

Reactions of Dimethyltitanocene with Alkynes and Nitriles

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Summary: Thermolysis of dimethyltitanocene in the presence of internal alkynes formed the corresponding titanacyclobutenes cleanly and efficiently. This reaction was shown to be first order in dimethyltitanocene with a primary kinetic isotope effect. When diphenylacetylene was reacted with dimethyltitanocene at lower temperatures, a competitive migratory insertion process took place, forming a vinyl-substituted titanocene species. An analogous reaction with 2 equiv of nitriles formed the known 1,3-diaza-2-titana-1,4-cyclohexadiene derivatives.

Introduction

The chemistry of transition-metal alkylidenes and metallacycles has attracted much recent attention¹ and has resulted in a number of useful synthetic transformations. Among the titanium complexes, the Tebbe reagent² (1) has been used widely as a source of the parent methylidenetitanocene (3). Although compound 3 has not yet been observed in its pure form, its phosphine complexes have been isolated and characterized.³ Also, adducts of 3 with olefins, acetylenes, and allenes were implicated in various reactions.⁴ Methylidenetitanocene (3) generated from 1 is a highly reactive species, which methylenates carbonyl compounds (4 → 5)⁵ and reversibly converts alkenes (6) to titanacyclobutenes (7).^{1c,5b,6} It also reacts with 2 equiv of nitriles (8), to form 1,3-diaza-2-titana-1,4-cyclohexadienes (9),^{1e,7} and with alkynes (10), to form

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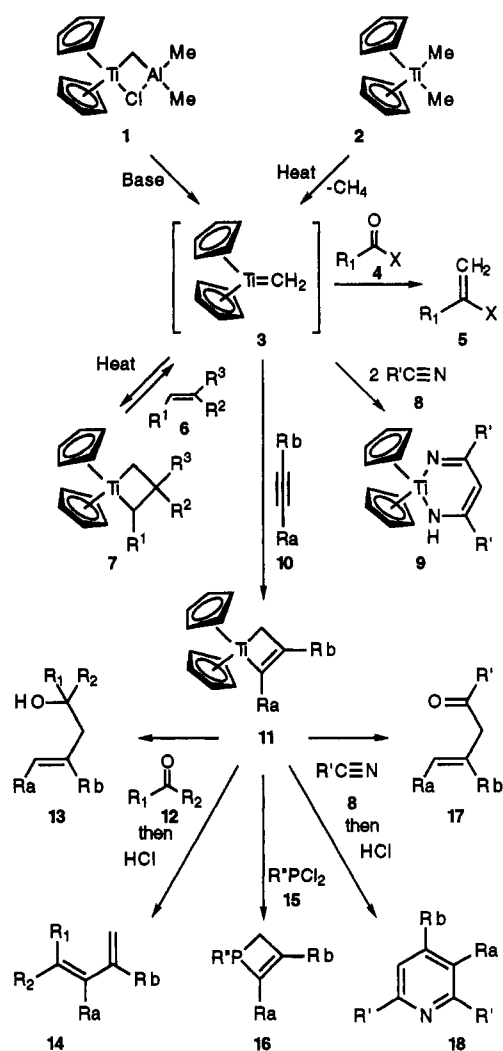
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Scheme 1



titanacyclobutenes (11).^{1e,4,6a,b,8,9} The latter give various titanium-free products (13,¹⁰ 14,¹¹ 16,¹² 17,^{10,13} 18¹³) upon reaction with aldehydes and ketones (12), phosphorus dichlorides (15), and nitriles (8).

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We have recently reported¹⁴ that dimethyltitanocene (2) constitutes a synthetically convenient alternative to 1 and 7 for the methylenation of a variety of carbonyls,¹⁵ including aldehydes, ketones, esters, lactones, and amides. We have also reported similar reactivity with the dibenzyl-,¹⁶ bis((trimethylsilyl)methyl)-,¹⁷ and bis(cyclopropyl)-titanocenes,¹⁸ which are readily prepared from titanocene dichloride and the appropriate organometallic reagents. Moreover, we have found that 2 is able to initiate the ring-opening metathesis polymerization of norbornene,¹⁹ a process previously studied with titanacyclobutenes (7).²⁰ This finding confirmed the formation of a methylidene-titanocene species (3) during the thermolysis of 2. In order to gain additional mechanistic information on the thermolysis of dialkyltitanocenes and in an effort to enhance their synthetic utility, we studied in detail the reactions of 2 with alkynes and nitriles, which we report herein.^{21,22}

