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Mechanistic Insight into Fragmentation Reactions of Titanapinacolate Complexes

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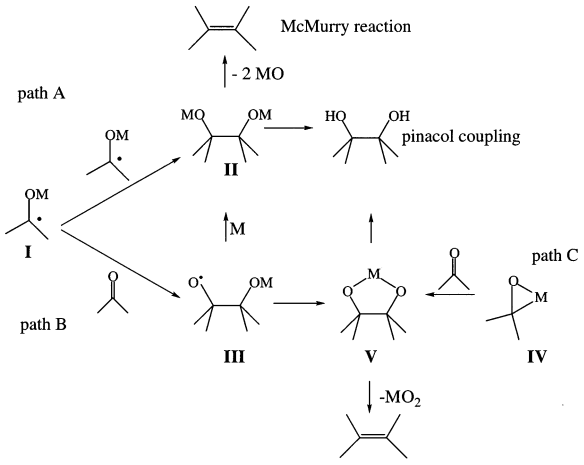
Abstract: Reactions between terminal alkynes or aromatic ketones and titanapinacolate complexes (DMSC)-Ti($OCAr_2CAr_2O$) (**2**, Ar = Ph, and **3**, Ar = *p*-MeC_6H_4; DMSC = 1,2-alternate dimethylsilyl-bridged *p-tert*-butylcalix[4]arene dianion) occur via rupture of the C−C bond of the titanacycle. Thus, reactions of **2** and **3** with terminal alkynes produce 2-oxatitanacyclopent-4-ene or 2-oxatitanacycloheptadiene complexes along with free Ar_2CO. These compounds have been characterized spectroscopically and by X-ray crystallography. Because metallapinacolate intermediates have been implicated in important C−C bond-forming reactions, such as pinacol coupling and McMurry chemistry, the mechanism of the fragmentation reactions was studied. Analysis of the kinetics of the reaction of (DMSC)Ti{$OC(p\text{-}MeC_6H_4)_2C(p\text{-}MeC_6H_4)_2O$} (**3**) with $Bu^tC{\equiv}CH$ revealed that the fragmentation reactions proceed via a preequilibrium mechanism, involving reversible dissociation of titanapinacolate complexes into (DMSC)Ti(η^2-$OCAr_2$) species with release of a ketone molecule, followed by rate-limiting reaction of (DMSC)Ti(η^2-$OCAr_2$) species with an alkyne or ketone molecule.

Introduction

The pinacol coupling reaction (reductive coupling of carbonyl compounds to yield 1,2-diols, mediated by a variety of metals in low oxidation state) and the McMurry reaction (reductive coupling of carbonyl compounds to yield alkenes, promoted by low-valent titanium reagents) are among the most powerful methods for constructing carbon−carbon bonds.[1−3] Metallapinacolate intermediates have been implicated in both of these reactions (Scheme 1).[1,4] For example, Villiers and Ephritikhine[4a,4c] have isolated and characterized a pinacolate intermediate $\{UCl_3(thf)_2\}_2(\mu\text{-}OCMe_2CMe_2O)$ in uranium-mediated reductive coupling of acetone at 20 °C, and deoxygenation of the metallapinacolate into tetramethylethylene was observed at higher temperature. We recently reported the synthesis of titanapinacolate complexes (DMSC)Ti($OCAr_2CAr_2O$) (**2**, Ar = Ph, and **3**, Ar = *p*-MeC_6H_4; DMSC = 1,2-alternate dimethylsilyl-bridged *p-tert*-butylcalix[4]arene dianion, eq 1).[5] Structural characterization of **2** by X-ray crystallography revealed that the unit cell contained two independent molecules and that the $OCPh_2CPh_2O$ fragment of each molecule possessed an unusually long C−C bond [1.628(6) and 1.652(5) Å].[5] Whether this rather

Scheme 1



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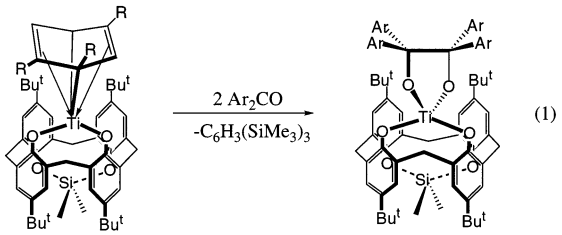

(1)

1, R = $SiMe_3$

2, Ar = Ph

3, Ar = *p*-MeC_6H_4

peculiar structural feature portends intriguing reaction chemistry for titanapinacolate complexes **2** and **3** was of interest to us, especially since **2** and **3** are titanium derivatives of **V** (Scheme 1). We have found that DMSC-based titanapinacolates **2** and **3** undergo remarkably facile fragmentation of the metallacyclic C−C bond upon reaction with unsaturated organic molecules, such as terminal alkynes and ketones. Whereas reversible cleavage of the C−C bond of some metallapinacolate intermediates has been invoked to explain their behavior in McMurry reactions,[4c,6−8] facile fragmentation of well-characterized metallapinacolate complexes by terminal alkynes is unprecedented to the best of our knowledge. More importantly, there is currently very little understanding of the mechanism(s) of metallapinacolate C−C bond rupture. In this paper, we present an analysis of the mechanism of fragmentation reactions of titanapinacolate compounds **2** and **3** on the basis of their structural properties and kinetic studies.

Experimental Section

General Methods. All experiments were performed under dry nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres, Inc., glovebox. Tetrahydrofuran, ether, and toluene were distilled twice from sodium benzophenone ketyl. Pentane was distilled twice from sodium benzophenone ketyl with addition of 1 mL/L of tetraethylene glycol dimethyl ether as a solubilizing agent. Benzene-d_6 was distilled from sodium benzophenone ketyl. All solvents were stored in the glovebox over 4 Å molecular sieves that were dried in a vacuum oven at 150 °C for at least 48 h prior to use. $Ph_2{}^{13}CO$ and alkynes were purchased from Aldrich. All of the alkynes were distilled from CaH_2 prior to use. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 spectrometer or a Varian VXR-400 spectrometer at ca. 22 °C. ^1H and ^{13}C chemical shifts were referenced to residual solvent peaks. GC-MS analyses were performed on a Hewlett-Packard 5890 series II gas chromatograph with a Hewlett-Packard 5972 series mass selective detector at an ionizing potential of 70 eV. Alternately, mass spectral data were obtained from the University of Kentucky Mass Spectrometry Center. Elemental analyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ. The kinetic data were fitted using the MacCurveFit program (version 1.1).

(DMSC)Ti{OC(*p*-MeC_6H_4)$_2$C(*p*-MeC_6H_4)$_2$O} (3). To a solution of (DMSC)Ti{1,2,4-$(Me_3Si)_3C_6H_3$} (**1**)[9] (1.015 g, 0.970 mmol) in dry heptane (20 mL) was added 4,4′-dimethylbenzophenone (0.408 g, 1.94 mmol). The brown slurry was heated at 65 °C with constant stirring for 1 h, using an oil bath. The clear yellow solution was cooled to room temperature, and the solvent was removed under reduced pressure to give a sticky yellow residue. A 5 mL volume of cold pentane was added into the flask, and the solution was stirred for 10 min. The yellow powder isolated by filtration was dried under vacuum. Yield: 1.042 g (92%). Both ^1H and ^{13}C NMR data are identical to that previously reported.[5]

