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Synthesis, characterization, and alkyne cyclotrimerization chemistry of titanium complexes supported by calixarene-derived bis(aryloxide) ligation ☆

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Abstract

Proximally bridged calix[4]arene compounds (DESC)H_2 (**3**), (DMSHC)H_2 (**4**), (DMSMC)H_2 (**5**), and (DPSC)H_2 (**6**), in which one R_2Si group (R = alkyl or aryl) bridges adjacent oxygens, were synthesized via reaction between dialkyl- or diaryldichlorosilane and the corresponding calix[4]arene. Treatment of *p-tert*-butylcalix[4]arene with Ph_2SiCl_2 at room temperature or (*o*-$MeC_6H_4)_2SiCl_2$ at 80 °C gave $(ClPh_2SiCl)_2$Calix-H_2 (**7**) and (*o*-$Tol_2SiCl)_2$Calix-H_2 (**8**), respectively. Titanium dichloride complexes **9**–**12** (L_2TiCl_2, where L_2 = DESC, DMSHC, DMSMC, or DPSC) were prepared in high yield from reaction of **3**–**6** with $TiCl_4$. The molecular structures of **7** and **12** were established by single-crystal X-ray diffraction studies. Reduction of **9**, **11**, and **12** with activated magnesium (Mg*) in the presence of an excess of $Me_3SiC{\equiv}CH$ produced titananorbornadiene complexes $L_2Ti\{\eta^6$-1,2,4-$C_6H_3(SiMe_3)_3\}$ (**13**–**15**, L_2 = DESC, DMSMC, or DPSC), which were characterized in solution. Catalytic cyclotrimerization of both terminal and internal alkynes was achieved using catalyst systems derived from L_2TiCl_2 complexes **9**–**12** and Mg*. For unsymmetrically substituted internal alkynes, preference for 1,2,4-substitution decreased as the size difference of the substituent groups decreased. The cyclotrimerization of PhC≡CMe was more facile when the calixarene-derived bis(aryloxide) ligand was DPSC versus DMSMC, suggesting that the DPSC ligand may provide a less crowded titanium center and exert greater kinetic control over the course of the cyclotrimerization.
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Keywords: Calixarene compounds; Alkyne cyclotrimerization; Titanium(IV); Reduced titanium

1. Introduction

Metallocene complexes of the group 4 metals have been the focus of intense study, mainly because of their usefulness in organic and polymer chemistry [1]. Group 4 metal complexes containing non-cyclopentadienyl ligand arrays, such as aryloxides [2], chelating diamides [3], porphyrins [4], amine-bis(phenolate)s [5], bis(salicylaldiminate)s [6], carboranes [7], amidinates [8], boratabenzenes [9], Schiff bases [10], and calixarenes [11,12], have increasingly been investigated. While precise control of chemical reactivity is difficult, the expectation is that compounds with comparable or superior reactivity to group 4 metal metallocenes can be developed since steric and electronic properties of ancillary ligands profoundly influence the reactivity of transition metals.

We have been exploring the chemistry of titanium complexes supported by dianionic, proximally bridged *p-t*-butylcalix[4]arene ligands [12]. Previously, we reported the synthesis of conformationally stable Ti(IV)

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dichlorides that contain calixarene-derived bis(aryloxide) ligands in 1,2-alternate conformation, (DMSC)$TiCl_2$ (**1a**) [12b] and (*t*-BuPC)$TiCl_2$ (**1b**) [12a] (Fig. 1). In this conformation, a pair of bulky *tert*-butylated phenyl rings essentially define a cavity into which a coordination site at titanium must project. We found that **1a** catalyzes cyclotrimerization of terminal alkynes at 80 °C and in the presence of excess Na (with respect to Ti) to give high yields of 1,2,4-substituted benzenes with excellent regioselectivity [12b]. The reaction of **1a** with activated magnesium (Mg*) in the presence of an excess of $Me_3SiC{\equiv}CH$ produced (DMSC)Ti{η^6-1,2,4-$C_6H_3(SiMe_3)_3$} (**2a**, Fig. 1), which is an efficient catalyst for regioselective cyclotrimerization of terminal alkynes to 1,2,4-substituted benzenes at room temperature [12c]. The steric bulk of the alkyne affects both the rate and regioselectivity of the cyclotrimerization reaction. Bulky terminal alkynes, such as $Pr^i_3SiC{\equiv}CH$, and most internal alkynes react very sluggishly with **2a**, and are rarely cyclotrimerized even at elevated temperatures.

Our mechanistic investigations revealed that displacement of 1,2,4-$C_6H_3(SiMe_3)_3$ from **2a** by alkyne is rate-limiting. Furthermore, the observed 1,2,4-regioselectivity is best explained by the directing influence (kinetic control) of the DMSC ligand [12b,12c]. That is, the size of the cavity defined by the DMSC ligand sterically governs the preferred orientation of a coordinated alkyne molecule by influencing placement of its substituent group inside or outside of the cavity. Accordingly, whether a larger cavity size will permit efficient cyclotrimerization of internal alkynes is of interest. A careful analysis of the molecular structures of DMSC-based titanium complexes revealed that the bridging $SiMe_2$ group can adopt different orientations, and thereby permit some degree of flexibility in the calixarene ligand. Herein, we describe results from a study aimed at elucidating the effect of the steric properties of the SiR_2 bridging group of calixarene-derived bis(aryloxide) ligands on reactivity of titanium complexes.

