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# Carbometalation/Methane Elimination Reactions of Dimethyltitanocene. Formation of Titanocene Vinyl Complexes and Titanacyclobutenes

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*Summary: Dimethyltitanocene reacts with diphenylacetylene to afford the vinyl complex resulting from insertion of the alkyne into one of the titanium–methyl bonds. Thermolysis of this vinyl complex results in extrusion of methane and formation of the titanacyclobutene. Other alkynes similarly afford the corresponding titanacyclobutenes. In contrast, nitriles react with dimethyltitanocene to afford not azatitanacyclobutenes but rather diazatitanacyclohexadienes, incorporating 2 equiv of the nitrile.*

The conversion of organic carbonyl compounds to alkenes via methylenation reactions has been facilitated by the development of a number of powerful organotitanium-based reagents. For example, "Tebbe's reagent" $[Cp_2Ti{=}CH_2{\cdot}Al(CH_3)_2Cl]$[1] and the titanacyclobutanes derived therefrom[2] efficiently methylenate enolizable ketones, as well as esters, lactones, and amides, to the corresponding alkenes,[3] whereas the more basic traditional Wittig reagents afford only poor yields with such substrates.

Literature reports suggest that the thermal[4] and photochemical[5] decomposition of dimethyltitanocene may proceed via formation of the titanocene methylidene complex, the complex clearly indicated as the active methylenating species in the reactions of Tebbe's reagent and the titanacyclobutanes. On the basis of this suggestion, Petasis recently reported the use of dimethyltitanocene to effect the methylenation of carbonyl compounds.[6] Although alternative mechanisms not involving the titanocene methylidene complex as an intermediate may also be invoked for these methylenation reactions, we were prompted to examine the reactions of dimethyltitanocene with alkynes, with the expectation of formation of titanacyclobutenes, complexes of long-standing interest in our research group.[7]

Indeed, alkynes react thermally with dimethyltitanocene to afford the corresponding titanacyclobutenes.[8] Whereas these reactions may in some cases proceed via the intermediacy of the titanocene methylidene complex, in one case we have observed an intermediate resulting from thermal carbometalation of the alkyne by dimethyltitanocene,[9] with subsequent ring closure of the resulting vinyltitanocene complex to the corresponding titanacyclobutene occurring with concomitant loss of methane. Although alkane elimination reactions have frequently been observed to lead to the formation of saturated metallacycles and of metallacyclopropenes, we are aware of only a single account of the formation of a metallacyclobutene as the result of such a reaction.[10] Similarly, the initial carbometalation step, although precedented, is an example of a relatively rare[11] carbometalation by a neutral group IV metallocene alkyl, a reaction class much more commonly seen for cationic group IV metallocene alkyl complexes.[12,13]

## Experimental Section

**General Procedures.** All manipulations were carried out under either an argon or nitrogen atmosphere using standard Schlenk and glovebox techniques. Solvents were dried over sodium/benzophenone ketyl or Na/K alloy, vacuum transferred,

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and stored under dry nitrogen or argon. Dimethyltitanocene was prepared as described.[14]

**1,1-Bis(cyclopentadienyl)-2,3-bis(trimethylsilyl)-1-titanacyclobut-2-ene (1a).** In the drybox an NMR tube was charged with bis(trimethylsilyl)acetylene (21.1 mg, 0.124 mmol) followed by a solution of $Cp_2TiMe_2$ (25.7 mg, 1 equiv) in $C_6D_6$ (0.5 mL). The tube was capped with a rubber septum or flame-sealed, wrapped completely in aluminum foil to exclude light, and heated in an oil bath at 80 °C (±1 °C). The reaction was monitored periodically by $^1$H NMR and was found to be >95% complete after 8 h. Removal of solvent in vacuo afforded **1a** in quantitative yield, with spectral properties identical to those previously reported.[15] On a preparative scale, a 100-mL Schlenk flask containing $Cp_2TiMe_2$ (1.05 g, 5.0 mmol) and toluene (30 mL) was charged with bis(trimethylsilyl)acetylene (0.83 g, 1 equiv). The flask was wrapped in aluminum foil and heated in an oil bath at 80 °C for 14 h, at which point $^1$H NMR analysis of an aliquot showed clean conversion to **1a**. Solvent was removed in vacuo, yielding **1a** in a satisfactory state of purity as an oil in quantitative yield. Crystallization of this oil from hexanes at −30 °C yields **1a** as a dark-red solid (1.46 g, 80%). $^1$H NMR ($C_6D_6$, 300.152 MHz): $\delta$ 5.22 (s, 10H, Cp), 4.67 (s, 2H, $CH_2$), 0.32 [s, 9H, $Si(CH_3)_3$], 0.21 [s, 9H, $Si(CH_3)_3$]. $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75.48 MHz): $\delta$ 108.8 ($CH_2$), 107.6 (Cp), 2.80 ($CH_3$), 1.49 ($CH_3$).