(DMSC)$_2$Ti (4). (DMSC)H_2 (0.176 g, 0.250 mmol) was dissolved in 15 mL of toluene, and $(PhCH_2)_2Mg{\cdot}2THF$ (0.0875 g, 0.250 mmol) was added to it. The mixture was stirred for 15 min, during which time (DMSC)Mg started to precipitate. (DMSC)$TiCl_2$ (0.205 g, 0.250 mmol) was added to this heterogeneous mixture, along with 15 mL of THF. The resulting mixture was stirred at room temperature for 24 h. Next, the insolubles were filtered off and the amount of solvent was reduced to 10 mL. Pentane (7 mL) was then added to the solution, and the resulting precipitate was allowed to settle at −20 °C for 4 h. A bright-yellow precipitate was collected and dried. Yield: 0.220 g (60%). ^1H NMR (C_6D_6): δ 7.34 (d, 2H, arom CH), 7.09−7.25 (m, 10H, arom CH), 7.07 (d, 2H, arom CH), 6.93 (d, 2H, arom CH), 4.77 (d, J = 14.5 Hz, 2H, calix-CH_2), 4.41 (d, J = 15 Hz, 2H, calix-CH_2), 4.18 (d, J = 17 Hz, 2H, calix-CH_2), 4.01 (d, J = 17 Hz, 2H, calix-CH_2), 3.79 (d, J = 15 Hz, 2H, calix-CH_2), 3.77 (d, J = 16 Hz, 2H, calix-CH_2), 3.53 (d, J = 17 Hz, 2H, calix-CH_2), 3.44 (d, J = 16 Hz, 2H, calix-CH_2), 1.51 (s, 18H, t-Bu), 1.30 (s, 18H, t-Bu), 1.27 (s, 18H, *t*-Bu), 1.00 (s, 18H, *t*-Bu), 0.07 (s, 6H, *exo*-$SiCH_3$), −1.32 (s, 6H, *endo*-$SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 156.0 (TiOC), 159.5 (TiOC), 149.7, 149.2, 144.9, 143.8, 143.1, 143.0, 135.2, 131.1, 129.8, 129.2, 128.0 (br s), 127.3, 127.2, 126.9, 126.6, 125.9, 125.8, 125.6 (br s), 125.4, 124.8, 40.1 (calix-CH_2), 37.7 (calix-CH_2), 36.7 (calix-CH_2), 34.5 (calix-CH_2), 34.1 ($C(CH_3)_3$), 34.0 ($C(CH_3)_3$), 33.9 ($C(CH_3)_3$), 33.5 ($C(CH_3)_3$), 31.9 (C(CH_3)$_3$), 31.5 (br s, C(CH_3)$_3$), 30.9 (C(CH_3)$_3$), 2.4 (SiCH_3), −2.2 (SiCH_3). MS (*m*/*z*): M^+ (1454).

(DMSC)Ti{OC(*p*-MeC_6H_4)$_2$C$_2$Bu^{t}H} (5). (DMSC)Ti{OC(*p*-MeC_6H_4)$_2$C(*p*-MeC_6H_4)$_2$O} (**3**) (1.32 g, 1.13 mmol), Bu^{t}C≡CH (0.55 mL, 4.50 mmol), and 25 mL of heptane were charged into a 50 mL reaction vessel equipped with a Teflon stopcock. The vessel was closed off and heated at 75 °C for 2 h. The yellow solution was then allowed to gradually cool to ambient temperature and was left standing for 18 h. The volatiles were removed under reduced pressure, and the residue was dissolved in a minimal amount of pentane and placed in the glovebox freezer at −15 °C for 24 h. During this time, (*p*-MeC_6H_4)$_2$CO precipitated and was filtered off. The filtrate was stripped under reduced pressure, and the residue was dissolved in 3 mL of Et_2O and cooled at −15 °C. After 3 days, yellow crystalline precipitate was collected and recrystallized from pentane to give yellow crystals of pure **5**. Yield: 0.35 g (30%). The rather low isolated yield is primarily due to the very high solubility of the product. ^1H NMR (C_6D_6): δ 7.68 (s, 1H, C_β-H), 7.31 (d, 2H, J = 8 Hz, *p*-tolyl), 7.30 (d, 2H, J = 2 Hz, calix arom), 7.27 (d, 2H, J = 2 Hz, calix arom), 7.18 (d, 2H, J = 2 Hz, calix arom), 7.08 (d, 2H, J = 8 Hz, *p*-tolyl), 7.00 (d, 2H, J = 2 Hz, calix arom), 4.86 (d, 1H, J = 13 Hz, calix-CH_2), 4.27 (d, 1H, J = 16 Hz, calix-CH_2), 4.09 (d, 2H, J = 17 Hz, calix-CH_2), 3.90 (d, 2H, J = 17 Hz, calix-CH_2), 3.83 (d, 1H, J = 16 Hz, calix-CH_2), 3.52 (d, 1H, J = 13 Hz, calix-CH_2), 2.22 (s, 6H, *Me*C_6H_4), 1.27 (s, 18H, t-Bu), 1.19 (s, 18H, t-Bu), −0.21 (s, 3H, *exo*-SiMe), −1.57 (s, 3H, *endo*-SiMe). ^{13}C NMR (C_6D_6): δ 221.1 (TiC_α), 161.0 (TiO*C*), 151.3, 150.5, 145.4, 144.8, 144.5, 135.6, 130.8, 130.7, 129.0, 128.3 (br), 127.8 (br), 126.7, 125.9, 125.8, 85.9 ($C(MeC_6H_4)_2$), 39.9 (calix-CH_2), 38.4 (calix-CH_2), 37.8 (calix-CH_2), 34.1 ($C(CH_3)_3$), 33.9 ($C(CH_3)_3$), 31.54 (C(CH_3)$_3$), 31.46 (C(CH_3)$_3$), 21.0 (*Me*C_6H_4), 1.4 (*exo*-Si*Me*), −3.6 (*endo*-Si*Me*). Anal. Calcd for $C_{67}H_{82}O_5SiTi$: C, 77.13; H, 7.92. Found: C, 77.11; H, 8.01. A single crystal of **5** suitable for an X-ray diffraction study was obtained by cooling a pentane solution of **5** to −15 °C.

(DMSC)Ti{OCPh$_2$C$_2$(SiMe$_3$)H} (6). (DMSC)Ti($OCPh_2CPh_2O$) (**2**) was generated in situ from 0.020 mmol (20.9 mg) of (DMSC)Ti{η^6-1,2,4-$(Me_3Si)_3C_6H_3$} (**1**) and 0.040 mmol (7.28 mg) of Ph_2CO (C_6D_6 solution). To this solution 0.100 mmol (14.1 μL) of $Me_3SiC{\equiv}CH$ was added, and the reaction was heated at 80 °C and monitored by ^1H NMR. After 25 min, **2** was completely exhausted and **6** and **9** were observed in ca. 1:2 ratio as the only DMSC-containing species in solution. After

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2 h, the conversion of **6** into **9** was >95% complete. The resonances due to **6** were mostly obstructed by those of **9** although certain peaks could be identified. ^{1}H NMR (unobstructed resonances) (C_6D_6): δ 8.25 (s, 1H, C_β-H), 1.29 (s, 18H, *t*-Bu), 1.17 (s, 18H, *t*-Bu), 0.18 (s, 9H, $SiMe_3$), −0.23 (s, 3H, *exo*-SiMe), −1.60 (s, 3H, *endo*-SiMe).

In a similar reaction, the sample was hydrolyzed while some of **6** was still present in solution. The hydrolysis product $Ph_2C(OH)CH{=}CHSiMe_3$ was identified by GC-MS. EI-GC-MS (*m*/*z*): 282 (10, M^+), 267 (4, $M^+ - CH_3$), 209 (10, $M^+ - SiMe_3$), 192 (100, $M^+ - HOSiMe_3$), 182 (40, $M^+ - HC{=}CHSiMe_3$), 105 (75, $PhCO^+$), 73 (60, Me_3Si^+).

