Mechanistic Insight into Fragmentation Reactions of Titanapinacolate Complexes

Jesudoss V. Kingston, Oleg V. Ozerov,† Sean Parkin, Carolyn P. Brock, and Folami T. Ladipo*

Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055

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Abstract: Reactions between terminal alkynes or aromatic ketones and titanapinacolate complexes (DMSC)-Ti(OCAr2CAr2O) (2, Ar = Ph, and 3, Ar = p-MeC6H4; DMSC = 1,2-alternate dimethylsilyl-bridged p-tert-butylicalix[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-oxatitanacyclopentadiene complexes along with free Ar2CO. 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(O(p-MeC6H4)2C(p-MeC6H4)2O) (3) with BuC==CH revealed that the fragmentation reactions occur via a pre-equilibrium mechanism, involving reversible dissociation of titanapinacolate complexes into (DMSC)Ti(p2-OCAr2) species with release of a ketone molecule, followed by rate-limiting reaction of (DMSC)Ti(p2-OCAr2) species with an alkyn 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 Ephritikhine4c have isolated and characterized a pinacolate intermediate with terminal alkynes produce 2-oxatitanacyclopent-4-ene or 2-oxatitanacyclopentadiene complexes along with free Ar2CO. 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(OAr2CAr2O) (3) with BuC==CH revealed that the fragmentation reactions occur via a pre-equilibrium mechanism, involving reversible dissociation of titanapinacolate complexes into (DMSC)Ti(p2-OCAr2) species with release of a ketone molecule, followed by rate-limiting reaction of (DMSC)Ti(p2-OCAr2) species with an alkyn or ketone molecule.

* To whom correspondence should be addressed. E-mail: fladipo@uky.edu.

† Current address: Department of Chemistry, Brandeis University, MS#015, 415 South Street, Box 9110, Waltham, MA 02253-7228.


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 DS-MSC-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—compounds which have been invoked to explain their behavior in McMurry reactions,—has 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 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

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 purified by distillation from sodium benzophenone ketyl. Pentane was distilled from sodium benzophenone ketyl. All solvents were stored in a vacuum glovebox. Atmospheric air was excluded by pumping with a vacuum pump and flushing with nitrogen gas. All solvents were stored in a glovebox freezer at −15 °C. Elemental analyses were performed by Complete Analysis Center. 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)2Ti(OC(p-MeC6H4)2C6BBrH) (5). (DMSc)2Ti(OC(p-MeC6H4)2C6BBrH) was generated in situ from 0.020 mmol (20.9 mg) of (DMSc)2Ti(OCPh2CPh2O) (5). 1H NMR (CDCl3) δ 7.68 (s, 1H, C-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-C3H3), 4.27 (d, 1H, J = 16 Hz, calix-C3H3), 4.09 (d, 2H, J = 17 Hz, calix-C3H3), 3.90 (d, 2H, J = 17 Hz, calix-C3H3), 3.83 (d, 1H, J = 16 Hz, calix-C3H3), 3.52 (d, 1H, J = 13 Hz, calix-C3H3), 2.22 (s, 6H, MeC6H4), 1.27 (s, 18H, t-Bu), 1.19 (s, 18H, t-Bu), −0.21 (s, 3H, exo-SiMe3), −1.57 (s, 3H, endo-SiMe3). 13C NMR (CDCl3) δ 221.1 (TiC=O), 161.0 (TiC=O), 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, 85.9 (MeC6H4), 39.9 (calix-C3H3), 38.4 (calix-C3H3), 37.8 (calix-C3H3), 34.1 (C(CH3)3), 33.9 (C(CH3)3), 31.54 (C(CH3)3), 31.46 (C(CH3)3), 21.0 (MeC6H4), 1.4 (exo-SiMe3), −3.6 (endo-SiMe3). Anal. Calcd for C48H32O3SiTi: 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)2Ti[(OCPh2C6BBrH)2] (6). (DMSc)2Ti[(OCPh2C6BBrH)2] was generated in situ from 0.020 mmol (20.9 mg) of (DMSc)2Ti[(p-(Me3Si)C6H3)2] (1) and 0.040 mmol (7.28 mg) of PbCl2(C6D6) solution. To this solution 0.100 mmol (14.1 μL) of Me3SiCl 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

2 h, the conversion of 6 into 9 was >95% complete. The resonances due to 6 were mostly obscured by those of 9 although certain peaks could be identified. 1H NMR (unobstructed resonances) (C6D6): δ 8.25 (s, 1H, C6-H), 1.29 (s, 18H, t-Bu), 1.17 (s, 18H, r-Bu), 0.18 (s, 18H, SiMe3), −0.23 (s, 3H, exo-SiMe3), −1.60 (s, 3H, endo-SiMe3).