**1,1-Bis(cyclopentadienyl)-2-methyl-3-(trimethylsilyl)-1-titanacyclobut-2-ene and 1,1-Bis(cyclopentadienyl)-3-methyl-2-(trimethylsilyl)-1-titanacyclobut-2-ene.** In the drybox an NMR tube was charged with 1-(trimethylsilyl)propyne (18.3 mg, 0.16 mmol) followed by a solution of $Cp_2TiMe_2$ (34 mg, 1 equiv) in $C_6D_6$ (0.5 mL). The tube was capped with a rubber septum or flame-sealed, wrapped completely in aluminum foil to exclude light, and heated in an oil bath at 60 °C (±1 °C). The reaction was monitored periodically by $^1$H NMR and was found to be >95% complete after 7 days. A 43:57 mixture of the two regioisomeric metallacycles was formed. Major isomer: $^1$H NMR ($C_6D_6$, 300.152 MHz) $\delta$ 5.23 (s, 10H, Cp), 4.04 (q, 2H, $J$ = 1.8 Hz, $CH_2$), 2.60 (t, 3H, $J$ = 1.8 Hz, $CH_3$), 0.18 [s, 9H, $Si(CH_3)_3$]; $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75.48 MHz) $\delta$ 128 (under $C_6D_6$, Ti—*C*=C), 110.5 (Cp), 85.4 (Ti—$CH_2$), 77.6 (Ti—C=*C*), 25.2 ($CH_3$), 1.54 [$Si(CH_3)_3$]. Minor isomer: $^1$H NMR ($C_6D_6$, 300.152 MHz) $\delta$ 5.51 (s, 10H, Cp), 3.35 (s, 2H, $CH_2$), 1.69 (s, 3H, $CH_3$), 0.21 [s, 9H, $Si(CH_3)_3$]; $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75.48 MHz) $\delta$ 221.3 (Ti—*C*=C), 112.3 (Ti—C=*C*), 107.6 (Cp), 97.8 (Ti—$CH_2$), 20.2 ($CH_3$), 0.97 [$Si(CH_3)_3$]. Anal. Calcd for $C_{17}H_{24}SiTi$: C, 67.09; H, 7.95. Found: C, 67.03; H, 7.91.