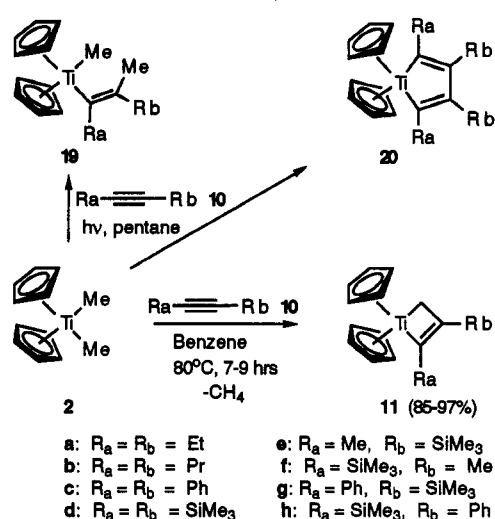
Results and Discussion

The reaction of dimethyltitanocene (2) with diphenylacetylene (10c) under photolytic conditions was previously shown²³ to give mainly the titanacyclopentadiene adduct (20c)²⁴ and small amounts of the vinyl insertion product (19c).^{23b}

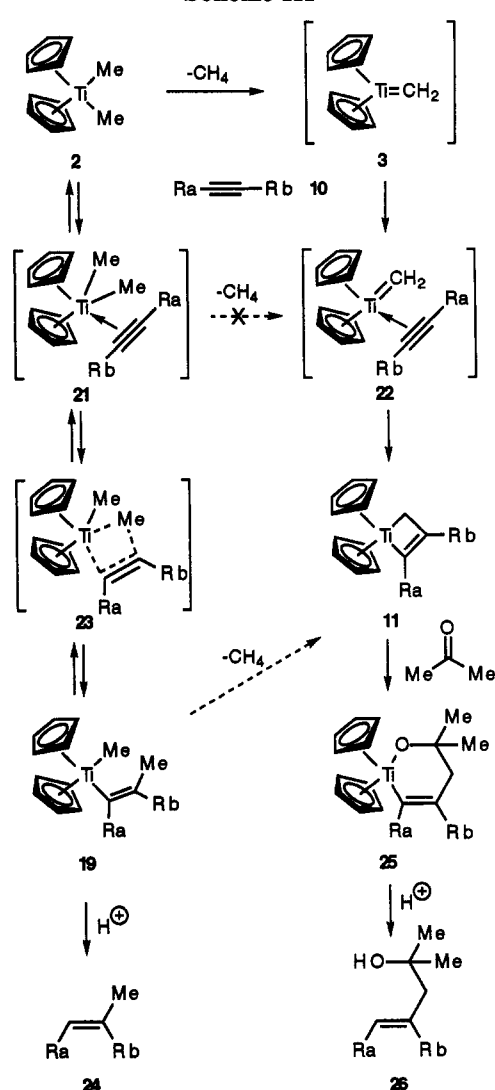
We have found that under thermal conditions (benzene, 80 °C, 7–9 h) the main products of the reaction of 2 with various alkynes (10) are the titanacyclobutenes (11). For example, thermolysis of 2 in the presence of symmetrical alkynes (10a–d) resulted in the clean and efficient preparation of 11a–d in near-quantitative conversions. Variable amounts of the vinyl derivative 19c were also observed when diphenylacetylene (10c) was reacted with 2. Although only very small quantities of 19c were formed when 10c and 2 were reacted in equimolar amounts, the portion of 19c increased dramatically when the temperatures were lowered (70 °C) and when excess 10c was used. The reactions of 2 with unsymmetrical alkynes proceeded with mixed regioselectivities. Thus, while alkyne 10e gave a 1:1 mixture of the two regioisomers 11e and 11f, the reaction with alkyne 10g afforded a 4.8:1 ratio of 11g and 11h.

Some mechanistic aspects of the conversion of 2 to 11 are noteworthy. Most likely, this reaction involves a rate-determining loss of methane to generate a methylidene-titanocene intermediate, either in its free form (3) or as a complex with methane or the solvent. Subsequent

Scheme II



Scheme III



trapping of 3 with the alkyne, probably via the alkyne complex 22, would rapidly lead to 11. Strong evidence for the involvement of complexes such as 22 was previously provided in the detailed study by Anslyn and Grubbs^{4b} of the reactions of alkynes with various other sources of 3.