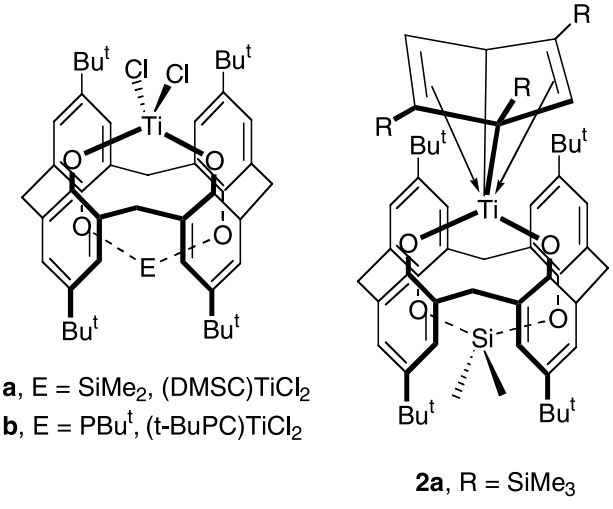


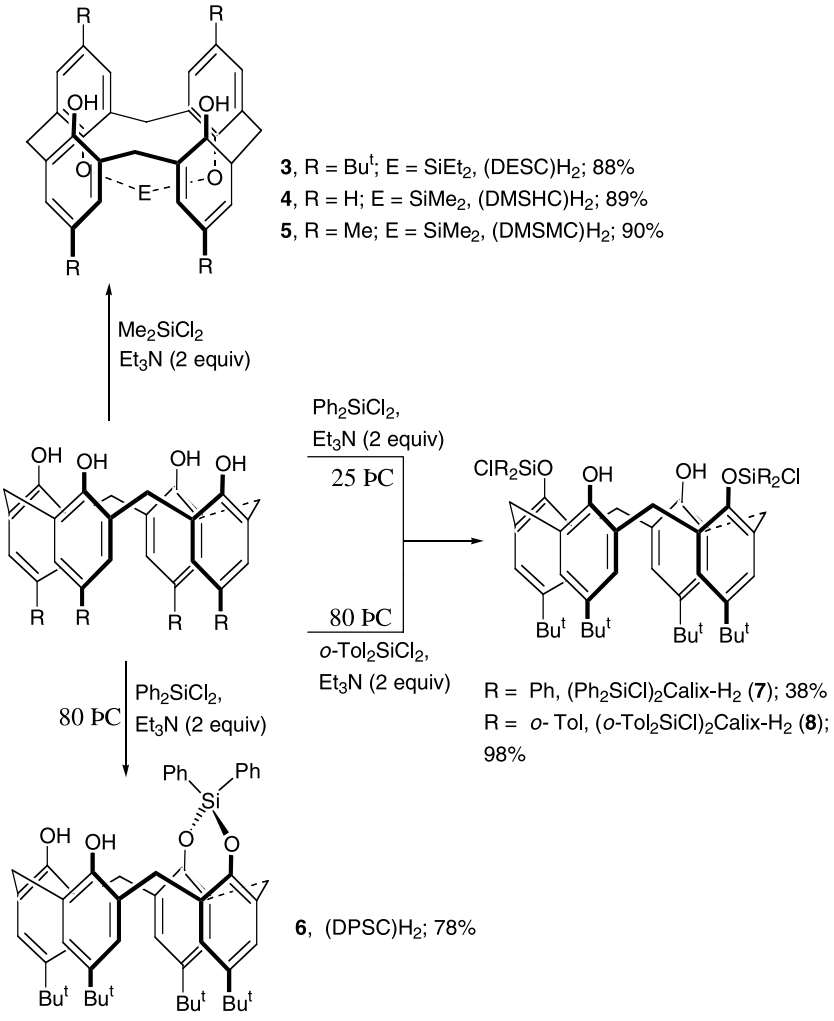
Fig. 1.

2. Results and discussion

2.1. Calix[4]arene derivatives

The synthesis of proximally bridged calix[4]arene compounds **3**–**6** is summarized in Scheme 1. The method reported by Lattman and colleagues [13] for the synthesis of (DMSC)H_2 was adapted to prepare **3**–**5**. At room temperature, reaction between Me_2SiCl_2 or Et_2SiCl_2 and the appropriate calix[4]arene derivative in the presence of 2 equiv of Et_3N for 24–48 h gave **3**–**5** in high yield after work-up. No reaction was observed between *p-tert*-butylcalix[4]arene and $Pr^i_2SiCl_2$ or $Bu^t_2SiCl_2$ under identical conditions while reaction with Ph_2SiCl_2 mainly produced $(ClPh_2Si)_2$Calix-H_2 (**7**, Scheme 1), along with minor amounts of (DPSC)H_2 (**6**). It is likely that formation of **7** occurs by sequential substitution of *p-tert*-butylcalix[4]arene with $ClPh_2Si$ groups. This suggests that at room temperature intermolecular reaction of the presumed mono-substituted intermediate ($ClPh_2Si$)Calix-H_3 with Ph_2SiCl_2 to give **7** proceeds at a faster rate than intramolecular chloride substitution to produce (DPSC)H_2 (**6**). Reasoning that both initial substitution of *p-tert*-butylcalix[4]arene to give ($ClPh_2Si$)Calix-H_3 and "HCl" elimination from ($ClPh_2Si$)Calix-H_3 should be more facile at higher temperatures, we conducted the reaction at 80 °C and isolated (DPSC)H_2 (**6**) in 78% yield. In contrast, reaction between *p-tert*-butylcalix[4]arene and more bulky (*o*-$MeC_6H_4)_2SiCl_2$ at 80 °C gave (*o*-$Tol_2SiCl)_2$Calix-H_2 (**8**) in excellent yield (Scheme 1). Compounds **3**–**8** are air-stable, hygroscopic white solids. While **3** and **5**–**8** are fairly soluble in aromatic hydrocarbon solvents, such as benzene and toluene, and in polar hydrocarbon solvents, such as ether, THF, chloroform, and dichloromethane (DMSHC)H_2 (**4**) is only sparingly soluble in these solvents. All of the compounds are considerably less soluble in aliphatic hydrocarbon solvents.

Mass spectral and solution NMR data of **3**–**8** are consistent with their proposed formulation and structure. The NMR data for **3**–**5** demonstrate that they possess C_s symmetry and adopt 1,2-alternate conformation in solution. ^1H and ^{13}C NMR resonances for the *endo*-SiR group (located inside the calixarene cavity) of 1,2-alternate R_2Si-bridged calix[4]arene compounds are always strongly shielded compared to signals for the *exo*-SiR group (located outside the calixarene cavity) [12,13], due probably to ring current effect [14]. For example, ^1H NMR resonances for the *endo*-$SiCH_2CH_3$ group of (DESC)H_2 (**3**) show as a triplet at δ 0.65



Scheme 1.

($SiCH_2CH_3$) and a quartet at δ −0.63 ($SiCH_2CH_3$) while the *exo*-$SiCH_2CH_3$ group is observed as a multiplet at δ 0.86–0.96. Similarly, in the ^{13}C NMR spectrum of **3**, two resonances at δ 7.2 ($SiCH_2CH_3$) and δ 4.9 ($SiCH_2CH_3$) are observed for the *endo*-$SiCH_2CH_3$ group while resonances for the *exo*-$SiCH_2CH_3$ group are observed at δ 8.2 ($SiCH_2CH_3$) and 7.4 ($SiCH_2CH_3$). ^1H NMR spectra of **3**–**5** also show two pairs of doublets and an AB system for the bridging CH_2 protons. The AB system integrates as four protons and represents CH_2 groups not included in the mirror plane. Furthermore, coupling constants (J_{H-H} ~16 Hz) for the AB system are typical of 1,2-alternate conformation (16–17 Hz) [12a,12b].

The poor solubility of $(DMSHC)H_2$ (**4**) prevented acquisition of its solution ^{13}C NMR data. However, ^{13}C NMR spectra of **3** and **5** showed three resonances for the bridging methylene carbons at δ 32.8, 36.2, and 37.4 (doubly intense) (**3**) and δ 31.9, 35.2, and 36.1 (doubly intense) (**5**). These data parallel ^{13}C NMR data reported for several calix[4]arene derivatives [13,15], which show that methylene carbons of calix[4]arenes are characterized by a resonance around δ 31 ppm when the attached phenol rings are oriented *syn*. Whereas, a resonance around δ 37 ppm is characteristic when the phenol rings adopt *anti* orientation (Fig. 2). NMR data for $(DPSC)H_2$ (**6**) confirm its C_s symmetry in solution and show that it adopts the cone conformation. Hence two singlets and three pairs of doublets are observed in its

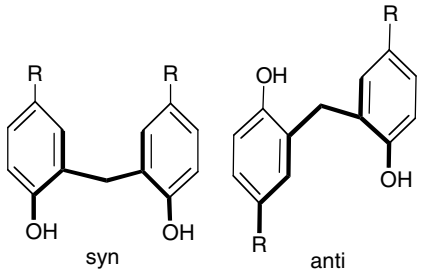


Fig. 2.