**Methyl(1,2-diphenyl-1-propenyl)titanocene (2) and 1,1-Bis(cyclopentadienyl)-2,3-diphenyl-1-titanacyclobut-2-ene (1b).** To a Schlenk flask containing a solution of $Cp_2TiMe_2$ (1.00 g, 4.80 mmol) in toluene (25 mL) was added diphenylacetylene (1.71 g, 9.59 mmol, 2.0 equiv). The flask was wrapped in aluminum foil to exclude light and heated at 72 °C for 5 h. The solution underwent a color change from orange to deep-red. The solvent was then removed in vacuo, affording a brownish solid. This solid was mixed with 10 mL of hexanes and cooled at −20 °C for 2 days. The mother liquor was removed from the so-precipitated solid by cannula, affording **2** as a reddish solid (400 mg, 22%).[18] $^1$H NMR ($C_6D_6$, 300.152 MHz): $\delta$ 7.01–6.91 (m, 4H, ArH), 6.87–6.82 (m, 4H, ArH), 6.73–6.70 (d, 2H, $^3J_{HH}$ = 7.5 Hz, ArH), 5.84 (s, 10H, Cp), 1.45 (s, 3H, C—$CH_3$), −0.42 (s, 3H, Ti—$CH_3$). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75.48 MHz): $\delta$ 189.6 (Ti—*C*=C), 147.2 (Ar), 146.4 (Ar), 135.5 (Ti—C=*C*), 128.3 (Ar), 127.5 (Ar), 127.3 (Ar), 124.9 (Ar), 123.9 (Ar), 123.7 (Ar), 112.5 (Cp), 50.3 (Ti—$CH_3$), 25.7 ($CH_3$). $^{13}$C NMR ($C_6D_6$, 75.48 MHz): $\delta$ 189.6 (s), 147.2 (s), 146.4 (s), 135.5 (s), 128.3 (d, $^1J_{CH}$ = 161.1 Hz), 127.5 (d, $^1J_{CH}$ = 158.0 Hz), 127.3 (d, $^1J_{CH}$ = 161.2 Hz), 124.9 (d, $^1J_{CH}$ = 162.9 Hz), 123.9 (t, $^3J_{CH}$ = 7.5 Hz), 123.7 (d, $^1J_{CH}$ = 159.5 Hz), 112.5 (d, $^1J_{CH}$ = 174.1 Hz), 50.3 (q, $^1J_{CH}$ = 125.8 Hz), 25.7 (q, $^1J_{CH}$ = 125.0 Hz). HRMS: calcd for $C_{26}H_{26}Ti$, 386.1514; found, 386.1508. Anal. Calcd for $C_{26}H_{26}Ti$: C, 80.82; H, 6.78. Found: C, 80.67; H, 6.86.

Thermolysis of solutions of **2** in benzene or toluene at 70 °C for 3 days resulted in clean conversion to a deep-red solution of **1b** and 1 equiv of methane [$^1$H NMR ($C_6D_6$): $\delta$ 0.15]. Removal of solvent in vacuo afforded **1b** in quantitative yield, with spectral properties identical to those previously reported.[15] $^1$H NMR ($C_6D_6$, 300.152 MHz): $\delta$ 7.33–7.31 (d, 2H, ArH), 7.14–6.91 (m, 8H, ArH), 5.67 (s, 10H, Cp), 3.45 (s, 2H, $CH_2$). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75.48 MHz): $\delta$ 210.9 (Ti—*C*=C), 147.6 (Ar), 138.7 (Ar), 129.6 (Ar), 129.5 (Ar), 126.2 (Ar), 125.9 (Ar), 124.5 (Ar), 112.4 (Cp), 100.63 (Ti—C=*C*), 73.4 ($CH_2$).

Metallacyclobutene **1b** may also be prepared without isolation of intermediate **2**. Thus, $Cp_2TiMe_2$ (0.998 g, 4.79 mmol) reacted with 0.902 g of diphenylacetylene (5.06 mmol, 1.06 equiv) in 10 mL of toluene to afford, after heating for 16 h at 65–68 °C and removal of solvent in vacuo, a dark-purple solid (1.815 g, 98%) composed of **2** (ca. 80%) and **1b** (ca. 20%). This material was redissolved in 10 mL of toluene and heated for 12–14 h at 80–85 °C. Removal of solvent in vacuo afforded quantitative recovery of crude metallacycle **2**. Crystallization of the crude product twice from hexanes afforded **2** as a nicely crystalline, purple solid (60%).