In a similar reaction, the sample was hydrolyzed while some of 6 was still present in solution. The hydrolysis product Ph2C(OH)CH=CHSiMe2 was identified by GC-MS. El-GC-MS (m/z): 282 (10, M+), 267 (4, M+ − CH3), 209 (10, M+ − SiMe3), 192 (100, M+ − HO3SiMe3), 182 (40, M− − HCH=CHSiMe3), 105 (75, PhC(OH)+), 73 (60, Me3Si). 1H NMR (C6D6): δ 7.62 (d, 1H, J = 2 Hz, calix arorn), 7.56 (pseudo d, 2H, J = 7 Hz, Ph), 7.42 (d, 1H, J = 2 Hz, calix arorn), 7.33 (2 AB doublets, 2H, calix arorn), 7.24 (d, 1H, J = 2 Hz, calix arorn), 7.0−7.2 (m, 12H), 6.85−6.92 (m, 2H), 6.59 (s, 1H), 4.69 (d, 1H, J = 14 Hz, calix arorn), 4.54 (d, 1H, J = 17 Hz, calix arorn), 4.50 (d, 2H, J = 15 Hz, calix arorn), 4.44 (d, 1H, J = 17 Hz, calix arorn), 4.35 (d, 1H, J = 14 Hz, calix arorn), 3.87 (d, 1H, J = 17 Hz, calix arorn), 3.70 (d, 1H, J = 14 Hz, calix arorn), 3.62 (d, 1H, J = 15 Hz, calix arorn), 3.68 (d, 1H, J = 14 Hz, calix arorn), 1.32 (s, 9H, t-Bu), 1.30 (s, 9H, r-Bu), 1.252 (s, 9H, r-Bu), 1.249 (s, 9H, r-Bu), 0.14 (s, 3H, exo-SiMe3), 0.07 (s, 9H, SiMe3), −0.02 (s, 9H, SiMe3), −1.40 (s, 3H, endo-SiMe3). 13C NMR (C6D6): δ 212.5 (TCS), 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, 127.3, 127.9, 127.8, 127.7, 127.4, 127.1, 126.1, 126.2, 126.0, 125.6, 125.1, 86.5 (CPh3), 41.2 (calix arorn), 38.4 (calix arorn), 37.7 (calix arorn), 34.23 (C(CH3)3), 34.18 (C(CH3)3), 34.12 (C(CH3)3), 33.94 (C(CH3)3), 31.82 (C(CH3)3), 31.78 (C(CH3)3), 31.61 (C(CH3)3), 31.55 (C(CH3)3), 2.3 (exo-SiMe3), −0.3 (SiMe3), −2.0 (SiMe3), −2.6 (endo-SiMe3). Anal. Calcd for (DMSC)Ti(OCp(CpMe2)CH2C2Bu(H)C(H2)3): 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 H2O 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. Ph2C(OH)CH=CHSiMe2 was the only species observed. El-GC-MS (m/z): 380 (1, M+), 362 (1, M+ − H2O), 307 (12, M+ − SiMe3), 281 (5, M+ − HCH=CHSiMe3), 259 (M+ − 121), 217 (M+ − OH, −2SiMe3), 187 (9, M+ − 193), 147 (8, M+ − 233), 105 (18, PhCO+), 73 (100, Me3Si).