(DMSC)Ti{OC(*p*-MeC$_6$H$_4$)$_2$C$_2$(SiMe$_3$)H} (7) and (DMSC)Ti{OC(*p*-MeC$_6$H$_4$)$_2$C$_4$(SiMe$_3$)$_2$H$_2$} (10). (DMSC)Ti{OC(*p*-MeC_6H_4)$_2$C(*p*-MeC_6H_4)$_2$O} (**3**) (23.4 mg, 0.020 mmol) was dissolved in 0.6 mL of C_6D_6, and $Me_3SiC{\equiv}CH$ (11.3 μL, 0.080 mmol) was added to it. The reaction is slow at 22 °C; the solution contained **3**, **7**, and **10** in ca. 50:45:5 ratio after 5 h. Under all the reaction conditions attempted, the final product mixture was ca. 85% of **10** and 15% of a DMSC-based compound. Whereas aromatic and calixarene CH_2 resonances are difficult to assign to specific components of the mixture due to spectra overlap, the remaining peaks could be identified and assigned. ^{1}H NMR (unobstructed resonances of **7**) (C_6D_6): δ 8.24 (s, 1H, C_β-H), 2.20 (s, 6H, *Me*C_6H_4), 1.29 (s, 18H, *t*-Bu), 1.17 (s, 18H, *t*-Bu), 0.16 (s, 9H, $SiMe_3$), −0.19 (s, 3H, *exo*-SiMe), −1.58 (s, 3H, *endo*-SiMe). ^{1}H NMR (unobstructed resonances of **10**) (C_6D_6): δ 6.59 (s, 1H), 2.27 (s, 6H, *Me*C_6H_4), 2.10 (s, 6H, *Me*C_6H_4), 1.31 (s, 9H, *t*-Bu), 1.29 (s, 9H, *t*-Bu), 1.28 (s, 9H, *t*-Bu), 1.23 (s, 9H, *t*-Bu), 0.14 (s, 3H, *exo*-SiMe), 0.07 (s, 9H, $SiMe_3$), −0.03 (s, 9H, $SiMe_3$), −1.40 (s, 3H, *endo*-SiMe).

(DMSC)Ti{OC(*p*-MeC$_6$H$_4$)$_2$C$_4$Bu^t(SiMe$_3$)H$_2$} (8). $Me_3SiC{\equiv}CH$ (0.20 mL, 1.415 mmol) and (DMSC)Ti{OC(*p*-MeC_6H_4)$_2$C$_2$Bu^{t}H} (**5**) (0.450 g, 0.431 mmol) were dissolved in 10 mL of toluene in a heavy-walled pressure tube equipped with a Teflon stopcock. The solution was stirred for 2 days at room temperature, and then the volatiles were removed under reduced pressure. The residue was washed with pentane and dried under vacuum to give 0.360 g (74%) of **8** as a pure yellow solid. ^{1}H NMR (C_6D_6): δ 7.63 (d, 1H, J = 2 Hz, calix arom), 7.41 (d, 2H, J = 8 Hz, *p*-tolyl), 7.40 (d, 1H, J = 2 Hz, calix arom), 7.37 (d, 1H, J = 2 Hz, calix arom), 7.33 (d, 1H, J = 2 Hz, calix arom), 7.22 (d, 1H, J = 2 Hz, calix arom), 7.14 (d, 1H, J = 2 Hz, calix arom), 7.13 (d, 1H, J = 2 Hz, calix arom), 7.04 (s, 1H), 7.03 (d, 1H, J = 2 Hz, calix arom), 6.98 (d, 2H, J = 8 Hz, *p*-tolyl), 6.96 (d, 2H, J = 8 Hz, *p*-tolyl), 6.86 (d, 2H, J = 8 Hz, *p*-tolyl), 6.21 (s, 1H), 4.61 (d, 1H, J = 14 Hz, calix-CH_2), 4.55 (d, 1H, J = 17 Hz, calix-CH_2), 4.49 (d, 2H, J = 15 Hz, calix-CH_2), 4.43 (d, 1H, J = 17 Hz, calix-CH_2), 4.36 (d, 1H, J = 17 Hz, calix-CH_2), 3.88 (d, 1H, J = 17 Hz, calix-CH_2), 3.68 (d, 1H, J = 14 Hz, calix-CH_2), 3.63 (d, 1H, J = 15 Hz, calix-CH_2), 2.26 (s, 3H, *Me*C_6H_4), 2.10 (s, 3H, *Me*C_6H_4), 1.31 (s, 9H, *t*-Bu), 1.29 (s, 9H, *t*-Bu), 1.29 (s, 9H, *t*-Bu), 1.21 (s, 9H, *t*-Bu), 1.06 (s, 9H, *t*-Bu), 0.14 (s, 3H, *exo*-SiMe), −0.03 (s, 9H, $SiMe_3$), −1.40 (s, 3H, *endo*-SiMe). ^{13}C NMR (C_6D_6): δ 214.3 (TiC_α), 159.7 (TiO*C*), 159.5 (TiO*C*), 155.1, 150.8, 149.6, 146.9, 146.2, 144.9, 144.8, 143.9, 143.2, 142.7, 137.4, 135.5, 135.0, 133.4, 130.9, 130.0, 129.5, 129.1, 128.5, 127.8, 127.7, 127.5, 127.4 (br), 127.0, 126.2, 126.0, 125.9, 125.8, 125.2, 86.0 (*C*Ph_2), 41.2 (calix-CH_2), 38.4 (calix-CH_2), 38.1 (calix-CH_2), 37.7 (calix-CH_2), 34.39 (*C*$(CH_3)_3$), 34.36 (*C*$(CH_3)_3$), 34.22 (*C*$(CH_3)_3$), 34.15 (*C*$(CH_3)_3$), 33.89 (*C*$(CH_3)_3$), 31.9 (C(*C*$H_3)_3$), 31.8 (C(*C*$H_3)_3$), 31.6 (C(*C*$H_3)_3$), 31.5 (C(*C*$H_3)_3$), 29.4 (C(*C*$H_3)_3$), 21.1 (*Me*C_6H_4), 20.9 (*Me*C_6H_4), 2.5 (*exo*-Si*Me*), −0.3 ($SiMe_3$), −2.6 (*endo*-Si*Me*). Anal. Calcd for $C_{71}H_{89}O_5Si_2Ti$: C, 75.70; H, 7.96. Found: C, 75.47; H, 8.06.

(DMSC)Ti{OCPh$_2$C$_4$(SiMe$_3$)$_2$H$_2$} (9). (DMSC)Ti($OCPh_2CPh_2O$) (**2**) (0.600 g, 0.535 mmol), $Me_3SiC{\equiv}CH$ (0.5 mL, ca. 3.50 mmol), and 10 mL of heptane were charged into a 50 mL reaction vessel equipped with a Teflon stopcock. The vessel was closed off and heated at 90 °C for 3 h. The volatiles were removed under reduced pressure, and then benzophenone was removed by sublimation. The sublimation residue was dissolved in 2 mL of pentane, and 0.5 mL of C_6D_6 was added to it. This solution was placed in the freezer at −15 °C for 24 h. The resulting precipitate was collected, washed with 2 mL of pentane, and dried under vacuum to give 0.56 g (92%) of solid yellow product. ^{1}H NMR (C_6D_6): δ 7.62 (d, 1H, J = 2 Hz, calix arom), 7.56 (pseudo d, 2H, J = 7 Hz, Ph), 7.42 (d, 1H, J = 2 Hz, calix arom), 7.33 (2 AB doublets, 2H, calix arom), 7.24 (d, 1H, J = 2 Hz, calix arom), 7.0−7.2 (m, 12 H), 6.85−6.92 (m, 2H), 6.59 (s, 1H), 4.69 (d, 1H, J = 14 Hz, calix-CH_2), 4.54 (d, 1H, J = 17 Hz, calix-CH_2), 4.50 (d, 2H, J = 15 Hz, calix-CH_2), 4.44 (d, 1H, J = 17 Hz, calix-CH_2), 4.35 (d, 1H, J = 17 Hz, calix-CH_2), 3.87 (d, 1H, J = 17 Hz, calix-CH_2), 3.70 (d, 1H, J = 14 Hz, calix-CH_2), 3.62 (d, 1H, J = 15 Hz, calix-CH_2), 1.32 (s, 9H, *t*-Bu), 1.30 (s, 9H, *t*-Bu), 1.252 (s, 9H, *t*-Bu), 1.249 (s, 9H, *t*-Bu), 0.14 (s, 3H, *exo*-SiMe), 0.07 (s, 9H, $SiMe_3$), −0.02 (s, 9H, $SiMe_3$), −1.40 (s, 3H, *endo*-SiMe). ^{13}C NMR (C_6D_6): δ 212.5 (TiC_α), 159.9, 159.7, 151.0, 150.9, 149.7, 148.7, 148.6, 146.9, 145.0, 143.9, 143.2, 142.8, 137.3, 133.4, 130.8, 130.1, 128.5, 128.3, 127.9, 127.8, 127.7, 127.4, 127.3, 127.1, 126.6, 126.2, 126.0, 125.6, 125.1, 86.5 (*C*Ph_2), 41.2 (calix-CH_2), 38.4 (calix-CH_2), 37.7 (calix-CH_2), 37.6 (calix-CH_2), 34.23 (*C*$(CH_3)_3$), 34.18 (*C*$(CH_3)_3$), 34.12 (*C*$(CH_3)_3$), 33.94 (*C*$(CH_3)_3$), 31.82 (C(*C*$H_3)_3$), 31.78 (C(*C*$H_3)_3$), 31.61 (C(*C*$H_3)_3$), 31.55 (C(*C*$H_3)_3$), 2.3 (*exo*-Si*Me*), −0.3 ($SiMe_3$), −2.0 ($SiMe_3$), −2.6 (*endo*-Si*Me*). Anal. Calcd for (DMSC)Ti{$OCPh_2C_4(SiMe_3)_2H_2$}(C_6D_6)(pentane)$_{0.5}$, $C_{77.5}H_{94}D_6O_5Si_3Ti$: C, 74.48; H, 8.55. Found: C, 74.76; H, 8.46.