**1,1-Bis(cyclopentadienyl)-2,3-diethyl-1-titanacyclobut-2-ene.** A solution of $Cp_2TiMe_2$ (0.5 g, 2.4 mmol) and dry toluene (5 mL) in a Schlenk flask wrapped in foil to exclude light was placed in a 71 °C (±1 °C) oil bath. To the heated mixture was added 3-hexyne (324 $\mu$L, 2.9 mmol). After continued heating at 71 °C for 12 h, during which time the flask was left open to a bubbler to prevent methane pressure buildup, the mixture was cooled to room temperature. Removal of solvent in vacuo, extraction with 10 mL of hexanes, filtration, and removal of solvent from the filtrate in vacuo afforded the diethyltitanacyclobutene as an oily paste (350 mg, 70%), in a satisfactory state of purity (ca. 98%), with spectral properties identical to those previously reported.[16] The product may be recrystallized from hexanes. $^1$H NMR ($C_6D_6$, 300.152 MHz): $\delta$ 5.53 (s, 10H, Cp), 3.30 (s, 2H, $CH_2$), 2.53 (q, 2H, $^3J_{HH}$ = 7.5 Hz, $CH_2$), 1.95 (q, 2H, $^3J_{HH}$ = 7.5 Hz, $CH_2$), 1.04 (t, 3H, $^3J_{HH}$ = 7.5 Hz, $CH_3$), 0.92 (t, 3H, $^3J_{HH}$ = 7.5 Hz, $CH_3$). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75.48 MHz): $\delta$ 221.0 (Ti—*C*=C), 110.0 (Cp), 92.5 (Ti—C=*C*), 77.6 (Ti—$CH_2$), 29.3 ($CH_2$), 22.4 ($CH_2$), 15.8 ($CH_3$), 12.4 ($CH_3$). $^{13}$C NMR ($C_6D_6$, 75.48 MHz): $\delta$ 221.0 (s), 110.0 (d, $^1J_{CH}$ = 172 Hz), 92.5 (s), 77.6 (t, $^1J_{CH}$ = 134 Hz), 29.3 (t, $^1J_{CH}$ = 124 Hz), 22.4 (t, $^1J_{CH}$ = 127 Hz), 15.8 (q, $^1J_{CH}$ = 125 Hz), 12.4 (q, $^1J_{CH}$ = 126 Hz).

**1,1-Bis(cyclopentadienyl)-3,5-bis(*tert*-butyl)-1-titana-2,6-diazacyclohexa-2,4-diene [4, R = $C(CH_3)_3$].** To a Schlenk flask containing $Cp_2TiMe_2$ (1.8 g, 8.6 mmol) and dry toluene (50 mL) was added pivalonitrile (1.43 g, 2.0 equiv) by syringe. The flask was wrapped in foil and heated at 65 °C for 5 days. The solvent was removed in vacuo and pentane (30 mL) was added. The reddish solution was cooled at −50 °C for 2 h, precipitating unreacted dimethyltitanocene. The mother liquor was transferred to another flask by cannula filtration. Removal of solvent in vacuo afforded **4** as a reddish oil (1.22 g, 40%). Spectral properties of this product were identical to those previously reported for **4**.[17] $^1$H NMR ($C_6D_6$, 300.152 MHz): $\delta$ 5.9 (br s, 1H, NH), 5.71 (s, 10H, Cp), 4.87 (d, $^4J_{HH}$ = 0.9 Hz, 1H, =CH), 1.21 [s, 9H, $C(CH_3)_3$], 1.02 [s, 9H, $C(CH_3)_3$]. $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75.48 MHz): $\delta$ 175.1 (*C*=N), 174.2 (=*C*-N), 110.0 (Cp), 87.8 (=CH), 37.7 [*C*$(CH_3)_3$], 37.1 [*C*$(CH_3)_3$], 29.8 ($CH_3$), 29.5 ($CH_3$). Anal. Calcd for $C_{21}H_{30}N_2Ti$: C, 70.38; H, 8.44; N, 7.82. Found: C, 68.68; H, 8.41; N, 6.98. HRMS: calcd for $C_{21}H_{30}N_2Ti$, 358.1888; found, 358.1872.

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**1,1-Bis(cyclopentadienyl)-3,5-bis($p$-methoxyphenyl)-1-titana-2,6-diazacyclohexa-2,4-diene (4, R = $p$-$CH_3OC_6H_4$).** To a Schlenk flask containing $Cp_2TiMe_2$ (1.0 g, 4.8 mmol) and dry toluene (40 mL) was added $p$-methoxybenzonitrile (1.28 g, 2.0 equiv) by syringe. The flask was wrapped in foil and heated at 65 °C for 5 days. After removal of solvent in vacuo, the residue was washed with 3 × 30 mL of pentane and filtered, affording the product as a bright-red solid, mp 162–167 °C (1.55 g, 70%). $^1H$ NMR ($C_6D_6$, 300.152 MHz): $\delta$ 7.84 (d, 2H, $^3J_{HH}$ = 8.4 Hz, ArH), 7.41 (d, 2H, $^3J_{HH}$ = 8.4 Hz, ArH), 6.88 (d, 2H, $^3J_{HH}$ = 9.3 Hz, ArH), 6.85 (d, 2H, $^3J_{HH}$ = 9.3 Hz, ArH), 6.05 (br s, 1H, NH), 5.78 (s, 10H, Cp), 5.71 (s, 1H, =CH) 3.34 (s, 3H, $OCH_3$), 3.29 (s, 3H, $OCH_3$). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75.48 MHz): $\delta$ 166.1 ($C$–$OCH_3$), 163.6 ($C$–$OCH_3$), 161.0 ($C$–$C_6H_4OCH_3$), 160.5 ($C$–$C_6H_4OCH_3$), 136.6 (ipso), 130.5 (ipso), 128.6 (Ar), 114.2 (Ar), 114.1 (Ar), 111.3 (Cp), 54.8 (2 × $OCH_3$). (One aromatic resonance was obscured by the solvent.) HRMS: calcd for $C_{27}H_{26}N_2O_2Ti$, 458.1474; found, 458.1449. Anal. Calcd for $C_{27}H_{26}N_2O_2Ti$: C, 70.74; H, 5.72; N, 6.11. Found: C, 70.68; H, 5.81; N, 6.15.