^{1}H NMR spectrum for Bu^t groups and methylene protons, respectively. The spectrum is distinct from the spectra of **3**–**5** in that an AB system is absent and the coupling constant (J_{H-H}) for the doubly intense pair of doublets is ~14 Hz while the corresponding J_{H-H} for **3**–**5** is ~16 Hz. In its ^{13}C NMR spectrum, the bridging methylene carbons resonate at δ 38.0, 33.8 (overlapped with $C(CH_3)_3$ resonance), and 32.8 (doubly intense). The resonance at 38.0 belongs to CH_2 carbon connecting *syn*-oriented Ph_2Si-bridged phenol rings. Similar data have previously been reported for proximally bridged calixarenes in cone conformation [12a,16].

^{1}H and ^{13}C NMR data for $(ClPh_2Si)_2$Calix-H_2 (**7**) and $(o\text{-}Tol_2SiCl)_2$Calix-H_2 (**8**) indicate that they are C_{2v} symmetric in solution. Their ^{1}H NMR spectra show two equally intense doublets for the calixarene CH_2 groups at δ 4.64 and 3.10 for **7** and at δ 4.57 and 3.10 for **8**. Their J_{H-H} coupling constants of ~14 Hz and the presence of a single resonance for calixarene CH_2 carbons in their ^{13}C NMR spectrum at δ 33.1 for **7** and δ 33.2 for **8** reveal that the compounds exist in cone conformation. The structure assigned for **7** by spectroscopy was confirmed by single-crystal X-ray crystallographic analysis: the molecule adopts cone conformation with the $ClPh_2Si$ groups substituted symmetrically. The molecular structure of **7** is shown in Fig. 3 and its crystallographic data and selected metrical parameters are presented in Tables 1 and 2. Metrical parameters for **7** are within the range observed for related calixarene compounds [12a,13,16].

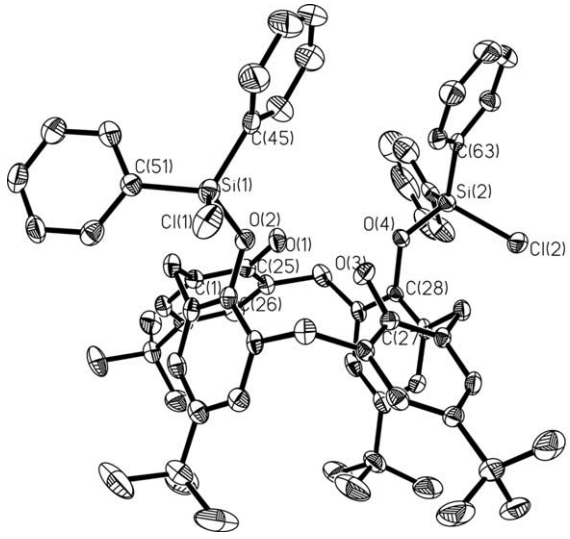


Fig. 3. An ORTEP diagram of the molecular structure of **7** showing 50% thermal ellipsoid probabilities.

2.2. Synthesis and reactivity of titanium complexes

Reaction between $TiCl_4$ and **3**–**6** produced L_2TiCl_2 complexes **9**–**12** (L_2 = DESC, DMSHC, DMSMC, or DPSC) in high yield Eq. (1), as air- and moisture-sensitive orange or orange-brown solids. Both microanalysis and NMR data strongly support the proposed formulation and structure of each compound. Compounds **9**, **11** and **12** are quite soluble in aromatic- and chlorinated hydrocarbon solvents while $(DMSHC)TiCl_2$ (**10**) is only sparingly soluble. All of the compounds are practically insoluble in aliphatic hydrocarbon solvents. ^{1}H and ^{13}C NMR data show that **9**–**12** exist in 1,2-

$$TiCl_4 \xrightarrow[-40\text{–}25\,^\circ C\ \text{pentane/ether}]{L_2H_2} L_2TiCl_2 \quad \begin{array}{l} \mathbf{9},\ L_2 = \text{DESC};\ 87\% \\ \mathbf{10},\ L_2 = \text{DMSHC};\ 84\% \\ \mathbf{11},\ L_2 = \text{DMSMC};\ 95\% \\ \mathbf{12},\ L_2 = \text{DPSC};\ 82\% \end{array} \qquad (1)$$

Table 1
Crystallographic data for **7**, **12**, and **16** · 1.5(C_5H_{12})

	7	**12**	**16** · 1.5(C_5H_{12})
Formula	$C_{68}H_{74}Cl_2O_4Si_2$	$C_{56}H_{62}Cl_2O_4SiTi$	$C_{85.50}H_{104}O_5SiTi$
Formula wt.	1082.35	945.97	1287.69
T (K)	144(1)	173(1)	173(1)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P21/n$
Z	2	2	4
a (Å)	11.093(2)	9.392(3)	11.0560(10)
b (Å)	14.490(2)	15.463(6)	30.443(3)
c (Å)	20.103(2)	19.154	22.699(2)
α (°)	87.288(10)	102.67(2)	90
β (°)	77.736(10)	91.60(2)	100.649(10)
γ (°)	76.081(10)	99.34(2)	90
V (Å^3)	3064.8(8)	2672.2(17)	7508.4(12)
d_{calc} (g/cm^3)	1.173	1.213	1.141
Final R indices [$I > 2\sigma(I)$]: R_1, wR_2	0.0657, 0.0919	0.0534, 0.1138	0.0818, 0.2188
wR_2, R_1 (all data)	0.1097, 0.1015	0.0855, 0.1267	0.1067, 0.2328

Table 2
Selected bond distances (Å) and angles (°) for **7**

Si(1)–O(2)	1.650(2)
Si(1)–C(45)	1.833(3)
Si(1)–C(51)	1.841(3)
Si(1)–Cl(1)	2.0522(13)
Si(2)–O(4)	1.643(2)
Si(2)–C(57)	1.837(3)
Si(2)–C(63)	1.841(3)
Si(2)–Cl(2)	2.0517(12)
O(1)–C(25)	1.384(3)
O(2)–C(26)	1.405(3)
O(3)–C(27)	1.385(3)
O(4)–C(28)	1.404(3)
C(26)–O(2)–Si(1)	125.67(17)
C(28)–O(4)–Si(2)	125.07(17)

Table 3
Selected bond distances (Å) and angles (°) for **12**

Ti–O(1)	1.766(2)
Ti–O(2)	1.769(2)
Ti–Cl(1)	2.1980(14)
Ti–Cl(2)	2.2332(14)
Si–O(4)	1.631(2)
Si–O(3)	1.642(2)
Si–C(45)	1.840(3)
Si–C(51)	1.867(4)
O(1)–Ti–O(2)	103.56(10)
O(1)–Ti–Cl(1)	110.06(8)
O(2)–Ti–Cl(1)	117.51(8)
O(1)–Ti–Cl(2)	108.90(9)
O(2)–Ti–Cl(2)	111.73(9)
Cl(1)–Ti–Cl(2)	104.95(5)

alternate conformation and possess C_s symmetry. Thus, a change in conformation of $(DPSC)H_2$ occurs when it reacts with $TiCl_4$ to form $(DPSC)TiCl_2$ (**12**) [17]. ^1H NMR spectra of **9**–**12** contain two pairs of doublets and an AB system (integrating as four protons) for the bridging CH_2 protons. Also, we could identify *endo*- and *exo*-SiR (R = Me or Et) resonances for **9**–**11** (see Section 3). ^{13}C NMR spectra of **9**, **11** and **12** showed methylenes bridging *anti*-oriented phenolic rings at around δ 40 ppm while methylenes bridging *syn*-oriented phenolic rings generally appeared at around δ 36 ppm, consistent with previously reported data for related 1,2-alternate calix[4]arene derivatives [12a,13,15]. A single-crystal X-ray crystallographic study of **12** established that the DPSC ligand adopts 1,2-alternate conformation and that the geometry about Ti is tetrahedral (Fig. 4). Similar to the DMSC ligand [12b], DPSC imposes distinct stereochemical environments about the titanium-bound chlorides. Thus, access to the *endo* chloride Cl(2) is more hindered relative to the *exo* chloride Cl(1). Bond distances and angles for **12** (Table 3) are within the expected ranges [18].