Another mechanistic pathway involves the initial complexation of 2 with the alkyne to give an 18-electron

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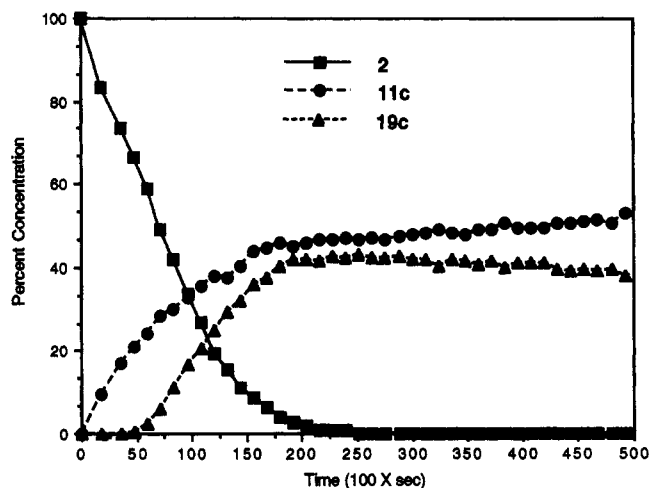


Figure 1. ^1H NMR monitoring of the reaction of dimethyltitanocene (**2**) with 10 equiv of diphenylacetylene (**10c**) in C_6D_6 . The concentrations of **2**, **11c**, and **19c** were determined in the probe at 76°C , in relationship to a ferrocene internal standard.

complex (**21**). This species can be directly converted to **22** via a ligand-promoted α -abstraction,²⁵ which may also involve a Cp ring slippage.²⁶ The same complex **21** is also capable of a migratory insertion process to form the vinyltitanocene species **19**, presumably via transition state (TS) **23**. While this type of insertion occurs readily with cationic titanium species,²⁷ it is not common with neutral complexes. Moreover, it is unlikely that **19** is formed via a heterolytic cleavage of **2** since, in contrast to the photochemical conditions which were shown to involve free-radical intermediates,²⁸ the thermally derived **19** was not accompanied by other coupling products.

An NMR experiment provided some indirect evidence for the involvement of an intermediate such as **21c** in the formation of **19c**. As shown in Figure 1, during the reaction of **10c** with **2**, an induction period preceded the formation of the vinyl derivative **19c**, while the titanacyclobutene **11c** began to increase immediately. This is an indication that an alkyne complex (**21c**) may be involved in the formation of **19c** but not **11c**, implying that the ligand-promoted abstraction is not required. Although the NMR spectra of the reaction mixture included new peaks that could be attributed to **21c**, these weak peaks could not be unambiguously assigned to this compound. Also, despite several unsuccessful attempts to isolate analytically pure samples of **19c**, its structure and geometry were confirmed by 2-D NMR experiments (NOESY and COSY) and high-resolution mass spectrometry. The *cis* addition of the Ti-CH₃ bond to the alkyne invokes an intramolecular migratory insertion process via TS **23**, rather than an intermolecular attack of **2** at **21c**.²⁹

Figure 1 provides information on another mechanistic possibility, involving the transformation of **19c** to **11c** via

a rare γ -abstraction step.³⁰ This process is unlikely to be the major pathway for the formation of **11c**, since prolonged heating at the same temperature of the final mixture of **19c** and **11c** showed only a small change in their relative ratios. While the conversion of **19c** to **11c** seems feasible either via a reversible loss of alkyne to give **2** or via a direct γ -abstraction, the rate of this transformation is clearly slower than the initial rate of formation of **11c** prior to the consumption of **2**.

Not surprisingly, the strained titanacyclobutene **11c** was more reactive toward electrophiles than was **19c**. For example, when a mixture of **19c** and **11c** was quenched with excess acetone, NMR indicated that **19c** remained intact while **11c** underwent complete carbonyl insertion to yield **25c**.^{10,11} Subsequent acid workup and purification afforded **24c** and **26c**.