**1,1-Bis(cyclopentadienyl)-3,5-bis(1-adamantyl)-1-titana-2,6-diazacyclohexa-2,4-diene (4, R = 1-Adamantyl).** An analogous procedure, using 0.87 g of $Cp_2TiMe_2$ and 2 equiv of 1-cyanoadamantane, afforded this metallacycle as a reddish-brown solid, mp 233–234 °C (1.56 g, 72%). $^1H$ NMR ($C_6D_6$, 300.152 MHz): $\delta$ 6.09 (br s, 1H, NH), 5.76 (s, 10H, Cp), 4.87 (s, 1H, =CH), 1.6–2.0 (m, 30H, adamantyl). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75.48 MHz): $\delta$ 176.1 (C—N), 175.4 (C=N), 111.0 (Cp), 87.2 (=CH), 42.0, 41.8, 39.8, 39.6, 37.5, 37.1, 29.5, 29.3. HRMS: calcd for $C_{33}H_{42}N_2Ti$, 514.2827; found, 514.2835. Anal. Calcd for $C_{33}H_{42}N_2Ti$: C, 77.02; H, 8.23; N, 5.44. Found: C, 76.87; H, 8.36; N, 5.40.

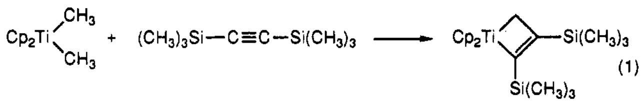
**1,1-Bis(cyclopentadienyl)-3,5-diphenyl-1-titana-2,6-diazacyclohexa-2,4-diene (4, R = $C_6H_5$).** An analogous procedure, using 0.050 g of $Cp_2TiMe_2$ and 2 equiv of benzonitrile, afforded this metallacycle as a red solid. $^1H$ NMR ($C_6D_6$, 300.152 MHz): $\delta$ 7.79 (d, 2H, $^3J_{HH}$ = 7.2 Hz, ArH), 7.43 (d, 2H, $^3J_{HH}$ = 6 Hz, ArH), 7.3–7.1 (m, 6H, ArH), 5.98 (br s, 1H, NH), 5.76 (s, 10H, Cp), 5.6 (s, 1H, =CH). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75.48 MHz): $\delta$ 166.2 (C—N), 163.7 (C=N), 144.0 (ipso), 137.9 (ipso), 128.8 (Ar), 128.7 (Ar), 128.6 (Ar), 127.9 (Ar), 127.3 (Ar), 126.7 (Ar), 111.5 (Cp), 92.9 (=CH). HRMS: Calcd for $C_{25}H_{22}N_2Ti$, 398.1262; found, 398.1248.