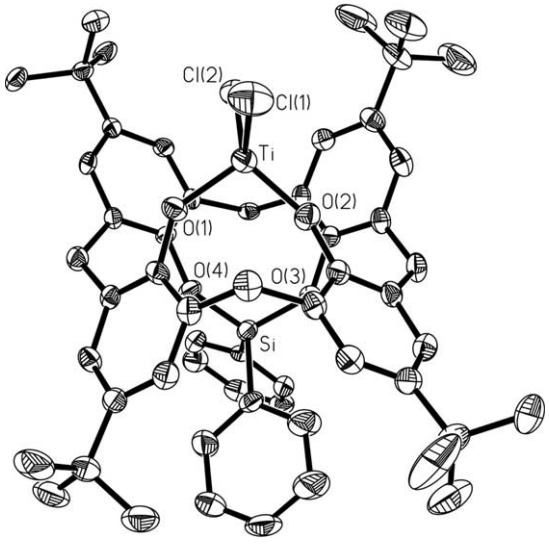


Fig. 4. An ORTEP diagram of the molecular structure of **12** showing 50% thermal ellipsoid probabilities.

Though the synthesis and chemistry of titananorbornadienes remain largely undeveloped [19], we have demonstrated that titananorbornadienes (DMSC)$Ti\{\eta^6$-1,2,4-$C_6H_3(SiMe_3)_3\}$ (**2a**) and (DMSC)$Ti(\eta^6$-1,3,5-$C_6H_3Bu^t_3)$ (**2b**) are excellent Ti(II) synthons [12b, 12c,12d]. Therefore, we saw benefit in extending the series of titananorbornadiene compounds and exploring their reactivity. Since **2a** was isolated from the black mixture that resulted upon reaction of $(DMSC)TiCl_2$ (**1a**) with an excess of $Me_3SiC{\equiv}CH$ and Mg* (generated by degradation of $C_{14}H_{10}Mg(THF)_3$ [20]) in toluene containing ~1–2% by volume of THF, we examined the reduction of L_2TiCl_2 complexes **9**–**12** with Mg* in the presence of 10 equivalents of $Me_3SiC{\equiv}CH$ in C_6D_6 containing ~1–2% by volume of THF. ^1H NMR analysis of the resulting black mixtures revealed that cyclotrimerization of $Me_3SiC{\equiv}CH$ occurred in all cases to give mixtures of 1,2,4- and 1,3,5-$C_6H_3(SiMe_3)_3$ (see Section 3). Moreover, titananorbornadiene complexes $L_2Ti\{\eta^6$-1,2,4-$C_6H_3(SiMe_3)_3\}$ (**13**–**15**) were observed in solution when L_2 = DESC, DMSMC, or DPSC Eq. (2). Efforts to prepare and cleanly isolate **13**–**15** via a variety of approaches have so far been unsuccessful because of low conversion of the L_2TiCl_2 precursors into a titananorbornadiene (vide infra). Therefore, the compounds were characterized only in solution by ^1H NMR data.

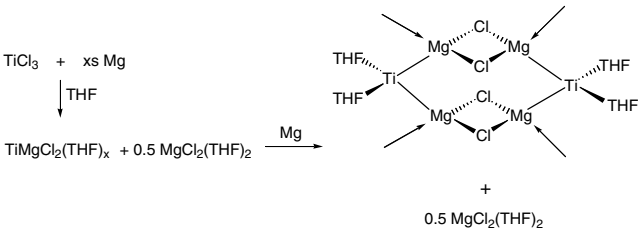
$$\begin{array}{l} L_2TiCl_2 \\ \textbf{9}, L_2 = \text{DESC} \\ \textbf{11}, L_2 = \text{DMSMC} \\ \textbf{12}, L_2 = \text{DPSC} \end{array} \xrightarrow[C_6D_6/THf]{\begin{array}{l}\text{(i) Mg}^* \\ \text{(ii) } Me_3SiC \equiv CH,\ \text{(xs)}\end{array}} \begin{array}{l} L_2Ti\{\eta^6\text{-}1,2,4\text{-}C_6H_3(SiMe_3)_3\} \\ \text{black solution} \\ \textbf{13}, L_2 = \text{DESC} \\ \textbf{14}, L_2 = \text{DMSMC} \\ \textbf{15}, L_2 = \text{DPSC} \end{array} \qquad (2)$$

The ^1H NMR data for **13**–**15** clearly demonstrate that they are C_1-symmetric in solution although some

resonances were obstructed by signals due to other products and THF (see Section 3). For instance, three singlets are observed in their ^{1}H NMR spectra for the inequivalent η^6-arene $SiMe_3$ groups. Furthermore, **13** and **15** each show four singlets between δ 1.2 and 1.6 ppm for Bu^t groups while the calixarene methyls of **14** show as four singlets between δ 2.0 and 2.4 ppm. That the calixarene ligand of **14** and **15** exists in 1,2-alternate conformation was deduced from the upfield shift of the *endo*-SiMe resonance (at δ −0.65 ppm for **14**) and/or from the magnitude of the coupling constants for the calixarene methylene protons (J_{H-H} typically equal 16-17 Hz for CH_2 groups bridging *anti*-oriented phenolic units, vide supra). Resonances for six of the eight calixarene methylene protons of **13** could be identified, four of which have coupling constants (J_{H-H} ∼16 Hz) typical of CH_2 groups bridging *anti*-oriented phenolic rings. However, a complex multiplet between δ 0.82–0.92 ppm was observed for $SiEt_2$ protons and an upfield resonance typical of an *endo*-SiR group was not observed. Unambiguous assignment of the conformation of the calixarene ligand of **13** must therefore await further data.