A single-crystal suitable for an X-ray diffraction study was obtained by inducing crystallization of **9** from hexamethyldisiloxane by addition of a small amount of benzene at ambient temperature. A sample of **9** was decomposed with H_2O in ether. The suspension was allowed to stand for 15 min, and then the insolubles were filtered off and the filtrate was analyzed by GC-MS. $Ph_2C(OH)CH{=}C(SiMe_3)CH{=}CH(SiMe_3)$ was the only species observed. EI-GC-MS (*m*/*z*): 380 (1, M^+), 362 (1, $M^+ - H_2O$), 307 (12, $M^+ - SiMe_3$), 281 (5, $M^+ - HC{=}CHSiMe_3$), 259 ($M^+ - 121$), 217 ($M^+ - OH, -2SiMe_3$), 187 (9, $M^+ - 193$), 147 (8, $M^+ - 233$), 105 (18, $PhCO^+$), 73 (100, Me_3Si^+).

Typical Procedure for Kinetic Study of the Reaction between (DMSC)Ti{OC(*p*-MeC$_6$H$_4$)$_2$C(*p*-MeC$_6$H$_4$)$_2$O} (3) and Bu^{t}C≡CH under Pseudo-First-Order Conditions. A 0.400 mL (0.0208 mmol) volume of a 0.0521 M stock solution of (DMSC)Ti{OC(*p*-MeC_6H_4)$_2$C(*p*-MeC_6H_4)$_2$O} (**3**) in C_6D_6 was added into a J. Young NMR tube, followed by 0.200 mL of a 2.00 M stock solution of Bu^{t}C≡CH (0.401 mmol, 19.3 equiv) and 0.300 mL of C_6D_6. This resulted in 0.900 mL of a 0.0232 M solution of **3** and a 0.445 M solution of Bu^{t}C≡CH. The tube was vigorously shaken and placed into the spectrometer at a set temperature (50 °C). The first ^{1}H NMR spectrum (at time = 0) was recorded immediately after inserting the sample in the spectrometer. Spectra were recorded every 10 min thereafter. The dependence of the reaction on [**3**] was determined by varying the concentration of **3** while conducting each experiment in C_6D_6 at 50 °C, using an identical amount of Bu^{t}C≡CH (0.200 mL, 0.401 mmol) and the same total volume (0.900 mL).

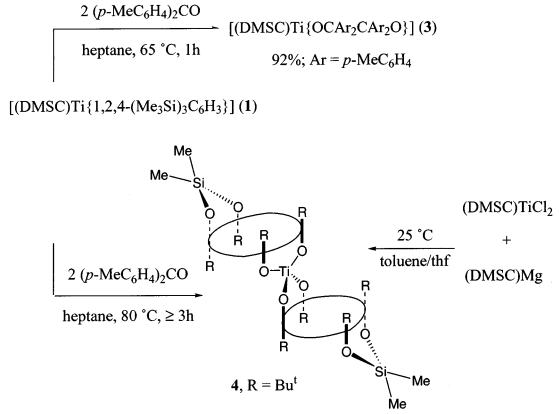
Typical Procedure for Determining the Reaction Dependence on the Concentration of Bu^{t}C≡CH. A 0.200 mL volume of a 0.0508 M stock solution of (DMSC)Ti{OC(*p*-MeC_6H_4)$_2$C(*p*-MeC_6H_4)$_2$O} (**3**) in C_6D_6 (0.0102 mmol) was added into a J. Young NMR tube, followed by 0.500 mL (0.500 mmol, 49.2 equiv) of a 1.00 M stock solution of Bu^{t}C≡CH and then 0.100 mL of C_6D_6. This resulted in 0.800 mL of a 0.0127 M solution of **3** and a 0.626 M solution of Bu^{t}C≡CH. The tube was vigorously shaken and placed into the spectrometer at 50 °C. The first ^{1}H NMR spectrum (at time = 0) was recorded immediately after inserting the sample in the spectrometer. Spectra were recorded for every 10 min thereafter. The dependence of the reaction on [Bu^{t}C≡CH] was obtained by varying the concentration of Bu^{t}C≡CH while conducting each experiment in C_6D_6 at the same temperature (50 °C), using an identical amount of **3** (0.200 mL, 0.0102 mmol) and the same total volume (0.800 mL).

Determining the Effect of Added (*p*-MeC$_6$H$_4$)$_2$CO on the Reaction between (DMSC)Ti{OC(*p*-MeC$_6$H$_4$)$_2$C(*p*-MeC$_6$H$_4$)$_2$O} (3) and Bu^{t}C≡

Table 1. Crystallographic Data for $5{\cdot}C_5H_{12}$ and $9{\cdot}2C_6H_6$

	$5{\cdot}C_5H_{12}$	$9{\cdot}2C_6H_6$
formula	$C_{72}H_{94}O_5SiTi$	$C_{81}H_{100}O_5Si_3Ti$
fw	1115.46	1285.78
T, K	173(1)	173(2)
cryst system	monoclinic	triclinic
space group	Pn	$P\bar{1}$
Z	2	2
a, Å	13.986(1)	11.242(2)
b, Å	11.690(1)	13.483(3)
c, Å	19.815(2)	25.368(5)
α, deg	90	79.350(10)
β, deg	97.94(1)	84.900(10)
γ, deg	90	76.400(10)
V, Å^3	3208.6(5)	3668.8(13)
d_{calcd}, g/cm^3	1.155	1.164
final *R* indices [$I > 2\sigma(I)$]: R1, wR2	0.047, 0.109	0.0970, 0.2522
wR2, R1 (all data)	0.113, 0.053	0.2558, 0.1071

Scheme 2



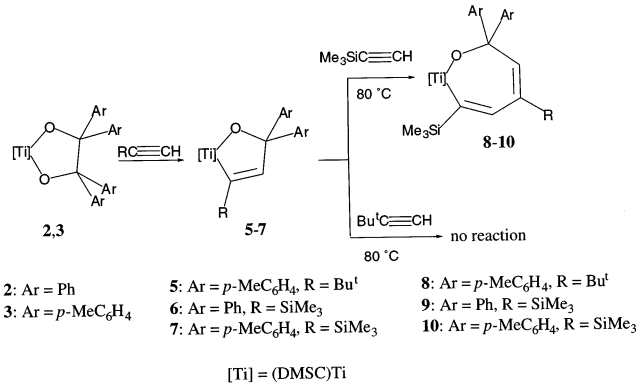
CH. A 0.200 mL (0.0101 mmol) volume of a 0.0507 M stock solution of (DMSC)Ti{OC(*p*-$MeC_6H_4)_2$C(*p*-$MeC_6H_4)_2$O} (**3**) in C_6D_6 was added into a J. Young NMR tube, followed by 0.250 mL of a 2.00 M stock solution of $Bu^tC{\equiv}CH$ (0.501 mmol, 49.5 equiv), 0.050 mL of a 0.203 M stock solution of (*p*-$MeC_6H_4)_2CO$ (0.0101 mmol), and 0.300 mL of C_6D_6. This resulted in 0.800 mL of a 0.0127 M solution of **3**, a 0.626 M solution of $Bu^tC{\equiv}CH$, and a 0.0127 M solution of (*p*-$MeC_6H_4)_2$-CO. The tube was vigorously shaken and placed into the spectrometer at 50 °C. The first ^{1}H NMR spectrum (at time = 0) was recorded immediately after inserting the sample in the spectrometer. Spectra were recorded for every 5 min thereafter. A second experiment was conducted in C_6D_6 and at 50 °C, using identical amounts of **3** and $Bu^tC{\equiv}CH$ as above, 0.0303 mmol (3 equiv) of (*p*-$MeC_6H_4)_2CO$, and the same total volume (0.800 mL).