**1,1-Bis(cyclopentadienyl)-3,5-diethyl-1-titana-2,6-diazacyclohexa-2,4-diene (4, R = $CH_2CH_3$).** An analogous procedure, using 0.050 g of $Cp_2TiMe_2$ and 2 equiv of propionitrile, afforded a dark-red solution of this metallacycle. Attempted isolation resulted in decomposition. $^1H$ NMR ($C_6D_6$, 300.152 MHz): $\delta$ 5.70 (s, 10H, Cp), 5.41 (br s, 1H, NH), 4.50 (s, 1H, =CH), 2.03 (q, 2H, $^3J_{HH}$ = 7.2 Hz, $CH_2$), 1.87 (q, 2H, $^3J_{HH}$ = 7.2 Hz, $CH_2$), 1.13 (t, 3H, $^3J_{HH}$ = 7.2 Hz, $CH_3$), 0.90 (t, 3H, $^3J_{HH}$ = 7.2 Hz, $CH_3$). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75.48 MHz): $\delta$ 169.9 (C—N), 169.1 (C=N), 111.0 (Cp), 94.3 (=CH), 34.0 ($CH_2$), 33.8 ($CH_2$), 11.2 ($CH_3$), 10.8 ($CH_3$).

**1,1-Bis(cyclopentadienyl)-3,5-dimethyl-1-titana-2,6-diazacyclohexa-2,4-diene (4, R = $CH_3$).** An analogous procedure, using 0.050 g of $Cp_2TiMe_2$ and 2 equiv of acetonitrile, afforded a dark-red solution of this metallacycle. Attempted isolation resulted in decomposition. $^1H$ NMR ($C_6D_6$, 300.152 MHz): $\delta$ 5.70 (s, 10H, Cp), 5.3 (br s, 1H, NH), 4.49 (s, 1H, =CH), 1.73 (s, 3H, $CH_3$), 1.62 (s, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75.48 MHz): $\delta$ 164.6 (C—N), 163.2 (C=N), 110.7 (Cp), 96.2 (=CH), 27.9 ($CH_3$), 25.6 ($CH_3$).

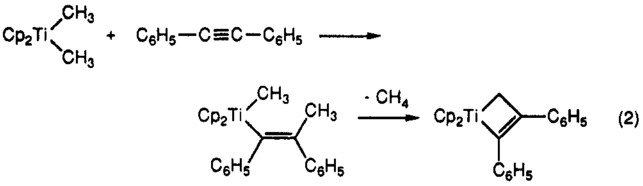
## Results and Discussion

Dimethyltitanocene reacts readily with bis(trimethylsilyl)acetylene in dry, deoxygenated benzene (80 °C, 10 h) to afford the known[15] bis(trimethylsilyl)titanacyclobutene (**1a**, eq 1). Workup is trivial, with material of satisfactory purity obtainable in essentially quantitative yield upon simple removal of solvent in vacuo and recrystallization from hexanes. This high yield and ease of workup, together with the ease of preparation of dimethyltitanocene, combine to make this the method of choice for the preparation of this titanacyclobutene.



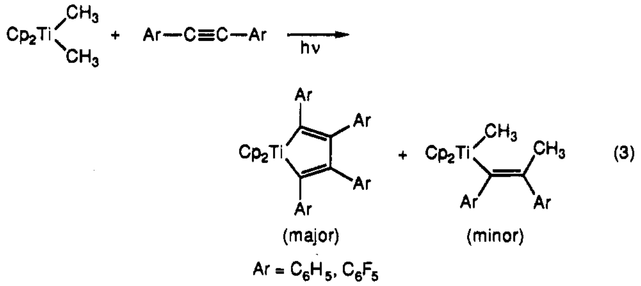
(1)

No intermediates are observed spectrally during the course of the reaction with bis(trimethylsilyl)acetylene. However, when dimethyltitanocene is treated with diphenylacetylene at 35 °C, near-quantitative conversion to the simple insertion product (**2**) is observed (eq 2),[18] with the only contaminant being the diphenyltitanacyclobutene (**1b**). Complex **2** may be isolated at this point in analytically pure form, although the yield of isolated **2** is rather low due to its good solubility even in cold hydrocarbon solvents. Continued thermolysis at higher temperatures (65–85 °C) completes the conversion of vinyl complex **2** to the titanacyclobutene. Formation of the titanacyclobutene is accompanied by the appearance of methane in the reaction mixture. Thermolysis of **2** in the presence of bis($p$-chlorophenyl)acetylene affords metallacycle **1b** cleanly, ruling out reversion of **2** to dimethyltitanocene via loss of alkyne under these reaction conditions.