The reduction of L_2TiCl_2 complexes **9**, **11**, and **12** in the presence of alkyne ($\geqslant$10 equiv) was studied at different temperatures in a variety of solvents, including toluene, THF, and 1,4-dioxane. The reaction was investigated for a range of reducing agents (such as activated Zn [21], Na, activated Ca [22], Mg*, and C_8K [23]) and alkynes (such as $Me_3SiC{\equiv}CH$, *p*-$MeC_6H_4C{\equiv}CH$, $Bu^tC{\equiv}CH$, $MeC{\equiv}CMe$, and $PhC{\equiv}CMe$). Titananorbornadiene complexes were formed in significant amount only when the reductant was Mg*, the alkyne was $Me_3SiC{\equiv}CH$, and the reaction was conducted at room temperature in toluene containing 1–2% (by volume) of THF. Although catalytic cyclotrimerization of the alkynes occurred using other reducing agents, harsher conditions were generally required and reduction of L_2TiCl_2 proceeded at a slower rate than alkyne cyclotrimerization. High conversion of L_2TiCl_2 complexes **9**, **11**, and **12** into corresponding titananorbornadienes (**13**–**15**) requires complete reduction of the L_2TiCl_2 precursor prior to catalytic $Me_3SiC{\equiv}CH$ cyclotrimerization. Otherwise, reduced titanium species formed in the initial stages of L_2TiCl_2 reduction will consume all of the alkyne before the reduction was complete (since alkyne cyclotrimerization is catalytic).

Bogdanovic and colleagues [24] have reported that reduction of $TiCl_x$ ($x = 3$ or 4) with Mg in THF produced black solutions containing paramagnetic Ti–Mg species $TiMgCl_2(THF)_x$ and $[Ti(MgCl)_2(THF)_x]_y$ (the local structure about Ti in the latter species was characterized by EXAFS, Eq. (3)). Since reactions of L_2TiCl_2 complexes **9**–**12** with Mg* and $Me_3SiC{\equiv}CH$ (10 equiv) in toluene or C_6D_6 containing 1–2% of THF proceed immediately to form black



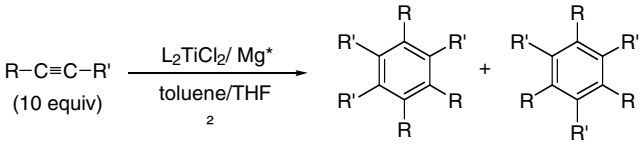
(3)

solutions, it is likely that the solutions also contained paramagnetic species similar to those proposed by Bogdanovic and colleagues. We presume that titananorbornadiene and paramagnetic calixarene-containing species are produced via competing pathways since black solutions result immediately upon addition of THF to a suspension of L_2TiCl_2 (**9**–**12**), Mg* and $Me_3SiC{\equiv}CH$ in toluene or C_6D_6. In contrast, very sluggish reaction of (DMSMC)$TiCl_2$ (**11**) or (DPSC)$TiCl_2$ (**12**) with Mg* and $Me_3SiC{\equiv}CH$ (10 equiv) occurred in toluene (in the absence of THF). The orange suspensions did not change color for 1.5 h and ^{1}H NMR revealed plenty of unreacted titanium dichloride.

We reasoned that increased $MgCl_2$ precipitation from reactions of L_2TiCl_2 complexes **9**–**12** with Mg* and $Me_3SiC{\equiv}CH$ should favor titananorbornadiene formation. Therefore, we explored reactions of (DESC)$TiCl_2$ (**9**) with Mg* and $Me_3SiC{\equiv}CH$ ($\geqslant$10 equiv) in toluene/THF containing different amounts of 1,4-dioxane. While precipitation of $MgCl_2(dioxane)_n$ did improve conversion to(DESC)Ti{η^6-1,2,4-C_6H_3(Si Me_3)$_3$} (**13**), the experimental results were irreproducible and depended on the mixing rate, the reaction scale, and solvent ratios. Finally, we explored reactions of various alkynes with $L_2Ti(\eta^2$-alkene) or $L_2Ti(\eta^2$-alkyne) species (prepared in situ via modifications of the Neghishi [25], Eisch [26], or Sato [27] protocols). Titananorbornadiene formation was very seldom observed and in very small amount.

In an effort to examine the effect of calixarene-derived bis(aryloxide) ligands on reactivity of titanium, we decided to examine the scope of alkynes that can be cyclotrimerized using L_2TiCl_2 complexes **9**–**12** in the presence of Mg* as catalyst (see Section 3). Table 4 outlines results from our preliminary investigations and show that both terminal and internal alkynes can be cyclotrimerized. Terminal alkynes are cyclotrimerized with high regioselectivity (Table 4, entries 1 and 2) while steric properties of the substituent groups of internal alkynes greatly influence both efficacy and regioselectivity of the reaction. Thus, an ethyl or phenyl unit is about the limit of a substituent that may be placed inside the calixarene cavity and still observe catalytic cyclotrimerization under our conditions (Table 4, entries 3–15). In the case of unsymmetrically substituted internal alkynes, preference for 1,2,4-substitution decreased as the size difference of the

Table 4
Catalytic alkyne cyclotrimerization



No.	Alkyne	L_2TiCl_2	% Isomer[c]		C_6R_6	Rxn. time[e]
			1,2,4-	1,3,5-		
1	*p*-$MeC_6H_4C{\equiv}CH$[a]	**12**	92	8		~2 h at 75 °C
2	$PhC{\equiv}CH$[a]	**12**	>92	<8[d]		~2 h at 75 °C
3	$PhC{\equiv}CMe$[a]	**11**	72	28		~24 h at 70 °C
4	$PhC{\equiv}CMe$[b]	**12**	90	10		~1 h at 70 °C
5	$PhC{\equiv}CEt$[a]	**11**	69	31		~24 h at 70 °C
6	$PhC{\equiv}CEt$	**12**	68	32		~24 h at 70 °C
7	$MeC{\equiv}CMe$[a]	**11**			100	~18 h at 70 °C
8	$MeC{\equiv}CMe$[a]	**12**			100	~2 h at 75 °C
9	$MeC{\equiv}CEt$[b]	**12**	~75	~25		~2 h at 75 °C
10	$MeC{\equiv}CEt$[a]	**11**	75	25		~20 h at 70 °C
11	$EtC{\equiv}CEt$[a]	**11**			100	~48 h at 70 °C
12	$EtC{\equiv}CEt$[b]	**12**			100	~48 h at 70 °C
13	$Me_2NCH_2C{\equiv}CEt$[a]	**9–12**	–	–		5 days at 70–100 °C
14	$Me_3SiC{\equiv}CMe$[a]	**9–12**	–	–		5 days at 70–100 °C
15	$Me_3SiC{\equiv}CSiMe_3$[a]	**9–12**			–	5 days at 70–100 °C

[a] A screw-capped NMR tube was charged with $C_{14}H_{10}Mg(THF)_3$ along with all other reactants and C_6D_6 in a glovebox. The NMR tube was then heated at 70–75 °C. See Section 3 (method 1) for full details.

[b] $C_{14}H_{10}Mg(THF)_3$ was first decomposed in C_6D_6 at 80 °C to Mg* and anthracene. All other reactants were added after cooling to ambient temperature. See Section 3 (method 2) for full details.

[c] Isomer ratios were determined from GC-MS and ^1H NMR data. For unsymmetrical alkynes $RC{\equiv}CR'$, 1,2,4-substitution refers to substitution of R at 1-, 2-, and 4-positions of the benzene ring.

[d] The yield of 1,3,5-$Ph_3C_6H_3$ was estimated based on the result obtained for *p*-tolylacetylene. ^{12}C NMR data confirmed the major product as 1,2,4-substituted isomer and GC-MS showed only one peak. ^1H NMR data could not be used to characterize the 1,3,5-substituted isomer, presumably because of extensive peak overlap.