Crystallographic Studies. The crystal data for $5{\cdot}C_5H_{12}$ and $9{\cdot}2C_6H_6$ are collected in Table 1. Further details of the crystallographic study are given in the Supporting Information.

Results and Discussion

Reaction of (DMSC)Ti{1,2,4-($Me_3Si)_3C_6H_3$} (1) with (*p*-$MeC_6H_4)_2CO$. We previously reported that reaction of (DMSC)-Ti{1,2,4-($Me_3Si)_3C_6H_3$} (**1**) with Ph_2CO or (*p*-$MeC_6H_4)_2CO$ in heptane proceeded to completion in under 3 h at 80 °C to produce titanapinacolates **2** and **3**, respectively.[5] Whereas these conditions are efficient for the preparation of **2**, we have since discovered that **3** is more reliably produced by carrying out the reaction at 65 °C for 1 h (Scheme 2). The predominant product formed in the reaction of **1** with (*p*-$MeC_6H_4)_2CO$ (2 equiv) at

Scheme 3



80 °C is $(DMSC)_2Ti$ (**4**),[10] which can be obtained in a more direct fashion by reaction between (DMSC)Mg[11] and (DMSC)-$TiCl_2$[12] (Scheme 2). Compound **4** is quite soluble in aromatic and ethereal solvents but is only modestly soluble in aliphatic hydrocarbons. Both solution ^{1}H and ^{13}C NMR data are consistent with the existence of the DMSC ligand of **4** in 1,2-alternate conformation.[13] In the ^{1}H NMR spectrum of **4**, four Bu^t resonances of equal intensity, eight doublets of equal intensity (for calix[4]arene methylene protons), eight aromatic resonances of equal intensity, and two resonances (corresponding to *exo*- and *endo*-SiMe groups)[13] are observed (see Experimental Section). Each DMSC unit is therefore absent of any local symmetry, but the molecule possesses a C_2 axis which renders the two DMSC units equivalent. Thus, the geometry about titanium is pseudotetrahedral, with the two DMSC units oriented perpendicular to one another.

Reactions between (DMSC)Ti($OCAr_2CAr_2O$) (2, Ar = Ph, and 3, Ar = *p*-MeC_6H_4) Complexes and Terminal Alkynes. Reactions of terminal alkynes with titanapinacolates **2** and **3** proceed in a rather unusual manner, wherein alkynes displace one of the Ar_2CO units of the titanapinacolate (2,5-dioxatitanacyclopentane) complex to form 3,5-disubstituted 2-oxatitanacyclopent-4-enes[14] (**5**−**7**, Scheme 3). The reactions are quite slow at room temperature but proceed to completion in under

(10) Whether **4** was formed via comproportionation reaction of **3** was of interest to us. Thus, a toluene-d_8 solution of **3** was heated at 95 °C in a screw-capped NMR tube and monitored periodically by ^{1}H NMR. After ∼16 h, ^{1}H NMR revealed a complete disappearance of **3** and formation of several DMSC-containing products: **4** was the major DMSC-containing product (>50%). Importantly, only two singlets were observed in the *p*-tolyl region of the spectrum at δ 2.06 ppm (*p*-*Me*$C_6H_4)_2CO$ and 1.94 ppm in ∼2:3 ratio. We tentatively assign the latter singlet to the *p*-tolyl methyl groups of the presumed comproportionation coproduct Ti{OC(*p*-$MeC_6H_4)_2$C(*p*-$MeC_6H_4)_2O\}_2$. Consistent with this proposal, GC-MS analysis of the reaction mixture (after hydrolysis and filtration through a plug of silica) revealed (*p*-$MeC_6H_4)_2$C=C(*p*-$MeC_6H_4)_2$, (*p*-$MeC_6H_4)_2CO$, and HOC(*p*-$MeC_6H_4)_2$-C(*p*-$MeC_6H_4)_2$COH in ∼1:3:10 ratio as the only *p*-tolyl-containing organic products.

(11) Mg can be generated in solution, but it tends to precipitate out of solution after a short period of time. We have not been able to redissolve this precipitate.

(12) Ozerov, O. V.; Ladipo, F. T.; Patrick, B. O. *J. Am. Chem. Soc.* **1999**, *121*, 7941.

(13) That the DMSC ligand exists in 1,2-alternate conformation is apparent from the NMR resonances of the *endo*- and *exo*-methyls of the bridging $SiMe_2$ unit. Invariably, ^{1}H and ^{13}C NMR resonances for the *endo*-SiMe group (located inside of the calix[4]arene cavity) are strongly shielded compared to corresponding signals for the *exo*-SiMe group (located outside of the calix[4]arene cavity), due most probably to ring current effect. For a discussion of ring current effect, see: Gunther, H. *NMR Spectroscopy: An Introduction*; Wiley: New York, 1980; pp 77−86.

(14) Previous work in our group has demonstrated that DMSC ligation favors introduction of substituents at the 3- (*endo*-*β*) and 5- (*exo*-α) positions of disubstituted five-membered titanacycles. Such location of one substituent outside (*exo*) of the calixarene cavity and the other substituent at the *endo*-*β* (inside the cavity) position apparently reduces unfavorable steric interactions.[9]

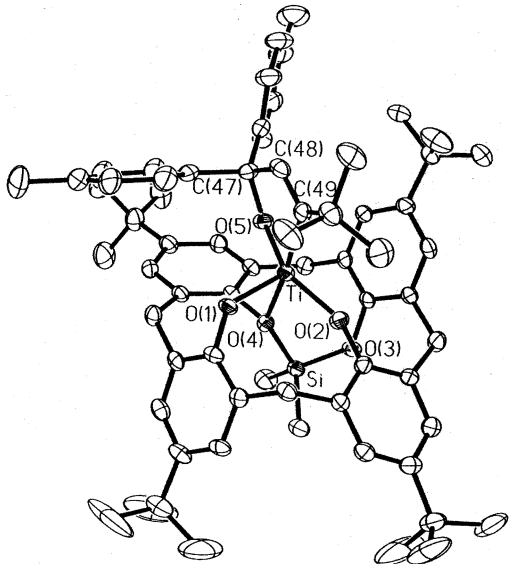


Figure 1. Molecular structure of (DMSC)Ti{OC(*p*-MeC_6H_4)$_2$$C_2$Bu^{t}H} (**5**) (50% probability ellipsoids).

