward methyltitanation reaction is observed even with a mixture of **4** and Me_2AlCl. It is also noteworthy that, unlike **6** which was reported to slowly produce **5**[4,5] presumably via intramolecular γ C−H activation, **10** did not show any sign of γ C−H activation leading to the formation of **5**. In contrast with MeLi and methylmagnesium halides, Me_3Al does not readily methylate monoorganyltitanocene chlorides. In principle, **10** could undergo bimetallic γ C−H activation. A related bimetallic α C−H activation shown in Scheme 4 is known,[6] and we have recently demonstrated that bimetallic β C−H activation can play a significant role in Zr-catalyzed carboalumination of alkynes.[10] These processes are thought to be six-centered and seven-centered, respectively. If **10** were to undergo a related bimetallic γ C−H activation, such a process would be eight-centered and hence potentially unfavorable (Scheme 9).

Bimetallic and Stoichiometric Nature of the Methyltitanation of Diphenylacetylene. Neither methylalanes,[11] *i.e.*, Me_3Al, Me_2AlCl, and $MeAlCl_2$, nor preformed $MeTiCp_2Cl$ reacts with diphenylacetylene under the conditions that are satisfactory for the reaction of diphenylacetylene with Me_nAlCl_{3-n}−Cl_2TiCp_2, where $n = 3$ or 2, clearly indicating that both Al and Ti are necessary at the crucial step of methyltitanation (net addition of Me and Ti to alkynes or alkenes regardless of its precise mechanism). The fact that the products are alkenyltitanocene derivatives, *e.g.*, **10**, has established the stoichiometric nature of the reaction with respect to Ti. Indeed, the reaction of diphenylacetylene with 3 equiv of Me_3Al with 0.2 equiv of Cl_2TiCp_2 produced, after protonolysis, (*Z*)- and (*E*)-1,2-diphenylproprene only in 14 and 4% yields, respectively. This is a sharp contrast with the catalytic nature of the corresponding reaction of Me_nAlCl_{3-n}−Cl_2ZrCp_2 with respect to Zr[7] and the reaction of alkenes with Et_2AlCl catalyzed by titanium tetraalkoxides.[12] The methyltitanation reaction reported herein is not catalytic in Al either. Thus, the reaction of diphenylacetylene with 1 equiv of preformed $MeTiCp_2Cl$[8] and 0.2 equiv of Me_3Al or Me_2AlCl gave the desired carbotitanation product only up to 20% yield based on Ti. Methylalanes are therefore stoichiometric promoters. Our attempts to find alternate promoters or potential catalysts have thus far failed. Specifically, no desired methyltitanation products were obtained in the reactions of diphenylacetylene with 1 equiv of $MeTiCp_2Cl$ in the presence of BCl_3 or $SnCl_4$, further pointing to the uniquely effective nature of the Al−Ti bimetallic systems. We tentatively propose a mechanism involving a concerted direct addition of the C−Ti bond activated by Al represented by Scheme 10, but a few other alternatives including some six-centered processes cannot be rigorously ruled out on the basis of the currently available data.

Scheme 10



Scheme 11



R = *n*-Bu, R′= *n*-Pr, X_2 = Me_2 or MeCl.

Reactions of 5-Decyne and 1-Octyne with Me_3Al−Cl_2TiCp_2. The reactions of alkyl-substituted internal and terminal alkynes have been only briefly investigated. The following results are presented here mainly to provide a proper perspective of the scope and limitations of the carbotitanation of alkynes with Me_3Al−Cl_2TiCp_2, even though full delineation of the scope will require extensive further studies. The reaction of 5-decyne with 2 equiv each of Me_3Al and Cl_2TiCp_2 in 1,2-dichloroethane at 22 °C for 3 h produced, after hydrolytic workup, a 92% GLC yield of 6-methyl-4,5-decadiene (**12**) exhibiting a well-defined ^1H NMR multiplet at 4.7−5.1 ppm, ^{13}C NMR signals at 90.08, 99.12, and 191.00 ppm, and an IR absorption at 1970 (w) cm^{-1} characteristic of an allene. Attempted iodination and deuteration of the presumed intermediate **13** did not produce **14** and **15**, respectively, indicating that **13** must have been converted into **12** before workup (Scheme 11). Thus, although potentially attractive as a method for the preparation of allenes, the reaction with Me_3Al−Cl_2TiCp_2 reagent system does not provide alkenylmetals as products.