[e] For 100% conversion.

substituent groups decreased (Table 4, entries 2, 4, and 6). Nonetheless, 1,2,4-substitution was favored over 1,3,5-substitution in all cases by about 3:1.

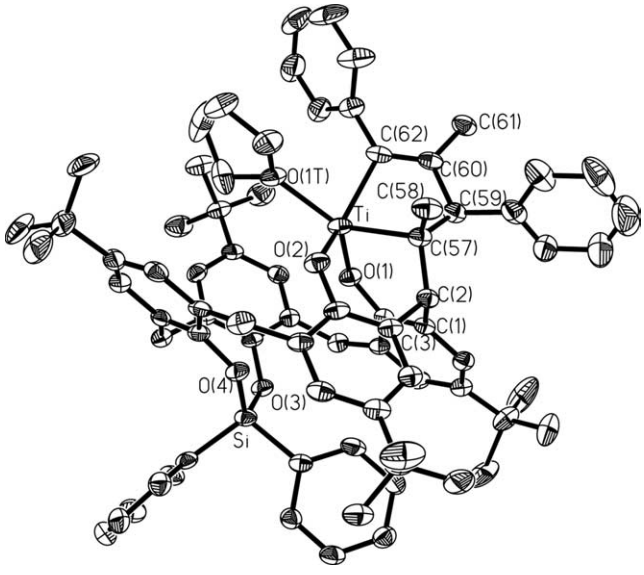


Fig. 5. An ORTEP diagram of the molecular structure of **16** showing 50% thermal ellipsoid probabilities.

It is noteworthy that cyclotrimerization of 1-phenyl-1-propyne was more facile when the calixarene-derived bis(aryloxide) ligand was DPSC versus DMSMC (Table 4, entries 3 and 4). This result suggests that the DPSC ligand may provide a less crowded titanium center and thereby reduce steric inhibition of alkyne coordination. Thus, the DPSC ligand may exert greater kinetic control over the course of cyclotrimerization and thereby explain the high regioselectivity [28]. When the reaction of $(DPSC)TiCl_2$ (**12**) with Mg* and $PhC{\equiv}CMe$ (3 equiv) was conducted on a preparative scale in toluene/THF, we isolated a small amount of a titanacyclopent-2-ene derivative **16** [29]. The molecular structure of **16** (Fig. 5) was characterized by X-ray diffraction study and its crystallographic data are listed in Table 1. The poor crystal quality could be due to a small amount of unresolved twinning, and limits the accuracy of geometrical parameters. Nevertheless, connectivity is unambiguous and bond lengths and angles (Table 5) are within expected ranges [2h,2k,30]. Remarkably, the molecular structure of **16** revealed that the DPSC ligand has undergone activation of one of its methylene C-H bonds and that the methylene carbon is bonded to the α-sp^3-carbon of the titanacyclopent-2-ene. The calixarene

Table 5
Selected bond distances (Å) and angles (°) for **16** · 1.5(C_5H_{12})

O(1)–Ti	1.817(3)	O(1)–Ti–C(57)	90.54(15)
O(2)–Ti	1.853(3)	O(2)–Ti–C(57)	85.94(15)
Ti–O(1T)	2.105(3)	O(1T)–Ti–C(57)	138.55(15)
Ti–C(57)	2.143(5)	O(1)–Ti–C(62)	110.31(16)
Ti–C(62)	2.177(4)	O(2)–Ti–C(62)	141.03(16)
C(2)–C(57)	1.534(6)	O(1T)–Ti–C(62)	85.23(16)
C(1)–C(2)	1.528(6)	C(57)–Ti–C(62)	77.27(17)
C(2)–C(3)	1.536(6)	C(1)–C(2)–C(57)	114.3(3)
C(57)–C(58)	1.528(6)	C(1)–C(2)–C(3)	109.8(3)
C(57)–C(59)	1.552(6)	C(57)–C(2)–C(3)	114.9(4)
C(59)–C(60)	1.520(6)	C(58)–C(57)–C(2)	111.1(4)
C(60)–C(62)	1.337(7)	C(58)–C(57)–C(59)	113.5(4)
C(60)–C(61)	1.497(6)	C(2)–C(57)–C(59)	112.2(4)
O(1)–Ti–O(2)	104.68(14)	C(58)–C(57)–Ti	109.1(3)
O(1)–Ti–O(1T)	130.88(13)	C(2)–C(57)–Ti	105.6(3)
O(2)–Ti–O(1T)	84.67(13)	C(59)–C(57)–Ti	104.9(3)

ligand exists in 1,2-alternate conformation and the geometry about Ti can be described as distorted square pyramidal, with the basal plane defined by C57, C62, O2, and O1(T). Equally surprising, a phenyl substituent is positioned at the α-position of the titanacycle on the same side as a THF molecule coordinated on the *endo*-face of titanium (directed toward the calixarene cavity) [31]. We propose that orientation of one of the phenyl units of the $SiPh_2$ bridging group such that it can fit between two phenolic units of the calixarene ligand (Fig. 5) allows the DPSC ligand to open up its cavity and accommodate more bulky substituents than the DMSC or DMSMC ligands.

In summary, it seems likely that the size of the cavity provided by proximally bridged calixarene ligands may be tuned through proper choice of bridging group. The observed regioselectivity for alkyne cyclotrimerization in the present study probably represent the lower-limit since paramagnetic calixarene-containing species that catalyze alkyne cyclotrimerization (with modest regioselectivity) are also generated under our reaction conditions. Efforts to isolate titananorbornadiene complexes and investigate their chemistry are continuing in our laboratory.

3. Experimental

3.1. General

All experiments were performed under dry nitrogen atmosphere using standard Schlenk techniques or in a MBraun glovebox. All of the solvents were dried and distilled by standard methods [33] then stored in the glovebox over 4A molecular sieves, which had been dried under vacuum at 150 °C for at least 48 h prior to use. Alkynes were purchased from Aldrich or GFS Chemicals, Inc. and were distilled from CaH_2 prior to use. Calix[4]arene [34], *p*-methylcalix[4]arene [35], $C_{14}H_{10}Mg(THF)_3$ [20], and $(o\text{-}MeC_6H_4)_2SiCl_2$ [36] were prepared by literature methods. All other chemicals were purchased from Aldrich Chemical Co. and used without further purification (unless otherwise stated). The calix[4]arene starting materials were dried in a vacuum oven at 150 °C for 48 h prior to use. ^1H and ^{12}C NMR spectra were recorded on a Varian Gemini-200 spectrometer or a Varian VXR-400 spectrometer at ca. 22 °C. ^1H and ^{12}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. Other mass spectral data were obtained from the University of Kentucky Mass Spectrometry Center on a Thermo Finnigan (San Jose, CA) Polaris Q (quadruple ion trap) spectrometer. Elemental analyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ.