Table 2. Selected Bond Distances (Å) and Angles (deg) for **5** and **9**

5		**9**	
Ti−O(1)	1.801(3)	Ti−O(1)	1.785(5)
Ti−O(2)	1.815(3)	Ti−O(2)	1.808(5)
Ti−O(4)	2.497(3)	Ti−O(5)	1.834(5)
Ti−O(5)	1.835(3)	Ti−C(51)	2.077(8)
Ti−C(49)	2.122(4)	C(47)−C(48)	1.536(11)
C(48)−C(49)	1.328(6),	C(48)−C(49)	1.314(11)
O(1)−Ti−O(2)	105.43(13)	C(49)−C(50)	1.496(11)
O(1)−Ti−O(4)	85.09(11)	C(50)−C(51)	1.341(11)
O(1)−Ti−O(5)	108.43(14)	O(1)−Ti−O(2)	105.6(2)
O(2)−Ti−O(4)	84.57(12)	O(1)−Ti−O(5)	115.2(2)
O(2)−Ti−O(5)	142.94(13)	O(2)−Ti−O(5)	118.6(2)
O(4)−Ti−O(5)	83.75(11)	O(1)−Ti−C(51)	102.3(3)
O(1)−Ti−C(49)	103.19(15)	O(2)−Ti−C(51)	114.9(3)
O(2)−Ti−C(49)	104.39(16)	O(5)−Ti−C(51)	99.4(3)
O(4)−Ti−C(49)	165.38(14)		
O(5)−Ti−C(49)	82.20(16)		

3 h at 80 °C. Although the very high solubility of **5** in hydrocarbon solvents hampered its isolation in high yield, it was obtained as yellow crystals and fully characterized. Both microanalysis and solution NMR (^{1}H and ^{13}C) data for **5** are consistent with the proposed formulation. In the ^{13}C NMR spectrum, the α-carbon of **5** and the Ar_2C carbon (Ar = *p*-MeC_6H_4) resonate at δ 221.1 and 85.9 ppm, respectively. Analogous data (δ 219.7 ppm for C_α and δ 95.8 ppm for Ph_2C) were reported for the related 2-oxatitanacyclopentene $(ArO)_2$Ti(CEtCEtCPh_2O) (Ar = 2,6-$Ph_2C_6H_3$).[15]

The molecular structure of **5** was determined by single-crystal X-ray diffraction analysis (Figure 1), and selected metrical parameters are listed in Table 2. The geometry about Ti is best described as distorted trigonal bipyramidal with the α-carbon of the 2-oxatitanacyclopent-4-ene ring [C(49)] occupying one of the axial positions and one of the silicon-bridged oxygen atoms [O(4)] occupying the other [O(4)−Ti−C(49) angle = 165.38(14)°]. The Ti−O(4) bond is long at 2.497(3) Å and indicative of a weak interaction. The Ti center of **5** is not very electrophilic hence coordination of O(4) to Ti is an unexpected peculiarity of the structure. It is most likely due to distortion of the DMSC ligand by unfavorable steric interaction between the Bu^t group of one of the *p-tert*-butylcalix[4]arene phenol units and tolyl substituents of the 2-oxatitanacyclopent-4-ene ring. This evidently causes the phenol unit to bend away and bring the oxygen close to titanium (Figure 1). The bond lengths within the five-membered titanacycle are within the expected ranges;[15,16] the C(48)−C(49) bond distance of 1.328(6) Å is comparable to that reported [1.332(6) Å] for the doubly bonded carbons in the related 2-oxatitanacyclopentene Cp_2Ti(CPhCPhCMe_2O).[16] The distortion of the DMSC ligand of **5**, observed in the solid-state structure, is also manifested in solution. In C_6D_6, the ^{1}H NMR chemical shifts of both the *exo*- and *endo*-SiMe groups are unusually upfield at δ −0.21 and −1.57 ppm, respectively.[17] The Ti−O(4) interaction apparently draws the *endo*-SiMe group deeper inside the calix[4]arene cavity, increasing the ring current effect, due to the two proximal aromatic rings, that it experiences. On the other hand, the aromatic ring of the phenol unit that is bent away by unfavorable steric interaction with the Ar_2C unit exerts a certain ring current effect on the *exo*-SiMe group.

In contrast to **5**, exclusive formation of 2-oxatitanacyclopent-4-enes **6** and **7** did not occur. Instead, **6** and **7** undergo further reaction with alkyne to yield oxatitanacycloheptadienes **9** and **10**, respectively (Scheme 3). Consequently, **2** (**3**), **6** (**7**), and **9** (**10**) are all present in solution for some time. Our attempts to favor predominant formation of **6** (**7**) by varying the reaction conditions have so far met with limited success. Consequently, a completely unobstructed ^{1}H NMR spectrum could not be observed for **6** or **7**. However, only one Me_3Si group belonging to **6** (**7**) could be observed by ^{1}H NMR and the chemical shifts of the *endo*- and *exo*-SiMe groups and the Bu^t groups of the DMSC ligand of **6** (**7**) are very close to those observed for **5**, supporting their structural similarity. Reaction of 2-oxatitanacyclopent-4-enes **5**−**7** with Me_3SiC≡CH proceeds via formal insertion into the Ti−C bond to yield the corresponding 2-oxatitanacycloheptadienes **8**−**10** (Scheme 3). In contrast, **5**−**7** did not react with Bu^{t}C≡CH under identical conditions. The latter result probably reflects steric effect of the 2-oxatitanacyclopentene α-carbon substituent as well as differences in steric and electronic properties between the two alkynes.[18] While the conversion of **5** to **8** is quantitative (by ^{1}H NMR), a minor side product is formed together with **9** and **10** (in <5% and ∼15% yield, respectively). On the basis of the ^{1}H NMR data, we assume that the side product is an isomeric species, possessing a different disposition of the Me_3Si groups on the metallacycle. The amount of side product formed in each case does not increase with reaction temperature between 20 and 80 °C. When an alkyne such as HC≡CCH_2OSiMe_3, with a less bulky substituent, is allowed to react with **2**, a mixture of three (DMSC)Ti-based compounds is produced along with 1 equiv of Ph_2CO. Analysis of the ^{1}H NMR data revealed that each of the products possessed two Me_3Si groups (from the correlation of the intensities of the *endo*-SiMe and the SiMe_3 resonances).

(15) Hill, J. E.; Balaich, G. J.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2911.

(16) Shur, V. B.; Burlakov, V. V.; Yanovsky, A. I.; Petrovsky, P. V.; Struchkov, Yu. T.; Vol'pin, M. E. *J. Organomet. Chem.* **1985**, *297*, 51.

(17) For typical *exo*- and *endo*-SiMe group chemical shifts, see for example: Ozerov, O. V.; Ladipo, F. T.: Rath, N. P. *J. Organomet. Chem.* **1999**, *586*, 223.

(18) The polarization in the π^* orbital of alkyl- and silylacetylenes has been calculated (see: Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952). The π^* orbital of terminal alkylacetylene has its largest lobe on the substituted carbon while the π^* orbital of terminal silylacetylene has its largest lobe on the unsubstituted carbon.

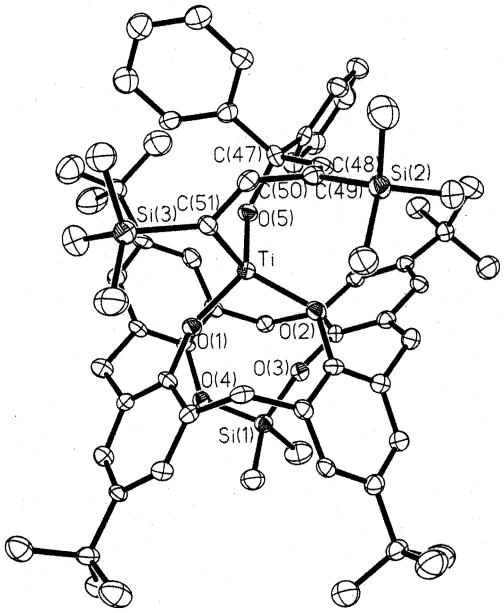
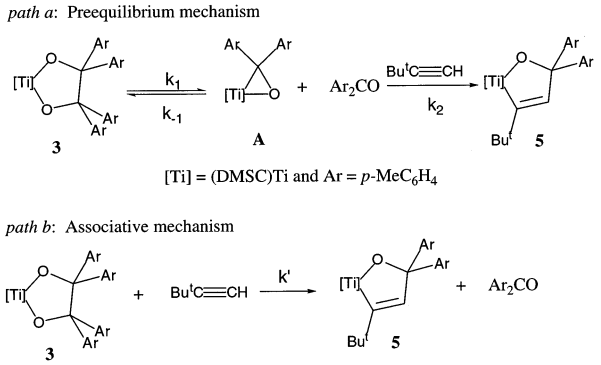


Figure 2. Molecular structure of (DMSC)Ti{$OCPh_2C_4(SiMe_3)_2H_2$} (**9**) (50% probability ellipsoids).