The increased relative amounts of **19c** vs **11c**, observed at lower temperatures and at higher concentrations of alkyne **10c**, are consistent with the intermediacy of an alkyne complex. However, a vinyltitanocene species such as **19c** was not formed with other alkynes, indicating difficulties in the formation of **21** or **23**. As previously suggested,^{8b} the polarization of the acetylene moiety in the case of diphenyltitanocene is facilitated by an orthogonal positioning of the two phenyl rings, while a similar arrangement is not possible with alkyl-substituted alkynes. An analogous nonplanar disposition of the phenyl ring in **22g** may be responsible for the selective formation of **11g** vs **11h** and the lack of selectivity in the case of **11e** vs **11f**.

Additional mechanistic information was obtained by kinetic studies of the reaction of bis(trimethylsilyl)acetylene (**10d**) with **2**, as well as the corresponding *d*₃ and *d*₆ derivatives. As indicated in Figure 2, the reaction is first order in the titanocene and there is a significant kinetic isotope effect. A $k_{\text{H}}/k_{\text{D}}$ ratio of 6.4 is reflected in the relative rates between **2-d**₀ and **2-d**₆. This isotope effect presumably includes both a primary and a secondary component. The primary isotope effect results from the breaking of a C-H bond during the rate-determining step, while the change in hybridization from sp^3 in **2** to sp^2 in **3** is responsible for the secondary isotope effect. Figure 2 also shows that the relative rate between **2-d**₀ and **2-d**₃ is 2.0, which is consistent with the fact that **2-d**₀ has twice as many ways of forming the protio intermediate **3** (at either -CH₃ group). In the case of **2-d**₃ a mixture of products **11d-d**₀ and **11d-d**₂ was obtained in a ratio of 5.9. Similarly, the relative rate between **2-d**₃ and **2-d**₆ was 3.2, half of the isotope effect between **2-d**₀ and **2-d**₆. Also consistent with these isotope effects are the results of a competition experiment of a 1:1:1 mixture of **2-d**₀, **2-d**₆, and **10d**, which afforded **11d-d**₀ and **11d-d**₂ in a ratio of 5.6.

We have also carried out a competition experiment between diphenylacetylene (**10c**) and 4-octyne (**10b**). It was previously shown^{4b} that **10b** is a much better methylidene-titanocene trap than **10c**, leading to a **11b**:**11c** ratio in the range of 5–23, depending on the source of **3**. We have observed similar results in the case of **2**. Thus, when a 1:5:5 mixture of **2**, **10b**, and **10c** was subjected to the typical thermolysis conditions, it gave a mixture of **11b**:**11c**:**19c** in a ratio of 18:1:18. The preferred formation of **11b** vs **11c** cannot be attributed to product equilibration via a reversible conversion of **11** to **22**, since upon heating

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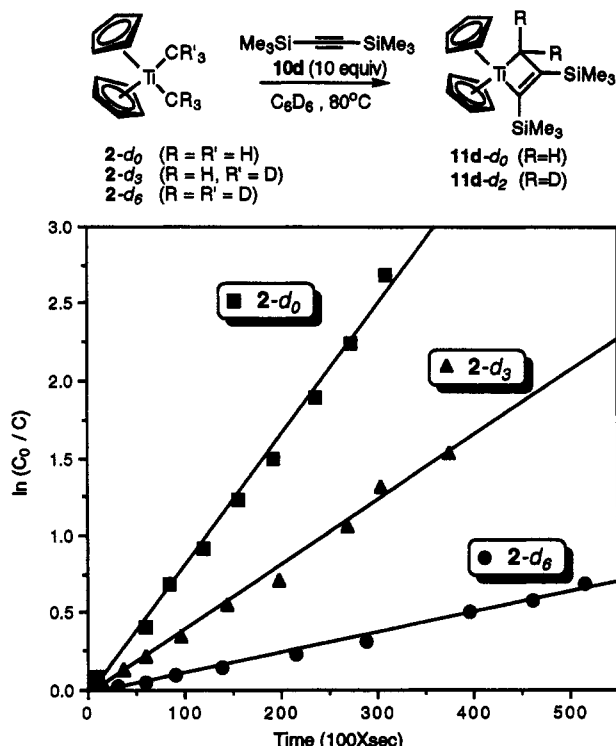
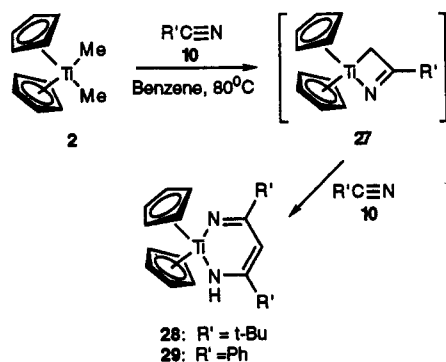