3.2. Synthesis of calix[4]arene derivatives **3**–**8**

3.2.1. (DESC)H_2 (**3**)

6.58 g (10.1 mmol) of *p*-*t*-Bu-calix[4]arene was charged into a 250 mL Schlenk flask followed by toluene (120 mL) and then 1.52 mL (10.1 mmol) of Et_2SiCl_2 in toluene (6 mL). Next, a solution of Et_3N (2.82 mL, 10.3 mmol) in toluene (10 mL) was added dropwise to the suspension over a 20 min period. After stirring for 48 h, the reaction mixture was filtered and Et_3NHCl was extracted with additional toluene (10 mL) and pentane (20 mL). The filtrate and extracts were combined and stripped to dryness under reduced pressure. The resulting white solid was washed with pentane (3×10 mL) and dried under vacuum. Yield: 6.51 g, 88%. ^1H NMR (C_6D_6) δ: 7.24 (d, $J = 2.6$ Hz, 2H, arom CH), 7.17 (d, 2H, $J = 2.6$ Hz, arom CH), 7.11 (d, $J = 2.6$ Hz, 2H, arom CH), 6.98 (d, 2H, $J = 2.6$ Hz, arom CH), 6.15 (s, 2H, OH), 4.38 (d, $J = 14$ Hz, 1H, calix-CH_2), 4.27 (d, $J = 16.2$ Hz, 2H, calix-CH_2), 4.08 (d, $J = 13.6$ Hz, 1H, calix-CH_2), 3.82 (d, $J = 16.2$ Hz, 2H, calix-CH_2), 3.44 (d, $J = 14$ Hz, 1H, calix-CH_2), 3.41 (d, $J = 14.8$ Hz, 1H, calix-CH_2), 1.29 (s, 18H, *t*-Bu), 1.24 (s, 18H, *t*-Bu), 0.86–0.96 (m, 5H, *exo*-SiCH_2CH_3), 0.65 (t, 3H, *endo*-$SiCH_2CH_3$), −0.63 (q, 2H, *endo*-SiCH_2CH_3). ^{13}C NMR (C_6D_6): 150.6, 150.5, 145.0, 143.4, 130.1, 130.0, 128.8, 127.5, 126.9, 126.2, 126.1, 125.8, 37.4 (calix-CH_2), 36.2 (calix-CH_2), 34.5 ($C(CH_3)_3$), 34.4 ($C(CH_3)_3$, 32.8 (calix-CH_2), 32.1 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$), 8.2 (*exo*-SiCH_2CH_3), 7.4 (*exo*-$SiCH_2CH_3$), 7.2 (*endo*-$SiCH_2CH_3$), 4.9 (*endo*-SiCH_2CH_3). MS(EI): M^+ (732).

3.2.2. (DMSHC)H_2 (**4**)

2.37 g (5.58 mmol) of calix[4]arene was charged into a 250 mL Schlenk flask followed by toluene (60 mL) and

then 0.710 mL (5.86 mmol) of Me_2SiCl_2 in toluene (5 mL). Next, a solution of Et_3N (1.87 mL, 13.4 mmol) in toluene (10 mL) was added dropwise to the suspension over a 20 min period. After stirring for 48 h, the reaction mixture was filtered and the filtrate was stripped to dryness under reduced pressure. The resulting white solid was washed with pentane (3×15 mL) and dried under vacuum. Yield: 2.38 g, 89%. ^{1}H NMR (C_6D_6) δ: 6.78–6.96 (m, 8H, arom CH), 6.62–6.74 (m, 4H, arom CH), 6.10 (s, 2H, OH), 4.24 (d, $J = 14.4$ Hz, 1H, calix-CH_2), 4.18 (d, $J = 15.8$ Hz, 2H, calix-CH_2), 3.90 (d, $J = 14.4$ Hz, 1H, calix-CH_2), 3.64 (d, $J = 15.8$ Hz, 2H, calix-CH_2), 3.43 (d, $J = 14.4$ Hz, 1H, calix-CH_2), 3.23 (d, $J = 14.4$ Hz, 1H, calix-CH_2), 0.27 (s, 3H, *exo*-SiMe), −0.69 (s, 3H, *endo*-SiMe). MS(EI): M^+ (480).

3.2.3. (DMSMC)H_2 (**5**)

A toluene (90 mL) solution of Et_3N (1.07 mL, 7.68 mmol) and Me_2SiCl_2 (0.460 mL, 3.79 mmol) was added very slowly into a 500 mL toluene solution of *p*-methylcalix[4]arene (1.84 g, 3.83 mmol) at room temperature with vigorous stirring. After 24 h, the reaction mixture was filtered and the filtrate was stripped to dryness under reduced pressure. The residue was washed with cold pentane (3×10 mL) and dried under vacuum to give a pure white powder (1.83 g, 90%). ^{1}H NMR ($CDCl_3$) δ: 6.97 (br s, 4H, arom CH), 6.84 (br d, 2H, arom CH), 6.72 (br d, arom CH), 5.96 (s, 2H, OH), 4.25 (d, $J = 14.8$ Hz, 1H, calix-CH_2), 4.12 (d, $J = 16$ Hz, 2H, calix-CH_2), 3.90 (d, $J = 14$ Hz, 1H, calix-CH_2), 3.80 (d, $J = 16$ Hz, 2H, calix-CH_2), 3.43 (d, $J = 14$ Hz, 1H, calix-CH_2), 3.42 (d, $J = 14.8$ Hz, 1H, calix-CH_2), 2.26 (s, 6H, Me), 2.22 (s, 6H, Me), 0.42 (s, 3H, *exo*-SiMe), −0.97 (s, 3H, *endo*-SiMe). ^{13}C NMR ($CDCl_3$): 149.6, 131.4, 130.4, 130.3, 129.8, 129.6, 129.5, 129.3, 128.8, 128.5, 126.2, 36.1 (calix-CH_2), 35.2 (calix-CH_2), 31.9 (calix-CH_2), 20.8 (calix-Me), 20.7 (calix-Me), 2.8 (*exo*-SiCH_2CH$_3$), −2.06 (*endo*-SiCH_2CH$_3$). MS(EI): M^+ (536).

3.2.4. (DPSC)H_2 (**6**)

A toluene (30 mL) solution of Et_3N (6.45 mL, 46.2 mmol) and Ph_2SiCl_2 (4.86 mL, 23.1 mmol) was charged into an addition funnel. The addition funnel was connected via a reflux condenser to a 250 mL Schlenk flask containing a toluene (120 mL) solution of *p*-*t*-Bu-calix[4]arene (15.0 g, 23.1 mmol), which was heated at 80 °C. The Et_3N/Ph_2SiCl_2 solution was added dropwise into the *p*-*t*-Bu-calix[4]arene solution (over a 30 min period) and the resulting mixture was stirred at 80 °C for another 4h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was stripped to dryness under reduced pressure. The resulting white solid was washed with pentane (3×15 mL) and dried under vacuum. Yield: 15.0 g, 78%. ^{1}H NMR (C_6D_6) δ: 8.23 (m, 2H, arom CH), 7.80 (m, 2H, arom CH), 7.52 (s, 2H, OH), 7.20-7.30 (m, 4H, arom CH), 6.80–7.10 (m, 10H, $J = 2.6$ Hz, arom CH), 5.02 (d, $J = 14$ Hz, 1H, calix-CH_2), 4.94 (d, $J = 13.6$ Hz, 2H, calix-CH_2), 3.93 (d, $J = 14.4$ Hz, 1H, calix-CH_2), 3.59 (d, $J = 13.6$ Hz, 2H, calix-CH_2), 3.26 (d, $J = 14$ Hz, 1H, calix-CH_2), 3.15 (d, $J = 15.4$ Hz, 1H, calix-CH_2), 1.14 (s, 18H, *t*-Bu), 1.10 (s, 18H, *t*-Bu). ^{13}C NMR (C_6D_6): 148.9, 145.1, 142.9, 138.6, 134.7, 134.5, 132.5, 131.7, 130.6, 130.3, 129.3, 128.9, 128.2, 127.7, 127.1, 126.7, 125.6, 125.5, 38.0 (calix-CH_2), 33.8 {$C(CH_3)_3$ and calix-CH_2}, 32.8 (calix-CH_2), 31.4 (C(CH_3)$_3$), 31.2 (C(CH_3)$_3$). MS(EI): M^+ (828).