The reaction of 1-octyne with 2 equiv each of Me_3Al and Cl_2TiCp_2 under the same conditions as for the reaction of 5-decyne provided, after quenching with 3 N HCl, 2-methyl-1-octene in 25% GLC yield and a mixture of at least 3 higher boiling and apparently dimeric products which were not identified. Several attempts to improve the yield of 2-methyl-1-octene, such as running the reaction at −20 °C, were unsuccessful.

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[10] Negishi, E.; Kondakov, D. Y.; Choueiry, D.; Kasai, K.; Takahashi, T. *J. Am. Chem. Soc.* **1996**, *118*, 9577.

[11] At much higher temperatures organoalanes are known to undergo carboalumination with internal alkynes to give mainly oligomeric products, while terminal alkynes are mainly converted to alkynylalanes: (a) Mole, T.; Jeffery, E. A. *Organoaluminium Compounds*; Elsevier Publishing Co.: Amsterdam, 1972. (b) Zweifel, G.; Miller, J. A. *Org. React.* **1984**, *32*, 375.

[12] (a) Dzhemilev, U. M.; Ibragimov, A. G.; Vostrikova, O. S.; Tolstikov, G. A.; Zelenova, L. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 361. (b) Negishi, E.; Jensen, M. D.; Kondakov, D. Y.; Wang, S. *J. Am. Chem. Soc.* **1994**, *116*, 8404.

Conclusions

The multimechanistic nature of the reaction of diphenylacetylene with methylalane–titanocene reagent systems has been clarified in considerable detail.

1. One-to-one mixtures of Me_3Al or Me_2AlCl with Cl_2TiCp_2 provide $MeTiCp_2Cl$ derivatives. These mixtures react with diphenylacetylene to give (*E*)-1,2-diphenyl-1-propenyltitanocene derivatives via Al-promoted stoichiometric *syn*-methyltitanation. After removal of organoalanes as their ether complexes, pure (*E*)-1,2-diphenyl-1-propenyltitanocene chloride may be obtained in good yield. Its deuterolysis gives 1-deuterio-1,2-diphenylpropene.

2. The corresponding reaction of diphenylacetylene with a 2:1 mixture of Me_3Al and Cl_2TiCp_2 is much more complex and condition dependent. If Me_3Al and Cl_2TiCp_2 is premixed in a 2:1 ratio for 3 d to produce the Tebbe reagent and then reacted with diphenylacetylene in the presence of DMAP, the known formation of a titanacyclobutene **5** is observed. Deuterolysis of **5** indeed gives (*Z*)-1,3-dideuterio-1,2-diphenylpropene. In the absence of DMAP, however, the methyltitanation reaction takes place slowly over 24 h. If all three reagents are mixed essentially at once, only the methyltitanation reaction of diphenylacetylene is observed. However, an excess of Me_3Al induces partial stereoisomerization. When 2 equiv of Me_3Al and Cl_2TiCp_2 is mixed only for 24 h and then reacted with diphenylacetylene, the reaction proceeds partially to undergo methyltitanation and partially to produce a titanacyclobutene **5** in the presence of DMAP.

3. The reaction of 5-decyne with a 1:1 mixture of Me_3Al and Cl_2TiCp_2 gives 6-methyl-4,5-decadiene. Neither deuterium nor iodine is incorporated into the product. The corresponding reaction of 1-octyne gives, after protonolysis, 2-methyl-1-octene only in 25% yield along with at least three unidentified but apparently dimeric products.

Experimental Section

General Procedures. 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 was distilled from sodium benzophenone ketyl. $MeTiCp_2Cl$ was prepared according to the published procedure.[8] 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-500S, and GE QE PLUS 300 spectrometers.

Reaction of Cl_2TiCp_2 with Me_3Al.[6] To Cl_2TiCp_2 (0.25 g, 1 mmol) and 5 mL of C_6D_6 was added at 22 °C Me_3Al (0.5 mL, 2 M in toluene). The reaction mixture was stirred for 1 h at 22 °C. NMR examination indicated that **8** was formed quantitatively: ^1H NMR (C_6D_6, Me_4Si) δ −0.12 (br s, 6 H), 0.96 (s, 3 H), 5.79 (s, 10 H); ^{13}C NMR (C_6D_6, Me_4Si) δ 60.24, 117.33. After quenching of the reaction with THF (0.2 mL), NMR examination indicated that $MeTiCp_2Cl$[8] was formed quantitatively: ^1H NMR (C_6D_6, Me_4Si) δ 0.85 (s, 3 H), 5.76 (s, 10 H); ^{13}C NMR (C_6D_6, Me_4Si) δ 49.43, 115.69.