Figure 2. Reaction of dimethyltitanocene (2-*d*₀, 2-*d*₃, and 2-*d*₆) with 10 equiv of bis(trimethylsilyl)acetylene (10d) at 80 °C in C₆D₆. The relative dimethyltitanocene concentrations (C₀/C, where C₀ is the initial concentration) were determined by ¹H NMR, in relationship to a ferrocene internal standard. These plots have ρ values greater than 0.99 and indicate the following relative rates: $k_{2-d_0}/k_{2-d_3} = 2.0$; $k_{2-d_0}/k_{2-d_6} = 6.4$; $k_{2-d_3}/k_{2-d_6} = 3.2$.

Scheme IV



an equimolar mixture of 11c and 10b at 80 °C for 2 h, we could not detect any 11b. While these competition experiments provide support for an intermediate (or TS) such as 22, they do not necessarily confirm the ligand-promoted elimination of 21 to 22. The observed selectivity may be explained either by a competitive ligand exchange and equilibration prior to the irreversible conversion to 11 (trap scrambling) or by a significant difference in the rate of formation or ring closure of 22 (Curtin-Hammett principle).^{4b}

Additional evidence supporting the intermediacy of 3 is found in the fact that the reaction of 10d with 2 is zero order in alkyne. As shown in Figure 3, the observed reaction rates at various alkyne concentrations remained essentially the same.

Finally, we have examined the reactivity of 2 toward nitriles. We found that upon heating a mixture of 2 and

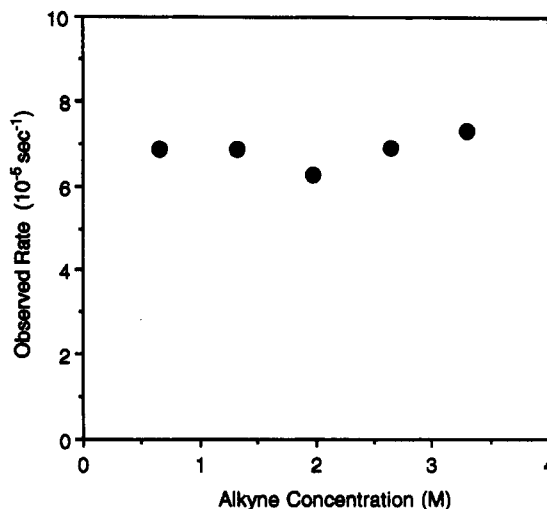


Figure 3. Reaction of dimethyltitanocene (2, 0.33 M) with various concentrations of bis(trimethylsilyl)acetylene (10d) at 80 °C in C₆D₆. The relative concentrations were determined by ¹H NMR, in relationship to a ferrocene internal standard. The observed rates were determined from the slope of first-order plots of the decrease in dimethyltitanocene concentration. All of these plots had ρ values greater than 0.99.

2 equiv of pivalonitrile or benzonitrile in benzene at 80 °C for several hours, the corresponding 1,3-diaza-2-titana-1,4-cyclohexadiene derivatives (28 and 29) were formed quantitatively. These compounds, previously obtained⁷ by using 1 or 7, are apparently produced via a sequential formation of the azatitanocyclobutene intermediate (27), which undergoes insertion of a second molecule of nitrile and tautomerization.⁷

Conclusions

We have shown that dimethyltitanocene reacts readily with alkynes to form titanacyclobutenes and with nitriles to give 1,3-diaza-2-titana-1,4-cyclohexadienes. The reaction with alkynes is first order in the titanocene and shows a primary kinetic isotope effect, consistent with an α-abstraction mechanism.

Our kinetic studies have suggested that the α-abstraction step takes place on the free dimethyltitanocene, which is converted to the methylidenetitanocene. This highly reactive species reacts rapidly with the alkyne to form a titanacyclobutene, which is finally transformed to the titanacyclobutene.

Although, in the case of diphenylacetylene, a dimethyltitanocene-alkyne complex was also invoked, this intermediate was associated with the formation of a vinyltitanocene product. This uncommon insertion pathway is presumably a consequence of the unique ability of diphenylacetylene to polarize and distort the acetylenic bond.