**Typical Procedure for Kinetic Study of the Reaction between (DMSC)Ti(OCp(Cp-Me2)CH2Cp-Me2)O (3) and Bu=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(OCp(Cp-Me2)CH2Cp-Me2)O (3) in C6D6 was added into a J. Young NMR tube, followed by 0.200 mL of a 2.000 M stock solution of Bu=C=CH (0.401 mmol, 19.3 equiv) and 0.300 mL of C6D6. This resulted in 0.900 mL of a 0.0232 M solution of 3 and a 0.445 M solution of Bu=C=CH. The tube was vigorously shaken and placed into the spectrometer at a temperature of 50 °C. The 1H 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 C6D6 at 50 °C, using an identical amount of Bu=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=C=CH.** A 0.200 mL volume of a 0.0508 M stock solution of (DMSC)Ti(OCp(Cp-Me2)CH2Cp-Me2)O (3) in C6D6 (0.0102 mmol) was added into a J. Young NMR tube, followed by 0.500 mL (0.500 mmol, 49.2 equiv) of a 1.000 M stock solution of Bu=C=CH and then 0.100 mL of C6D6. This resulted in 0.800 mL of a 0.0127 M solution of 3 and a 0.626 M solution of Bu=C=CH. The tube was vigorously shaken and placed into the spectrometer at 50 °C. The first 1H 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=C=CH] was obtained by varying the concentration of Bu=C=CH while conducting each experiment in C6D6 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-Me6C6H4)2CO on the Reaction between (DMSC)Ti(OCp(p-Me6C6H4)CH2Cp-Me2)O (3) and Bu=C=CH**...
Table 1. Crystallographic Data for 5-C6H12 and 9-2C6H6

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**Scheme 2**

CH. A 0.200 mL (0.0101 mmol) volume of a 0.0507 M stock solution of (DMSC)Ti[(OC(p-MeC6H4)2)C(p-MeC6H4-OC)] (3) in C6D6 was added into a J. Young NMR tube, followed by 0.250 mL of a 2.00 M stock solution of BuC=CH2 in C6D6. This resulted in a 0.800 mL of a 0.0127 M solution of 3, a 0.626 M solution of BuC=CH2, and a 0.0127 M solution of (p-MeC6H4)2CO. The tube was vigorously shaken and placed into the spectrometer at 50 °C. The first 1H 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 C6D6, and at 50 °C, using identical amounts of 3 and BuC=CH2 as above, 0.0303 mmol (3 equiv) of (p-MeC6H4)2CO, and the same total volume (0.800 mL).

**Crystallographic Studies**

The crystal data for 5-C6H12 and 9-2C6H6 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-(Me3Si)3C6H3) (1) with (p-MeC6H4)2CO.** We previously reported that reaction of (DMSC)Ti(1,2,4-(Me3Si)3C6H3) (1) with Ph2CO or (p-MeC6H4)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-MeC6H4)2CO (2 equiv) at 80 °C is (DMSC)2Ti (4),10 which can be obtained in a more direct fashion by reaction between (DMSC)Mg11 and (DMSC)-TiCl.12 (Scheme 2). Compound 4 is quite soluble in aromatic and ethereal solvents but is only modestly soluble in aliphatic hydrocarbons. Both solution 1H and 13C NMR data are consistent with the existence of the DMSC ligand of 4 in 1,2-alternate conformation.13 In the 1H NMR spectrum of 4, four Bu' resonances of equal intensity, eight doublets 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 C3 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.

**Scheme 3**

Reactions between (DMSC)Ti(OCAr2C2O) (2, Ar = Ph, and 3, Ar = p-MeC6H4) 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 Ar2CO units of the titanapinacolate (2,5-dioxatitana-cyclopentane) complex to form 3,5-disubstituted 2-oxatitana-cyclopent-4-enes14 (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-δ6 solution of 3 was heated at 95 °C in a screw-capped NMR tube and monitored periodically by 1H NMR. After ~16 h, 1H 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-MeC6H4-CHO) 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-MeC6H4)2C(p- MeC6H4-OC)); Consistent with this proposal, OCMAS analysis of the reaction mixture (after hydrolysis and filtration through a plug of silica) revealed (p-MeC6H4)2C=C(p-MeC6H4), (p-MeC6H4)2CO, and HOCl(p-MeC6H4); (p-MeC6H4)2CO 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.


(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 SiMe2 unit. Invariably, 1H and 13C 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.
peculiarity of the structure. It is most likely due to distortion of the DMSC ligand by unfavorable steric interaction between the Bu' 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 range;\textsuperscript{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 C\textsubscript{4}H\textsubscript{2}Ti(CPhCPhCHMe\textsubscript{2})O.\textsuperscript{16} The distortion of the DMSC ligand of 5, observed in the solid-state structure, is also manifested in solution. In C\textsubscript{4}D\textsubscript{8}, the \textsuperscript{1}H NMR chemical shifts of both the exo- and endo-SiMe\textsubscript{2} groups are unusually upfield at δ = −0.21 and −1.57 ppm, respectively.\textsuperscript{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\textsubscript{2}C 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 alkynyl 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 \textsuperscript{1}H NMR spectrum could not be observed for 6 or 7. However, only one Me\textsubscript{3}Si group belonging to 6 (7) could be observed by \textsuperscript{1}H NMR and the chemical shifts of the endo- and exo-SiMe\textsubscript{2} groups and the Bu' 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-ynes 5–7 with Me\textsubscript{3}Si(C\equivC)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'\textsubscript{3}SiCH 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.\textsuperscript{18} While the conversion of 5 to 8 is quantitative (by \textsuperscript{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 \textsuperscript{1}H NMR data, we assume that the side product is an isomeric species, possessing a different disposition of the Me\textsubscript{3}Si groups on the metalacycle. The amount of side product formed in each case does not increase with reaction temperature between 20 and 80 °C. When an alkynyl such as H\textsubscript{2}C\equivCPh or Me\textsubscript{3}SiC\equivCPh 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'\textsubscript{3}SiCH 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.\textsuperscript{18}