Reaction of Cl_2TiCp_2 with Me_2AlCl. To Cl_2TiCp_2 (0.25 g, 1 mmol) and 5 mL of C_6D_6 was added Me_2AlCl (1 mL, 1 M in hexanes). The reaction mixture was stirred for 1 h at 22 °C. NMR examination showed a single set of ^{13}C NMR signals: 64.56 (CH_3–Ti), 118.14 (Cp). After quenching of the reaction with THF (0.2 mL), NMR examination indicated that $MeTiCp_2Cl$ was formed in 66% yield along with Cl_2TiCp_2 (29%), as judged from the ^{13}C NMR signals of the Cp groups at δ 115.95 and 120.25, respectively.

Reaction of Cl_2TiCp_2 with $MeAlCl_2$. To Cl_2TiCp_2 (0.25 g, 1 mmol) and 5 mL of C_6D_6 was added $MeAlCl_2$ (1 mL, 1 M in hexanes). The reaction mixture was stirred for 1 h at 22 °C. After quenching of the reaction with THF (0.2 mL), NMR examination indicated that essentially all of that Cl_2TiCp_2 remained unreacted. The extent of the formation of $MeTiCp_2Cl$ was ≤2%.

Reaction of a 1:1 Mixture of Cl_2TiCp_2 and Me_3Al with Diphenylacetylene. To Cl_2TiCp_2 (0.25 g, 1 mmol), 5 mL of $(CH_2Cl)_2$, and diphenylacetylene (178 mg, 1 mmol) was added Me_3Al (0.5 mL, 2 M in toluene). The reaction mixture was stirred for 24 h at 22 °C. NMR examination indicated that 11% of $MeTiCp_2Cl \cdot AlMe_2Cl$ was present along with 81% of **9**, as judged by quantitative analysis of the ^1H NMR signals of the Cp groups: δ 6.03 and 6.15, respectively. The reaction mixture was treated with 5 mL of Et_2O, and the precipitate was allowed to settle. The clear supernatant layer was removed by canula decantation. This washing procedure was applied 3 times, and the residual red powder was dried under vacuum to give **10** (273 mg, 67%): ^1H NMR (CD_2Cl_2, Me_4Si) δ 1.65 (s, 3 H), 6.50 (s, 10 H), 6.80–7.30 (m, 10 H); ^{13}C NMR (CD_2Cl_2, Me_4Si) δ 27.50, 115.76, 124.24, 124.96, 127.20, 127.46, 128.21, 130.57, 138.35, 147.71, 149.60, 187.09. HRMS/FAB calcd for $C_{25}H_{23}Ti$ ([M − Cl]) m/z 371.1279, found m/z 371.1283.

Reaction of 10 with DCl–D_2O. A suspension of **10** (0.2 g, 0.5 mmol) in 5 mL of benzene was treated with 1 mL of 10% DCl in D_2O for 1 h at 22 °C. The reaction mixture was extracted with Et_2O, washed with water, dried over $MgSO_4$, filtered, and concentrated. Column chromatography on silica gel afforded 88 mg of **11** (90%): ^1H NMR ($CDCl_3$, Me_4Si) δ 2.15 (s, 3 H), 6.95–7.35 (m, 10 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 27.05, 126.03, 126.56 (t, J = 24 Hz), 126.84, 127.78, 128.09, 128.40, 128.89, 137.51, 138.57, 142.00.

Reaction of 10 with MeLi. A suspension of **10** (0.2 g, 0.5 mmol) in 5 mL of toluene was treated at 0 °C with MeLi (0.7 mL, 1.4 M in ether, 1.0 mmol). The reaction mixture was stirred at 22 °C for 1 h, and the solvent was evaporated. The resultant solid was dissolved in 5 mL of C_6D_6 and examined by NMR spectroscopy, which indicated that **6**[4,5] was formed in 77% yield: ^1H NMR (C_6D_6, Me_4Si) δ −0.41 (s, 3 H), 1.46 (s, 3 H), 5.86 (s, 10 H), 6.65–7.05 (m, 10 H).