The convenient preparation and handling of dimethyltitanocene, combined with its efficient application in the synthesis of titanacyclobutenes reported herein, may enhance the synthetic utility of the latter, particularly their reactions with carbonyls and other electrophiles.³¹

Experimental Section

General Considerations. ¹H and ¹³C NMR spectra were recorded on a Bruker AMX-500, AM-360, or AC-250 instrument,

(31) Other dialkyltitanocene derivatives, such as bis((trimethylsilyl)methyl)titanocene, also react with alkynes to form titanacyclobutenes. More details of this work will be reported in due course.

using CDCl_3 or C_6D_6 as the solvent. High-resolution mass spectra were obtained at the Southern California Mass Spectrometry Facility, University of California, Riverside, CA. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN. Dimethyltitanocene (2) was prepared by the literature method.³² The d_3 derivative (2- d_3) was prepared from Cp_2TiMeCl and $\text{CD}_3\text{-MgCl}$, whereas the d_6 derivative (2- d_6) was prepared from $\text{Cp}_2\text{-TiCl}_2$ and CD_3MgCl .

Titanacyclobutene 11a. Into a septum-sealed NMR tube filled with argon was syringe-transferred a solution of dimethyltitanocene (2; 48 mg, 0.24 mmol) and 3-hexyne (10a; 22 mg, 0.27 mmol) in C_6D_6 (0.8 mL). The reaction mixture was heated in the dark at 80 °C for 9 h. The titanacyclobutene 11a was obtained as a deep red solution, in nearly quantitative yield based on the alkyne. The yield was determined by ^1H NMR, using a relaxation time of 20 s. ^1H NMR (250 MHz, C_6D_6): δ 5.53 (s, 10H, Cp), 3.30 (s, 2H, TiCH_2), 2.54 (q, 2H, CH_2), 1.97 (q, 2H, CH_2), 1.05 (t, 3H, CH_3), 0.91 (t, 3H, CH_3). ^{13}C NMR (63 MHz, C_6D_6): δ 200.4 ($\text{TiC}=\text{C}$), 109.9 (Cp), 91.9 ($=\text{C}$), 77.5 (TiCH_2 , $J_{\text{CH}} = 139.9$ Hz), 29.3, 22.4, 15.9, 12.6. MS (CI): m/e 275.1274 (MH^+), calcd for $\text{C}_{17}\text{H}_{23}\text{Ti}$ 275.1279.

Titanacyclobutene 11b was prepared from dimethyltitanocene (2) and 4-octyne (10b) similarly to the preparation of 11a. ^1H NMR (250 MHz, C_6D_6): δ 5.54 (s, 10H, Cp), 3.28 (s, 2H, TiCH_2), 2.52 (q, 2H, CH_2), 1.92 (q, 2H, CH_2), 1.43 (m, 4H, CH_2), 0.98 (t, 3H, CH_3), 0.86 (t, 3H, CH_3). ^{13}C NMR (63 MHz, C_6D_6): δ 201.0 ($\text{TiC}=\text{C}$), 109.9 (Cp), 91.2 ($=\text{C}$), 78.2 (TiCH_2 , $J_{\text{CH}} = 139.9$ Hz), 39.5, 31.8, 24.6, 21.4, 15.1, 14.6. MS (EI): m/e 302.1503 (M^+), calcd for $\text{C}_{19}\text{H}_{25}\text{Ti}$ 302.1514.

Titanacyclobutene 11c was prepared from dimethyltitanocene (2) and diphenylacetylene (10c) similarly to the preparation of 11a. ^1H NMR (250 MHz, C_6D_6 , lit.^{8a}): δ 6.89–7.29 (m, 10H, Ph), 5.68 (s, 10H, Cp), 3.45 (s, 2H, TiCH_2). ^{13}C NMR (63 MHz, C_6D_6): δ 210.8 ($\text{TiC}=\text{C}$), 123–147 (Ph), 112.7 (Cp), 100.7 ($=\text{C}$), 73.4 (TiCH_2 , $J_{\text{CH}} = 139.0$ Hz). MS (CI): m/e 371.1296 (MH^+), calcd for $\text{C}_{26}\text{H}_{23}\text{Ti}$ 371.1279.