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

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<td>103.19(15)</td>
<td>O(2)–O(5) &amp; O(2)–O(5) &amp; O(2)–O(5)</td>
<td>105.6(2)</td>
</tr>
<tr>
<td>C(49)–O(4)</td>
<td>84.57(12)</td>
<td>O(1)–C(51) &amp; O(1)–C(51) &amp; O(1)–C(51)</td>
<td>102.3(3)</td>
</tr>
<tr>
<td>C(49)–O(2)</td>
<td>142.94(13)</td>
<td>O(2)–C(51) &amp; O(2)–C(51) &amp; O(2)–C(51)</td>
<td>114.9(3)</td>
</tr>
<tr>
<td>C(49)–O(5)</td>
<td>82.20(16)</td>
<td>C(49)–O(5) &amp; C(49)–O(5) &amp; C(49)–O(5)</td>
<td>94.3(3)</td>
</tr>
</tbody>
</table>

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 (\textsuperscript{1}H and \textsuperscript{13}C) data for 5 are consistent with the proposed formulation. In the \textsuperscript{13}C NMR spectrum, the α-carbon of 5 and the Ar\textsubscript{2}C carbon (Ar = p-MeC\textsubscript{6}H\textsubscript{4}) resonate at δ 221.7 and 85.9 ppm, respectively. Analogous data (δ 219.7 ppm for C\textsubscript{6}H\textsubscript{5}) were reported for the related 2-oxatitanacyclopentene (Ar\textsubscript{2}C\equivCPh)(C\equivCPhCHMe\textsubscript{2})O.\textsuperscript{16}

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


(17) For typical exo- and endo-SiMe\textsubscript{2} 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\textsuperscript{a} orbital of allyl- and silylacetylenes has been calculated (see: Stocks, A.; Hoffmann, R. J. Am. Chem. Soc. 1980, 102, 2952). The π\textsuperscript{a} orbital of terminal alkylalkylenes has its largest lobe on the substituted carbon while the π\textsuperscript{a} orbital of terminal silylacetylene has its largest lobe on the unsubstituted carbon.
It is reasonable to assume that the mixture consists of isomeric 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 C1 symmetry of 9 is maintained in C6D6 solution over the 22—80 °C temperature range. The 13C NMR resonances of the TiC̊ 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 Me3SiC̊CH 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 Me3Si substituents of the metallacycle, as was deduced from solution NMR data.

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, benzo-pinacol (HOCPh2CPh2-OH) and its derivatives have been shown to be amenable to photolytic and thermolytic fragmentation, as well as oxidation to benzophenone.19 However, L2Ti(OCPH2CMe2O) (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(η2-OCAr2) 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(OCAr2C=O) (2, Ar = Ph, and 3, Ar = p-MeC6H4) with Ph13CO (1.1 equiv) at room temperature by 13C NMR spectroscopy.21 Essentially, statistical scrambling of Ph13CO into both endo- and exo-positions of the titanapinacolates 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 BuC≡

(21) Had no incorporation of Ph13CO into the titanapinacolate ring been observed, a mechanism involving reversible formation of a (DMSC)Ti(η2-OCAr2) intermediate prior to the rate-limiting reaction with an alkyne or ketone molecule would have been ruled out.

Figure 2. Molecular structure of (DMSC)Ti(OCPH2C4(SiMe3)2H2) (9) (50% probability ellipsoids).