Reaction of a 1:1 Mixture of $MeTiCp_2Cl$ and Me_2AlCl with Diphenylacetylene. To $MeTiCp_2Cl$ (1.1 mL, 1 mmol, 0.9 M in C_6D_6), 5 mL of $(CH_2Cl)_2$, and diphenylacetylene (178 mg, 1 mmol) was added Me_2AlCl (1 mL, 1 M in hexanes). The reaction mixture was stirred for 24 h at 22 °C. NMR examination indicated that **9** was formed in 85% yield, as judged by quantitative analysis of the ^1H NMR signal of the Cp group (δ 6.15).

Reaction of a 1:1 Mixture of Cl_2TiCp_2 and Me_2AlCl with Diphenylacetylene. To Cl_2TiCp_2 (0.25 g, 1 mmol), 5 mL of $(CH_2Cl)_2$, and diphenylacetylene (178 mg, 1 mmol) was added Me_2AlCl (1 mL, 1 M in hexanes). The reaction mixture was stirred for 3 h at 22 °C. NMR examination indicated that **10** complexed with $MeAlCl_2$ was formed in 90% yield, as judged by quantitative analysis of the ^1H NMR signal of the Cp group (δ 6.20).

Reaction of a 1:1 Mixture of Cl_2TiCp_2 and $MeAlCl_2$ with Diphenylacetylene. To Cl_2TiCp_2 (0.25 g, 1 mmol), 5 mL of $(CH_2Cl)_2$, and diphenylacetylene (178 mg, 1 mmol) was added $MeAlCl_2$ (1 mL, 1 M in hexanes), and the reaction mixture was stirred for 3 h at 22 °C. NMR examination indicated that **10** complexed with a methylalane was formed in 27% yield, as judged by quantitative analysis of the ^1H NMR signal of the Cp group (δ 6.16). After 12 h at 22 °C no signals attributable to Cp were visible in the ^1H and ^{13}C spectra.

Reaction of 4 with Diphenylacetylene in the Presence of *N*,*N*-Dimethyl-4-aminopyridine (DMAP). Method a.

The following procedure is based on a previous study by Tebbe *et al.*[2,3] To Cl_2TiCp_2 (0.25 g, 1 mmol) and 5 mL of toluene was added Me_3Al (1.0 mL, 2 M in toluene, 2 mmol). After the mixture was stirred for 3 days at 22 °C, diphenylacetylene (178 mg, 1 mmol) and DMAP (0.49 g, 4 mmol) were successively added. After quenching of the reaction with 4% DCl in D_2O (5 mL) at 0 °C, the reaction mixture was extracted with Et_2O, washed with water, dried over $MgSO_4$, filtered, and concentrated. Column chromatography on silica gel (hexanes) afforded 182 mg (93%) of (*Z*)-1,3-dideuterio-1,2-diphenylpropene: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.13 (s, 2 H), 6.90−7.40 (m, 10 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 26.71 (t, $J = 20$ Hz), 126.03, 126.50 (t, $J = 23$ Hz), 126.84, 127.77, 128.07, 128.39, 128.86, 137.43, 138.43, 141.99.

Method b. Examination of the mixture of Me_3Al and Cl_2TiCp_2, prepared as described above, by NMR spectroscopy after 24 h at 22 °C indicated the formation of **4** (59%) and $MeTiCp_2Cl{\cdot}AlMe_nCl_{3-n}$ (29%), as judged by quantitative analysis of the Cp signals: ^{1}H δ 5.63, ^{13}C δ 112.27 and ^{1}H δ 5.67, ^{13}C δ 117.66, respectively. Diphenylacetylene (178 mg, 1 mmol) was added, and the reaction mixture was stirred for 1 h. After quenching of an aliquot (ca. 2 mL) with 3 N HCl at 0 °C, GLC examination showed that (Z)-1,2-diphenylpropene was formed in 45% yield, and diphenylacetylene remained unreacted to the extent of 50%. The reaction mixture was stirred for 3 h, treated with DMAP (0.25 g, 2 mmol), stirred for 1 h, and quenched with 4% DCl in D_2O. Examination by GLC and NMR spectroscopy showed that a mixture **11** and its 1,3-dideuterio analogue was formed in 95% combined yield (>90% D at C-1, 30% D at C-3).