It is reasonable to assume that the mixture consists of isomeric products resulting from different alkyne insertion regiochemistry. This result suggests that steric interaction between alkyne substituents, as well as with the Ar_2C moiety, influences the regiochemistry of **5**−**10**. It is worth pointing out that no reaction occurs between **5**−**7** and Ar_2CO. The Ar_2CO moiety that is part of the metallacycle is apparently not exchangeable. Consequently, **6** does not react with Ph_2CO. In addition, Ph_2CO is not incorporated in the products when the transformation of **6** into **9** is carried out in the presence of Ph_2CO.

2-Oxatitanacycloheptadienes **8** and **9** were isolated as yellow solids in high yield, while **10** was studied in situ. The solution NMR data for **9** are consistent with the existence of the DMSC ligand in 1,2-alternate conformation. The C_1 symmetry of **9** is maintained in C_6D_6 solution over the 22−80 °C temperature range. The ^{13}C NMR resonances of the TiC_α carbons of **8** and **9** are observed at δ 214.3 and 212.5 ppm, respectively, and compare well to the 210.8−215.8 ppm range reported for related oxatitanacycloheptadienes by Rothwell.[15] Only one of the metallacyclic CH hydrogen signals can be identified by ^1H NMR for **9** and **10** at δ 6.59 ppm (singlet); the other signal is obscured by the aromatic resonances. Both of these signals could be identified for **8** at δ 7.04 and 6.21 ppm; their near-zero coupling constant suggests head-to-tail incorporation of the $Me_3SiC{\equiv}CH$ units into the metalacycle. Compound **9** is extremely soluble in hydrocarbon solvents, and it proved impossible to induce its precipitation from pentane solution even after extended periods at −78 °C. Remarkably, the incorporation of a six-membered aromatic ring into the crystal lattice promotes the crystallization of **9**. Thus, addition of small amounts of benzene or pyridine to pentane solutions of **9** causes (within minutes) precipitation of crystalline solid. ^1H NMR data revealed that pyridine is not coordinated to **9** in solution. Neither 1,4-dioxane or toluene has the same effect on the crystallization of **9**. The molecular structure of **9** was determined by X-ray crystallography (Figure 2), and selected metrical parameters are listed in Table 2. The bond lengths within the titanacycle are within the expected ranges.[15] The asymmetric unit contained one molecule of **9** and two molecules of benzene. The geometry about Ti is best described as pseudotetrahedral, and the oxatitanacycloheptadiene ring is decidedly nonplanar. The solid-state structure confirmed the head-to-tail regiochemistry of the Me_3Si substituents of the metallacycle, as was deduced from solution NMR data.

Scheme 4



Mechanistic Considerations. The precise mechanism of the metallacyclic C−C bond rupture reported for titanapinacolates **2** and **3** in this study was of interest to us. The relative ease of fragmentation reactions of **2** and **3** is probably due to the long metallacyclic C−C bond. In fact, benzopinacol ($HOCPh_2CPh_2OH$) and its derivatives have been shown to be amenable to photolytic and thermolytic fragmentation, as well as oxidation to benzophenone.[19] However, $L_2Ti(OCPh_2CMe_2O)$ (L = *N*,*N*'-dimethylaminotroponiminate) possesses a metallacyclic C−C bond distance [1.610(2) Å] similar to that for **2**, and reactivity analogous to that observed for **2** and **3** was not reported.[20] The two most probable mechanisms that can be envisioned for fragmentation reactions of titanapinacolates **2** and **3** with terminal alkynes are (i) an associative mechanism, involving coordination of the alkyne to titanium prior to rate-limiting rupture of the titanacyclic C−C bond, and (ii) a preequilibrium mechanism, involving reversible formation of a (DMSC)Ti(η^2-$OCAr_2$) intermediate prior to rate-limiting reaction with alkyne (Scheme 4). In an attempt to differentiate between the two mechanistic possibilities, we monitored reactions of (DMSC)-$Ti(OCAr_2CAr_2O)$ (**2**, Ar = Ph, and **3**, Ar = *p*-MeC_6H_4) with $Ph_2{}^{13}CO$ (1.1 equiv) at room temperature by ^{13}C NMR spectroscopy.[21] Essentially, statistical scrambling of $Ph_2{}^{13}CO$ into both *endo*- and *exo*-positions of the titanapinacolate rings occurred within 30 min (eq 2). While this result did not allow the two mechanistic possibilities to be unambiguously differentiated,[22] it does demonstrate facile reversible fragmentation of well-characterized titanapinacolate complexes by benzophenone.

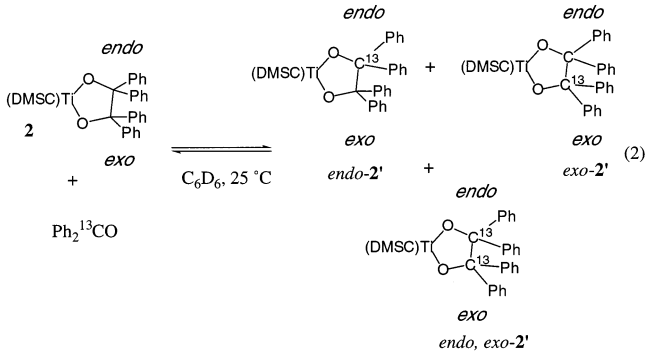
To elucidate the mechanism of these fragmentation reactions, we conducted a kinetic analysis of the reaction of **3** with $Bu^tC{\equiv}$

(19) Hillgartner, H.; Schroeder, B.; Neumann, W. P. *J. Organomet. Chem.* **1972**, *42*, C83. (b) Weiner, S. A. *J. Am. Chem. Soc.* **1971**, *93*, 6978. (c) Michielli, R.; Elving, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 6864.

(20) Steinhuebel, D. P.; Lippard, S. J. *J. Am. Chem. Soc.* **1999**, *121*, 11762.

(21) In a typical experiment, 15 mg (0.0134 mmol) of (DMSC)Ti($OCPh_2CPh_2O$) (**2**) and 3.00 mg (1.1 equiv) of $Ph_2{}^{13}CO$ were dissolved in 0.7 mL of C_6D_6 in a screw-capped NMR tube under N_2 atmosphere. The tube was vigorously shaken, and the reaction was monitored by ^{13}C NMR spectroscopy (1024 scans were recorded). Two singlet resonances at δ 110.1 and 111.1 ppm (for *endo*-C_β and *exo*-C_β metallacyclic carbons, respectively) and two doublet resonances centered at 110.1 and 111.1 ppm ($^2J_{C-C}$ = 36.6 Hz) were observed in approximately 2: 2: 1 ratio. Similar results were obtained when **3** was utilized.

(22) Had no incorporation of $Ph_2{}^{13}CO$ into the titanapinacolate ring been observed, a mechanism involving reversible formation of a (DMSC)Ti(η^2-$OCAr_2$) intermediate prior to the rate-limiting reaction with an alkyne or ketone molecule would have been ruled out.



endo-**2'**: *exo*-**2'**: *endo, exo*-**2'** = 2 : 2 : 1

CH. This reaction was chosen for study because **5** is the exclusive product (vide supra) and the reaction proceeds at a convenient rate over a broad temperature range. In addition, **3** affords two sets of signals through which the reaction could be easily monitored: *p*-tolyl methyl resonances, as well as *endo*- and *exo*-SiMe resonances. The kinetic studies were conducted at 50 °C, under pseudo-first-order conditions, by adding ∼20 equiv of Bu^{t}C≡CH to a benzene-d_6 solution of **3** and monitoring the reactions at various time intervals by ^{1}H NMR spectroscopy. The concentration of Bu^{t}C≡CH was then varied in a second set of experiments. Plots of the disappearance of **3** with time and of the observed rate constants (k_{obs}) versus [Bu^{t}C≡CH] are depicted in Figures 3 and 4, respectively. The reactions showed first-order dependence on both [**3**] and [Bu^{t}C≡CH], confirming that the rate-limiting step in the reaction involves both Bu^{t}C≡CH and a titanium species.