Titanacyclobutene 11d. Into a septum-sealed 50-mL flask charged with dimethyltitanocene (2; 2.08 g, 10 mmol) under argon was syringe-transferred a solution of bis(trimethylsilyl)acetylene (10d; 1.87 g, 11 mmol) in benzene (20 mL). The sealed mixture was covered with aluminum foil and heated in an oil bath at 80 °C. The reaction was monitored by the ^1H NMR of small aliquots (0.50 mL) from which the solvent was evaporated under vacuum and replaced with C_6D_6 . After 10 h the solvent was evaporated under vacuum to yield the crude titanacyclobutane 11d as a dark red solid (3.55 g, 98% crude). Even without further purification, this material was quite pure, with ^1H NMR showing greater than 95% conversion. Anal. Calcd for $\text{C}_{19}\text{H}_{30}\text{Si}_2\text{Ti}$: C, 62.95; H, 8.34. Found: C, 61.97; H, 7.99. ^1H NMR (250 MHz, C_6D_6 , lit.^{8a}): δ 5.22 (s, 10H, Cp), 4.68 (s, 2H, TiCH_2), 0.33 (s, 9H, SiMe_3), 0.21 (s, 9H, SiMe_3). ^{13}C NMR (63 MHz, C_6D_6 , lit.^{8a}): δ 246.8 ($\text{TiC}=\text{C}$), 108.8, (TiCH_2 , $J_{\text{CH}} = 141.6$ Hz), 107.6 (Cp), 102.9 ($=\text{C}$), 2.5 (SiMe_3), 1.5 (SiMe_3). MS (CI): m/e 363.1435 (MH^+), calcd for $\text{C}_{19}\text{H}_{31}\text{Si}_2\text{Ti}$ 363.1444.

Titanacyclobutenes 11e and 11f were prepared as a mixture from dimethyltitanocene (2) and 1-(trimethylsilyl)-1-propyne (10e) similarly to the preparation of 11a. NMR data for the mixture: ^1H NMR (500 MHz, C_6D_6) δ 5.68 (s, 10H, Cp), 5.57 (s, 10H, Cp), 4.03 (s, 2H, TiCH_2), 3.35 (s, 2H, TiCH_2), 2.60 (s, 3H, CH_3), 1.69 (s, 3H, CH_3), 0.21 (s, 9H, SiMe_3), 0.18 (s, 9H, SiMe_3); ^{13}C NMR (125.8 MHz, C_6D_6) δ 240.47 ($\text{TiC}=\text{C}$), 221.16 ($\text{TiC}=\text{C}$), 110.46 (Cp), 110.22 ($=\text{C}$), 107.48 (Cp), 93.83 (TiCH_2 , $J_{\text{CH}} = 141.5$ Hz), 85.29 (TiCH_2 , $J_{\text{CH}} = 138.7$ Hz), 77.19 ($=\text{C}$), 25.22 (CH_3), 20.57 (CH_3), 1.53 (SiMe_3), 0.98 (SiMe_3).

Titanacyclobutenes 11g and 11h were prepared as a mixture from dimethyltitanocene (2) and 1-phenyl-2-(trimethylsilyl)acetylene (10g) similarly to the preparation of 11a. NMR data for the mixture: ^1H NMR (500 MHz, C_6D_6) δ 6.89–7.20 (m, 5H, Ph), 5.59 (s, 10H, Cp), 5.31 (s, 10H, Cp), 4.19 (s, 2H, TiCH_2), 3.67 (s, 2H, TiCH_2), 0.05 (s, 9H, SiMe_3), 0.00 (s, 9H, SiMe_3); ^{13}C NMR

(125.8 MHz, C_6D_6) δ 238.06 ($\text{TiC}=\text{C}$), 225.60 ($\text{TiC}=\text{C}$), 123–150 (Ph), 115.32 ($=\text{C}$), 110.93 (Cp), 108.68 (Cp), 94.12 (TiCH_2 , $J_{\text{CH}} = 141.5$ Hz), 85.33 (TiCH_2 , $J_{\text{CH}} = 138.7$ Hz), 83.77 ($=\text{C}$), 2.06 (SiMe_3), 0.69 (SiMe_3).