Reaction of 4 with Diphenylacetylene in the Absence of DMAP. To Cl_2TiCp_2 (0.25 g, 1 mmol) and 5 mL of toluene was added Me_3Al (1.0 mL, 2 M in toluene, 2 mmol). After stirring of the mixture for 3 days at 22 °C, diphenylacetylene (178 mg, 1 mmol) was added. Examination of the reaction mixture by GLC revealed that diphenylacetylene was consumed after 24 h at 22 °C. After quenching of an aliquot (ca. 2 mL) with 4% DCl in D_2O at 0 °C, examination by GLC and NMR spectroscopy showed that **11** was formed in 86% yield (>90% D at C-1, <5% D at C-3). The rest of the reaction mixture was treated with DMAP (0.25 g, 2 mmol), stirred for 1 h, and quenched with 4% DCl in D_2O. Its analysis as above showed that **11** was formed in 86% yield (>90% D at C-1, <5% D at C-3) indicating that DMAP had no effect on the reaction.

Reaction of a 1:2 Mixture of Cl_2TiCp_2 and Me_3Al with Diphenylacetylene in the Absence of DMAP. To Cl_2TiCp_2 (0.25 g, 1 mmol) and 5 mL of toluene was added Me_3Al (1.0 mL, 2 M in toluene, 2 mmol). After stirring of the mixture for 2 min at 22 °C, diphenylacetylene (178 mg, 1 mmol) was added. After stirring of the reaction mixture for 24 h at 22 °C, quenching of an aliquot (ca. 2 mL) with 3 N HCl at 0 °C followed by GLC examination showed that **1** was formed in 85% yield along with an 8% yield of its *E* isomer. After being stirred for 5 days at 22 °C, the reaction mixture was quenched with 4% DCl in D_2O at 0 °C. Examination by GLC and NMR spectroscopy revealed that **11** was formed in 74% yield (94% D at C-1, < 5% D at C-3) along with a 17% yield of its *E* isomer.

Reaction of $MeTiCp_2Cl$ with Diphenylacetylene in the Absence of Alkylaluminum Compounds. Method a. To $MeTiCp_2Cl$ (0.23 g, 1 mmol) and 5 mL of $(CH_2Cl)_2$ was added diphenylacetylene (178 mg, 1 mmol). After the mixture was stirred for 24 h at 22 °C, analysis by NMR spectroscopy and GLC indicated that the starting materials remained intact to the extent of 95%. The reaction mixture was then heated for 4 h at 80 °C without any change in the NMR spectra.

Method b. The reaction mixture prepared as described above was treated with BCl_3 (1 mL, 1 mmol, 1 M in heptane) and stirred for 24 h at 22 °C. GLC analysis of a quenched (3 N HCl) aliquot indicated that diphenylacetylene remained unreacted to the extent of 95%. The amount of 1,2-diphenylpropene was below the detection limit of 1%.

Method c. The reaction mixture prepared as described above was treated with $SnCl_4$ (0.12 mL, 1 mmol) and stirred for 24 h at 22 °C. GLC analysis of a quenched (3 N HCl) aliquot indicated that diphenylacetylene remained unreacted to the extent of 95%. The amount of 1,2-diphenylpropene was below the detection limit of 1%.

Reaction of Diphenylacetylene with Me_3Al in the Presence of a Catalytic Amount of Cl_2TiCp_2. To Cl_2TiCp_2 (0.05 g, 0.2 mmol), 5 mL of $(CH_2Cl)_2$, and diphenylacetylene (178 mg, 1 mmol) was added Me_3Al (0.5 mL, 2 M in toluene, 1 mmol). The reaction mixture was stirred for 3 h at 60 °C. GLC analysis of a quenched (3 N HCl) aliquot indicated that 75% of diphenylacetylene remained unreacted. The yields of (*Z*)- and (*E*)-1,2-diphenylpropenes were 14 and 4%, respectively.

Reaction of Diphenylacetylene with Me_2AlCl in the Presence of a Catalytic Amount of $MeTiCp_2Cl$. To $MeTiCp_2Cl$ (0.046 g, 0.2 mmol), 5 mL of $(CH_2Cl)_2$, and diphenylacetylene (178 mg, 1 mmol) was added Me_2AlCl (1 mL, 1 M in hexanes, 1 mmol) The reaction mixture was stirred for 3 h at 60 °C. GLC analysis of a quenched (3 N HCl) aliquot indicated that 75% of diphenylacetylene remained unreacted. The yields of (*Z*)- and (*E*)-1,2-diphenylpropene were 17% and 4%, respectively.