Scheme 4

path a: Preequilibrium mechanism

path b: Associative mechanism
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 \( \sim 20 \) equiv of BuC\( \equiv \)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 BuC\( \equiv \)CH was then varied in a second set of experiments. Plots of the disappearance of 3 with time and of the observed rate constants (\( k_\text{obs} \)) versus [BuC\( \equiv \)CH] are depicted in Figures 3 and 4, respectively. The reactions showed first-order dependence on both [Ar\( _2 \)CO] and [BuC\( \equiv \)CH], confirming that the rate-limiting step in the reaction involves both BuC\( \equiv \)CH and a titanium species.

Clearly, if fragmentation reactions described in this study proceed via a preequilibrium pathway, the presumed (DMSC)-Ti(\( \eta^2 \)-OCAr\( _2 \)) intermediate (A) is so reactive that it does not accumulate to an appreciable level. Indeed, (DMSC)Ti(\( \eta^2 \)-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(\( \eta^2 \)-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)H(\( \eta^2 \)-OC(CH\( _3 \)Ph\( _2 \))) (where TC-3.5 = tropocorand ligand)\(^{23} \) and (OC\( _6 \)H\( _3 \)Ph\( _2 \)-2,6)-Ti(\( \eta^2 \)-Ph\( _2 \)CO)(PMe\( _3 \)).\(^{24} \) Since [BuC\( \equiv \)CH] \( \gg \) [3] and [A] \( \ll \) [3] under the conditions of our kinetic studies, the steady-state approximation\(^{25} \) can be applied to the concentration of the (DMSC)Ti(\( \eta^2 \)-OC(p MeC\( _6 \)H\( _4 \))\( _2 \)) intermediate (A) as follows:  

\[
\frac{d[A]}{dt} = k_3 [3] - k_{-1} [Ar_2 CO][A] - k_2 [BuC \equiv CH] = 0 
\]

\[
[A]_{ss} = \frac{k_3 [3]}{k_{-1} [Ar_2 CO] + k_2 [BuC \equiv CH]} 
\]

Thus,

\[
\frac{d[5]}{dt} = k_3 [A]_{ss} [BuC \equiv CH] = \frac{k_{-1} [Ar_2 CO] + k_2 [BuC \equiv CH]}{k_{-1} [Ar_2 CO] + k_2 [BuC \equiv CH]} \]

When \( k_3 [BuC \equiv CH] \gg k_{-1} [Ar_2 CO] \),

\[
\frac{d[5]}{dt} = k_3 [3] 
\]

\( Ar = p\text{-MeC}_6 \text{H}_4 \)

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 BuC\( \equiv \)CH (\( \sim 50 \) 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\( _2 \)C\( \equiv \)CO into endo- and exo-positions of titanapinacolates 2 and 3 (vide supra), strongly supports a mechanism.
involving reversible formation of a \((\text{DMSC})\text{Ti}[^3\text{OCAr}_2]\) 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 \((\text{DMSC})\text{Ti}\{\text{OC}(p\text{-MeC}_6\text{H}_4)_2\text{C}(p\text{-MeC}_6\text{H}_4)_2\text{O}\}\) (3) with BuC\(=\)CH are consistent with a mechanism that involves reversible dissociation of the titanapinacolate complexes into \((\text{DMSC})\text{Ti}[^3\text{OCAr}_2]\) species with release of a ketone molecule, followed by rate-limiting reaction of the \((\text{DMSC})\text{Ti}[^3\text{OCAr}_2]\) 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.

\(^{26}\) Since the reaction between 3 and \((p\text{-MeC}_6\text{H}_4)_2\text{CO}\) 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 \((\text{DMSC})\text{Ti}[^3\text{OC}(p\text{-MeC}_6\text{H}_4)_2]\) species (A) occurs but A is not an intermediate in the reaction between 3 and BuC\(=\)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 BuC\(=\)CH. In either case, the rate of formation of 5 will not be retarded by added ketone.

\[
\begin{align*}
(i) & \\
3 & \rightleftharpoons A + Ar_2CO \\
3 + [\text{BuC}=\text{CH}] & \rightarrow 5 + Ar_2CO
\end{align*}
\]

\[
\begin{align*}
(ii) & \\
3 + Ar_2CO & \rightleftharpoons [\text{(DMSC)}\text{Ti}(\text{OCAr}_2\text{CAr}_2\text{O})(\text{OCAr}_2)]^\uparrow \rightarrow 3 + Ar_2CO \\
3 + [\text{BuC}=\text{CH}] & \rightarrow 5 + Ar_2CO
\end{align*}
\]

Ar = p-MeC\(_6\)H\(_4\)