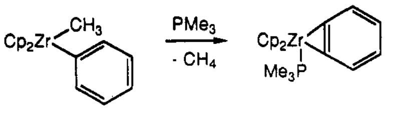
(2)

Vinyl complex **2** has previously been obtained as one of the products of the photolysis of dimethyltitanocene in the presence of diphenylacetylene, although the major product of the latter reaction was the result of reductive coupling of 2 equiv of the alkyne (eq 3), apparently by transiently-generated titanocene.[18] The thermal reaction of dimethyltitanocene with diphenylacetylene (eq 2) gives identical results whether carried out in the dark or with exposure to ambient fluorescent room light, suggesting that photochemical processes are not at play in this case. Formation of **2** is most easily explained by a direct insertion (carbometalation) of the alkyne into one of the Ti–$CH_3$ bonds of dimethyltitanocene, but may also result from homolysis of a Ti–$CH_3$ bond, followed by addition of $CH_3^{\bullet}$ to the alkyne and subsequent recombination of the so-formed vinyl radical with $Cp_2TiCH_3^{\bullet}$.



(3)

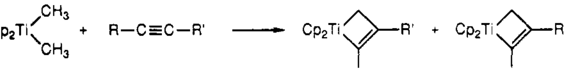
The methane elimination reaction leading from **2** to the titanacyclobutene is noteworthy. Similar reactions involving the coupling of a transition-metal bound methyl group with a proximal aromatic or vinylic hydrogen, affording methane and an aryne or alkyne complex, are well-precedented (e.g., eq 4).[19] However, we are aware of



(4)

only one previous report of the formation of metallacyclobutenes by such an alkane elimination reaction, in which thermolysis of dibenzylbis(pentamethylcyclopentadienyl)hafnocene afforded toluene and the benzohafnacyclobutene.[10] We are continuing to investigate the use of this general procedure for the preparation of differentially substituted metallacyclobutenes of titanium and other transition metals.

Other alkynes react analogously with dimethyltitanocene at elevated temperatures (ca. 70–80 °C), affording the corresponding titanacyclobutenes in good yield (eq 5). The reaction with 3-hexyne appears to give rise to



(5)

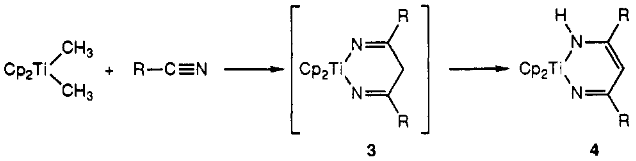
| R | R' | Yield (%) | |
|---|---|---|---|
| Me3Si | Me3Si | > 95 | |
| Ph | Ph | > 95 | |
| Et | Et | 70 | |
| Me | Me3Si | 43% | 57% |

alkyne polymerization competitively with formation of the corresponding titanacyclobutene. Even in this case, however, the yield of isolated titanacyclobutene is reasonable (ca. 70%), and the crude product is of satisfactory purity for further studies. (Alkyne polymerization appears to be a more significant problem in the reaction of dimethyltitanocene with 2-butyne. Given the irreproducible and variable yields of dimethyltitanacyclobutene obtained in this 2-butyne reaction, ranging from 30% to 70%, we do not report details of this reaction here.) Given the potential intermediacy of metallacyclobutenes in the polymerization of alkynes, first proposed by Chauser some 16 years ago, the observation of polymerization of alkynes in these reactions may prove to be significant. Whereas we have not yet observed vinyl complexes analogous to **2** as intermediates in these reactions of $Cp_2Ti(CH_3)_2$ with other alkynes, this is, we feel, indicative of a sensitive balance between carbometalation and methane elimination reaction rates rather than of a change in mechanism for these alkynes.

(Trimethylsilyl)propyne affords a 43:57 mixture of the two regioisomeric metallacyclobutenes, with the major isomer having the trimethylsilyl group in the $\alpha$-position. Tebbe's reagent reacts with this alkyne to form a similar mixture of regioisomers,[16] suggesting the possibility of a common intermediate (e.g., $Cp_2Ti{=}CH_2$) in the two reactions. However, expectedly similar steric influences in the [2 + 2] cycloaddition of the alkyne to $Cp_2Ti{=}CH_2$ and in its carbometalation by $Cp_2Ti(CH_3)_2$ would also lead to similar regioselectivities, without invoking a common intermediate for the two reactions. Treatment of the mixture of (trimethylsilyl)propyne metallacycle regioisomers with diphenylacetylene does not give the diphenyltitanacyclobutene, ruling out regioisomer equilibration as the source of the similar product ratios in the dimethyltitanocene and Tebbe's reagent reactions.[21]