Reaction of Cl_2TiCp_2 with (*E*)-(1-Butyl-2-methyl-1-hexenyl)dimethylalane. To Cl_2TiCp_2 (0.25 g, 1.0 mmol) and 5 mL of CH_2Cl_2 was added dropwise at −78 °C (*E*)-(1-butyl-2-methyl-1-hexenyl)dimethylalane (2 mL, *ca.* 0.5 M in CH_2Cl_2). The reaction mixture was warmed to 22 °C. After 15 min at 22 °C Cl_2TiCp_2 was fully dissolved. Examination of a quenched (THF) aliquot by NMR spectroscopy indicated the formation of an 85% yield of $MeTiCp_2Cl$: ^{1}H NMR ($C_6D_6-CH_2Cl_2$, Me_4Si) δ 0.93 (s, 3 H), 6.01 (s, 10 H); ^{13}C NMR (C_6D_6, Me_4Si) δ 49.38, 115.90. Examination of a quenched (3 N HCl) aliquot by GLC indicated that (*Z*)-5-methyl-5-decene was formed to the extent of 90% along with 6-methyl-4,5-decadiene (8%). After stirring of the reaction mixture for 3 h at 22 °C, examination by NMR spectroscopy and GLC indicated the formation of the following compounds in the yields shown in parentheses: $MeTiCp_2Cl$ (50%), (*Z*)-5-methyl-5-decene (60%), and 6-methyl-4,5-decadiene (20%). No ^{13}C NMR signal attributable to ${=}C{-}Ti$ was observed (detection limit <5%).

Reaction of Cl_2TiCp_2 with 2 equiv of (*Z*)-(1-Butyl-2-methyl-1-hexenyl)lithium Followed by 1 equiv of I_2. To Cl_2TiCp_2 (0.25 g, 1.0 mmol) and 5 mL of toluene was added dropwise at −78 °C (*Z*)-(1-butyl-2-methyl-1-hexenyl)lithium (5 mL, *ca.* 0.4 M in Et_2O/pentane, 2 mmol). The reaction mixture was warmed to −23 °C, stirred for 1 h, and treated with I_2 (2 mL, 0.5 M in THF, 1 mmol). After warming of the reaction mixture to 22 °C, the solvent was removed *in vacuo*. After addition of 2 mL of CD_2Cl_2, the product was examined by NMR spectroscopy. No ^{13}C NMR signal attributable to ${=}C{-}Ti$ was observed (detection limit <5%).

6-Methyl-4,5-decadiene via the Reaction of 5-Decyne with $Me_3Al-Cl_2TiCp_2$. To a brick-red colored slurry of Cl_2TiCp_2 (4.98 g, 20 mmol) in 30 mL of $(CH_2Cl)_2$ was added Me_3Al (1.92 mL, 20 mmol) at 22 °C. To the resultant deep dark orange solution was added 5-decyne (1.83 mL, 10 mmol). After 3 h at 22 °C, the blue-green reaction mixture was quenched with H_2O. Analysis by GLC indicated the clean formation of 6-methyl-4,5-decadiene in 92% yield. The standard workup and chromatographic isolation afforded a pure sample of the title compound: $n^{18.4}_{D}$ 1.4516; ^{1}H NMR (CCl_4, Me_4Si) δ 0.7−1.1 (m, 6 H), 1.1−1.6 (m, 6 H), 1.62 (d, $J = 3$ Hz, 3 H), 1.7−2.2 (m, 4 H), 4.7−5.1 (m with at least 9 signals centered at 4.90, $J = 3$ Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.75, 14.05, 19.36, 22.60, 22.79, 30.10, 31.82, 34.07, 90.08, 99.12, 191.00; IR (neat) 2900 (s), 1970 (w), 1460 (m), 1375 (w) cm^{-1}. Anal. Calcd for $C_{11}H_{20}$: C, 86.76; H, 20.16. Found: C, 86.49; H, 20.08.

Reaction of 1-Octene with 2 equiv Each of Me_3Al and Cl_2TiCp_2. The reaction of 1-octene (1.50 mL, 10 mmol) with

$Me_3Al-Cl_2TiCp_2$ as in the preceding experiment was mildly exothermic and complete within 1 h. After quenching of the reaction with 3 N HCl, analysis by GLC indicated the formation of 2-methyl-1-octene in 25% yield along with at least 3 unidentified and apparently dimeric compounds produced in considerable amounts. In view of the low yield of the desired product, the reaction was not further investigated.

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