Clearly, if fragmentation reactions described in this study proceed via a preequilibrium pathway, the presumed (DMSC)Ti(η^2-OCAr$_2$) intermediate (**A**) is so reactive that it does not accumulate to an appreciable level. Indeed, (DMSC)Ti(η^2-OCAr$_2$) species will most likely be unstable and can be expected to react rapidly with the released Ar$_2$CO molecule to regenerate the titanapinacolate complex. Consistent with this suggestion, no ligand-free (RO)$_2$Ti(η^2-ketone) (R = alkyl or aryl) complexes are known and very few well-characterized mononuclear group 4 metal−ketone complexes bearing alkyl or aryl substituents have been reported, including (TC-3,5)Hf(η^2-OC(CH$_2$Ph)$_2$) (where TC-3,5 = tropocorand ligand)[23] and (OC$_6$H$_3$Ph$_2$-2,6)$_2$-Ti (η^2-Ph$_2$CO)(PMe$_3$).[24] Since [Bu^{t}C≡CH] ≫ [**3**] and [**A**] ≪ [**3**] under the conditions of our kinetic studies, the *steady-state* approximation[25] can be applied to the concentration of the (DMSC)Ti{η^2-OC(*p* MeC$_6$H$_4$)$_2$} intermediate (**A**) as follows:

$$\frac{d[\mathbf{A}]}{dt} = k_1[\mathbf{3}] - k_{-1}[Ar_2CO][\mathbf{A}] - k_2[\mathbf{A}][Bu^tC{\equiv}CH] = 0$$

$$[\mathbf{A}]_{ss} = \frac{k_1[\mathbf{3}]}{k_{-1}[Ar_2CO] + k_2[Bu^tC{\equiv}CH]} \qquad (3)$$

Thus,

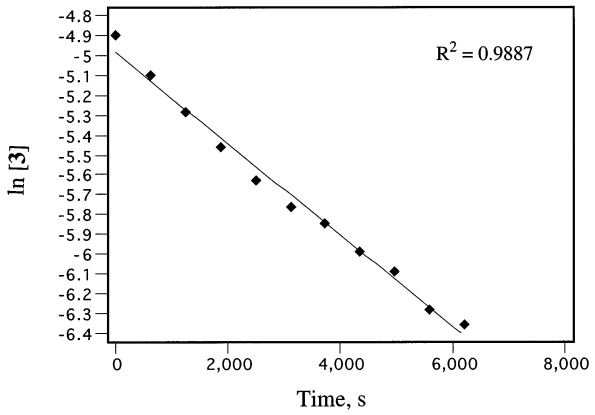


Figure 3. Plot showing the disappearance of (DMSC)Ti{OC(*p*-MeC$_6$H$_4$)$_2$-C(*p*-MeC$_6$H$_4$)$_2$O} (**3**) with time ([Bu^{t}C≡CH] = 20 equiv).

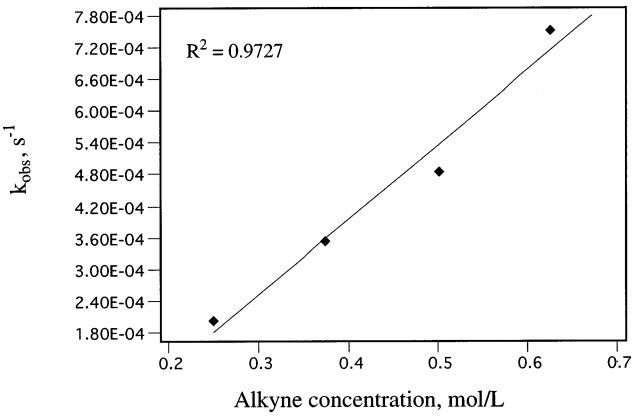


Figure 4. Plot of the observed rate constants (k_{obs}) versus [Bu^{t}C≡CH].

$$\frac{d[\mathbf{5}]}{dt} = k_2[\mathbf{A}]_{ss}[Bu^tC{\equiv}CH]$$

$$= \frac{k_2k_1[\mathbf{3}][Bu^tC{\equiv}CH]}{k_{-1}[Ar_2CO] + k_2[Bu^tC{\equiv}CH]}$$

When k_2[Bu^{t}C≡CH] ≫ k_{-1}[Ar$_2$CO],

$$\frac{d[\mathbf{5}]}{dt} = k_1[\mathbf{3}]$$

Ar = *p*-MeC$_6$H$_4$

It then follows that if the reaction proceeds via a preequilibrium pathway, the observed rate constant (k_{obs}) will equal k_1 (eq 3) and the reaction rate will be retarded by added ketone (path a, Scheme 4). On the other hand, the reaction rate will be independent of added ketone if the fragmentation reactions occur via an associative mechanism (path b, Scheme 4). When the reaction of **3** with Bu^{t}C≡CH (∼50 equiv) was monitored in the presence of 1 and 3 equiv of (*p*-MeC$_6$H$_4$)$_2$CO, we observed retardation of the reaction rate. Thus, $k_{obs} = 7.50 \times 10^{-4} \pm 4.84 \times 10^{-5}$ s^{-1} in the absence of added ketone while $k_{obs} = 2.34 \times 10^{-4} \pm 8.31 \times 10^{-6}$ s^{-1} and $9.95 \times 10^{-5} \pm 1.08 \times 10^{-6}$ s^{-1} in the presence of one and three equivalents of added ketone, respectively. This result, together with facile reversible exchange of Ph$_2{}^{13}$CO into *endo*- and *exo*-positions of titanapinacolates **2** and **3** (vide supra), strongly supports a mechanism

(23) Scott, M. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 3411.
(24) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1992**, *11*, 1771. (b) Thorn, M. G.; Hill, J. E.; Warantuke, S. A.; Johnson, E. S.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 8630.
(25) See for example: Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981.

involving reversible formation of a (DMSC)Ti(η^2-$OCAr_2$) species prior to rate-limiting reaction with an alkyne or ketone molecule.[26]

Conclusions

While fragmentation of metallapinacolate intermediates has previously been invoked to explain reactivity patterns in pinacol and McMurry reactions, the present studies demonstrate unambiguously the fragmentation of well-characterized titanapinacolate complexes by terminal alkynes and aromatic ketones. More importantly, both structural parameters of the titanapinacolate complexes and kinetic investigations of the reaction of (DMSC)Ti{OC(*p*-$MeC_6H_4)_2$C(*p*-$MeC_6H_4)_2$O} (**3**) with $Bu^tC{\equiv}$CH are consistent with a mechanism that involves reversible dissociation of the titanapinacolate complexes into (DMSC)-Ti(η^2-$OCAr_2$) species with release of a ketone molecule, followed by rate-limiting reaction of the (DMSC)Ti(η^2-$OCAr_2$) species with an alkyne or ketone molecule (i.e. a preequilibrium mechanism). Further studies of the reaction chemistry of these and related compounds with various unsaturated organic substrates are underway in our laboratory.

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Supporting Information Available: A summary of crystallographic parameters, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **5** and **9** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Since the reaction between **3** and (p-$MeC_6H_4)_2$CO is reversible, this result also rules out the two alternate mechanisms depicted below: (i) a mechanism in which reversible fragmentation of **3** to form the (DMSC)-Ti{η^2-OC(p-$MeC_6H_4)_2$} species (**A**) occurs but **A** is not an intermediate in the reaction between **3** and $Bu^tC{\equiv}$CH; (ii) a mechanism in which the reversible fragmentation of **3**, through a transition state species of increased coordination number, competes with the direct reaction of **3** with $Bu^tC{\equiv}$CH. In either case, the rate of formation of **5** will not be retarded by added ketone.

(i)

$$\mathbf{3} \rightleftharpoons \mathbf{A} + Ar_2CO$$

$$\mathbf{3} + [Bu^tC{\equiv}CH] \rightarrow \mathbf{5} + Ar_2CO$$

(ii)

$$\mathbf{3} + Ar_2CO \rightleftharpoons [(DMSC)Ti(OCAr_2CAr_2O)(OCAr_2)]^{\ddagger} \rightleftharpoons \mathbf{3} + Ar_2CO$$

$$\mathbf{3} + [Bu^tC{\equiv}CH] \rightarrow \mathbf{5} + Ar_2CO$$

$$Ar = p\text{-}MeC_6H_4$$