Earlier studies have suggested that thermolysis of dimethyltitanocene may be initiated by $\alpha$-elimination of methane, affording a thermally labile methylidene complex which decomposes under the thermolysis conditions.[4] This decomposition reaction is not simple, however, with autocatalysis and a biphasic reaction course evident, and the intermediacy of the methylidene complex has not been unequivocally established.[22] Our observation of the intermediate vinyl complex in the reaction of dimethyltitanocene with diphenylacetylene at temperatures (~35 °C) lower than ordinarily required for the thermal decomposition of dimethyltitanocene and demonstration that this vinyl complex serves as a precursor to the corresponding titanacyclobutene suggest that these reactions proceed, at least at lower temperatures, via insertion of the alkyne into one of the titanium–methyl bonds, followed by intramolecular elimination of methane. At higher temperatures, the reaction may proceed via competitive generation of the titanocene methylidene complex and trapping by alkyne. In support of this suggestion, the reaction of dimethyltitanocene with 2-butyne at temperatures lower than that reported above for formation of the titanacyclobutenes (ca. 35 °C instead of 70–80 °C) affords a product which appears to be formed via initial carbometalation followed by methane elimination not from the methyl group transferred from titanium to the alkyne but rather from an alternative allylic site in the intermediate vinyl complex. This chemistry will be discussed further elsewhere.[23]

Interestingly, dimethyltitanocene also affords entry into the nitrile coupling reactions we first reported to be effected by Tebbe's reagent.[17] Thus, treatment of dimethyltitanocene with 2 equiv of pivalonitrile affords the diazatitanacyclohexadiene [**4**, $R = C(CH_3)_3$, eq 6]. Other nitriles similarly cleanly afford the corresponding diazatitanacyclohexadienes.



R = $CH_3$, $CH_3CH_2$, $(CH_3)_3C$, $C_6H_5$, p-$CH_3O$-$C_6H_4$, 1-adamantyl (6)

Rather surprisingly, no intermediates are observable by $^1H$ NMR spectroscopy during the course of this reaction, whereas we have found that the reaction with Tebbe's reagent provides first the untautomerized metallacyclic product (**3**), which then undergoes a slow tautomerization to afford **4**.[17] Although related tautomerizations are becoming commonplace in organotransition-metal chem-

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[19] See, for example: (a) Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 7137–7141. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047–1058.

[20] Chauser, M. G.; Rodionov, Y. M.; Misin, V. M.; Cherkashin, M. I. *Russ. Chem. Rev.* (*Engl. Transl.*) **1976**, *45*, 348–374. See also: Katz, T. J.; Hacker, S. M.; Kendrick, R. D.; Yannoni, C. S. *J. Am. Chem. Soc.* **1985**, *107*, 2182–2183 and references therein.

[21] The bis(trimethylsilyl)titanacyclobutene displays structural properties and reactivity consistent with facile loss of alkyne to regenerate [$Cp_2Ti{=}CH_2$]: McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbaugh, T. S.; Tebbe, F. N. *J. Am. Chem. Soc.* **1981**, *103*, 5584–5586.

[22] The thermal decomposition of dimethylbis(pentamethylcyclopentadienyl)titanium, in contrast, appears well-behaved. McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629–1634.

[23] Doxsee, K. M.; Juliette, J. J. J.; Nieckarz, G.; Zientara, K. To be submitted.

istry,[24] they represent thermally unfavorable [1,3]-sigmatropic rearrangements and are generally presumed to occur through mediation by adventitious acids or bases or via multistep mechanisms. It is likely that the tautomerization of **3** to **4** follows a base-catalyzed pathway, which is slowed in the presence of Lewis acids such as the $(CH_3)_2AlCl$ generated as a byproduct in the reactions of Tebbe's reagent. Continued study of the aluminum-containing reagent via aluminum-free routes to the diazatitanacyclohexadienes may permit some light to be shed on the factors at play in this tautomerization.

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[24] See, e.g.: Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006–1014. Strickler, J. R.; Wigley, D. E. *Organometallics* **1990**, *9*, 1665–1669.