Identification of Insertion Product 19c. A solution of dimethyltitanocene (2; 203 mg, 1.0 mmol) and diphenylacetylene (10c; 161 mg, 0.91 mmol) in C_6D_6 (1.0 mL) was placed in a 10-mL flask. After it was degassed under vacuum at -78 °C, the solution was filled with argon, sealed, and placed in an oil bath heated at 70 °C for 16 h. The NMR spectrum of the mixture showed the presence of titanacyclobutene 11c and the insertion product 19c in a 60:40 ratio. Spectral data for 19c: ^1H NMR (360 MHz, C_6D_6) δ 6.89–7.39 (m, 10H, Ph), 5.86 (s, 10H, Cp), 1.47 (s, 3H, $=\text{CCH}_3$), -0.44 (s, 3H, TiCH_3); ^{13}C NMR (90 MHz, C_6D_6) δ 189.6 ($\text{TiC}=\text{C}$), 123–147 (Ph), 113.2 (Cp), 90.1 ($=\text{C}$), 50.2 (TiCH_3 , $J_{\text{CH}} = 125.7$ Hz), 25.7 (CH_3); MS (CI) m/e 387.1579 (MH^+), calcd for $\text{C}_{26}\text{H}_{27}\text{Ti}$ 387.1592.

Reaction of 11c with Acetone. The mixture of 11c and 19c, prepared as above, was treated with excess acetone and heated at 70 °C for another 1 h. At this time the reaction mixture turned from dark to red and NMR indicated the presence of 25c¹⁰ and unreacted 19c in a ratio of 60:40. Compound 25c could be isolated by column chromatography (neutral alumina, 10% ethyl acetate in hexane). Quenching the mixture of 19c and 25c with excess HCl in ether, followed by aqueous workup and flash column chromatography, gave 24c (68 mg) and 26c¹⁰ (125 mg). Spectral data for 25c: ^1H NMR (500 MHz, C_6D_6 , lit.¹⁰) δ 6.73–7.00 (m, 10H, Ph), 5.98 (s, 10H, Cp), 2.72 (s, 2H, CH_2), 1.27 (s, 6H, CH_3); ^{13}C NMR (125.8 MHz, C_6D_6 , lit.¹⁰) δ 190.0 ($\text{TiC}=\text{C}$), 153.8 ($=\text{C}$), 122.3–146.7 (Ph), 113.6 (Cp), 88.3 (CO), 58.5 (CH_2), 28.4 (CH_3); MS (EI) m/e 428.1612 (M^+), calcd for $\text{C}_{28}\text{H}_{28}\text{TiO}$ 428.1619.

Typical Kinetic Experiment. A solution of dimethyltitanocene (2; 40.6 mg, 0.20 mmol), bis(trimethylsilyl)acetylene (10d, 356 mg, 2 mmol), and ferrocene (18.6 mg) in C_6D_6 (0.5 mL) was placed in an NMR tube. The solution was degassed under vacuum; after it was cooled to -78 °C, the tube was filled with argon, sealed, and placed in an oil bath heated at 80 °C. The ^1H NMR (360 MHz) spectra of the mixture were recorded periodically. The relative concentrations (C) of the components were determined by dividing the peak integrals for the titanocene Cp with the integral of the ferrocene Cp. The *R* value for all of the reported plots was >0.99 .

Reaction of Dimethyltitanocene with Pivalonitrile. Into a septum-sealed NMR tube filled with argon was syringe-transferred a solution of dimethyltitanocene (2; 94 mg, 0.46 mmol) and pivalonitrile (60 mg, 0.72 mmol) in C_6D_6 (0.5 mL). The reaction mixture was heated at 80 °C for 6 h, forming 28 in 90% yield based on the nitrile. ^1H NMR (250 MHz, C_6D_6 , lit.⁷): δ 5.70 (s, 10H, Cp), 4.83 (s, 1H, $=\text{CH}$), 1.19 (s, 9H, ^tBu), 1.03 (s, 9H, ^tBu); ^{13}C NMR (63 MHz, C_6D_6 , lit.⁷) δ 175.0 ($\text{C}=\text{N}$), 111.0 (Cp), 87.6 ($\text{CH}=\text{C}$), 37.6 ($\text{C}-\text{Me}$), 37.0 ($\text{C}-\text{Me}$), 29.8 (Me), 29.5 (Me). MS (FAB): m/e 359.1976 (MH^+), calcd for $\text{C}_{21}\text{H}_{31}\text{N}_2\text{Ti}$ 359.1967.

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Supplementary Material Available: ^1H and ^{13}C NMR spectra for compounds 11a, 11b, 11c, 11d, 11e/11f, 11g/11h, 11c/19c, 25c, and 28 (9 pages). Ordering information is given on any current masthead page.