3.2.5. ($Ph_2SiCl)_2$Calix-H_2 (**7**)

5.00 g (7.70 mmol) of *p*-*t*-Bu-calix[4]arene was charged into a 250 mL Schlenk flask followed by toluene (100 mL) and then 1.62 mL (7.70 mmol) of Ph_2SiCl_2 in toluene (6 mL). Next, a solution of Et_3N (2.15 mL, 15.4 mmol) in toluene (10 mL) was added dropwise into the suspension over a 20 min period. After stirring for 48 h, the reaction mixture was filtered and the filtrate was stripped to dryness under reduced pressure. The resulting white solid was washed with pentane (3×15 mL), dried under vacuum, and identified as $(Ph_2SiCl)_2$Calix-H_2 (**7**) on the basis of NMR, MS, and X-ray diffraction data. Yield: 1.58 g (1.46 mmol), 38% on the basis of the maximum yield possible under these conditions (3.85 mmol). ^{1}H NMR (C_6D_6) δ: 7.98–8.10 (m, 8H, arom CH), 7.06–7.14 (m, 12H, arom CH), 7.03 (s, 4H, arom CH), 6.87 (s, 2H, OH), 6.78 (s, 4H, arom CH), 4.64 (d, $J = 13.4$ Hz, 4H, calix-CH_2), 3.10 (d, $J = 13.6$ Hz, 4H, calix-CH_2), 1.32 (s, 18H, *t*-Bu), 0.84 (s, 18H, *t*-Bu). ^{13}C NMR (C_6D_6): 151.2, 146.1, 144.8, 142.1, 135.4, 131.8, 131.6, 130.9, 128.9, 128.5, 126.0, 125.6, 33.8 ($C(CH_3)_3$), 33.7 ($C(CH_3)_3$, 33.1 (calix-CH_2), 31.8 (C(CH_3)$_3$), 30.9 (C(CH_3)$_3$). MS(EI): M^+ (1082).

The pentane washings were combined, concentrated under vacuum to ~5 mL, and then cooled at −78 °C for 30 min. The resulting solids were collected by filtration, dried under vacuum, and identified as (DPSC)H_2 (**6**). Yield of 0.68 g (0.82 mmol), 11% on the basis of the maximum yield possible (7.70 mmol).

3.2.6. (*o*-$Tol_2SiCl)_2$calix-H_2 (**8**)

A toluene (30 mL) solution of Et_3N (2.00 mL, 14.3 mmol) and *o*-Tol_2SiCl_2 (2.00 g, 7.11 mmol) was charged into an addition funnel. The addition funnel was connected via a reflux condenser to a 250 mL Schlenk flask containing a toluene (120 mL) solution of *p*-*t*-Bu-calix[4]arene (4.61 g, 7.11 mmol), which was heated at 80 °C. The Et_3N/*o*-Tol_2SiCl_2 solution was added dropwise into the *p*-*t*-Bu-calix[4]arene solution (over a 30 min period) and the resulting mixture was stirred at 80 °C for another 3h. After cooling to room temperature, the

reaction mixture was filtered and the filtrate was stripped to dryness under reduced pressure. The resulting white solid was washed with pentane (5 × 10 mL) and toluene (5 mL) then dried under vacuum. Yield: 4.00 g (3.51 mmol), 98% on the basis of the maximum yield possible under these conditions (3.56 mmol). ^{1}H NMR (C_6D_6) δ: 8.61 (m, 4H, arom CH), 7.10–7.20 (m, 8H, arom CH), 6.99 (s, 4H arom CH), 6.92 (m, 4H, arom CH), 6.79 (s, 4H arom CH), 6.22 (s, 2H, OH), 4.57 (d, $J = 14$ Hz, 4H, calix-CH_2), 3.10 (d, $J = 14$ Hz, 1H, calix-CH_2), 2.39 (s, 12H, *o-Me* C_6H_4), 1.28 (s, 18H, *t*-Bu), 0.93 (s, 18H, *t*-Bu). ^{13}C NMR (C_6D_6): 151.4, 146.4, 145.6, 144.6, 142.7, 136.8, 132.5, 132.1, 131.6, 131.3, 129.7, 126.7, 126.4, 125.9, 34.3 ($C(CH_3)_3$), 33.2 (calix-CH_2), 33.1 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$). MS(EI): M^+ (1138).

3.3. Synthesis of titanium complexes **9**–**12**

3.3.1. (DESC)$TiCl_2$ (**9**)

A pentane (10 mL) solution of $TiCl_4$ (0.544 g, 2.86 mmol) was added dropwise into a stirred suspension of (DESC)H_2 (2.00 g, 2.73 mmol) in ether (50 mL) at −40 °C. The mixture turned orange-brown and was warmed gradually to room temperature and let stir for 24 h. Volatiles were then removed under vacuum, the residue was washed with pentane (3 × 10 mL), and the orange product was dried in vacuo. Yield: 2.01 g, 87%. ^{1}H NMR ($CDCl_3$) δ: 7.23 (s, 2H, arom CH), 7.12 (s, 2H, arom CH), 7.10 (s, 2H, arom CH), 7.04 (s, 2H, arom CH), 4.40 (d, $J = 14$ Hz, 1H, calix-CH_2), 4.38 (d, $J = 14.2$ Hz, 1H, calix-CH_2), 4.02 (d, AB, $J = 16$ Hz, 2H, calix-CH_2), 3.96 (d, AB, $J = 16$ Hz, 2H, calix-CH_2), 3.60 (d, $J = 14.2$ Hz, 1H, calix-CH_2), 3.47 (d, $J = 14$ Hz, 1H, calix-CH_2), 1.32 (s, 18H, *t*-Bu), 1.31 (s, 18H, *t*-Bu), 0.88 (br m, 5H, *exo*-$SiCH_2CH_3$), 0.29 (t, 3H, *endo*-$SiCH_2CH_3$), -1.40 (q, 2H, *endo*-$SiCH_2CH_3$). ^{13}C NMR ($CDCl_3$): 162.2, 149.1, 147.9, 144.5, 137.5, 128.6, 128.5, 127.2, 126.9, 126.4, 125.6, 124.9, 39.9 (calix-CH_2), 36.6 (calix-CH_2), 35.9 (calix-CH_2), 34.6 ($C(CH_3)_3$), 34.2 ($C(CH_3)_3$, 31.7 ($C(CH_3)_3$), 31.6 ($C(CH_3)_3$), 8.9 (*exo*-$SiCH_2CH_3$), 7.6 (*exo*-$SiCH_2CH_3$), 6.9 (*endo*-$SiCH_2CH_3$), 3.8 (*endo*-$SiCH_2CH_3$). Anal. Calcd. for $C_{48}H_{62}O_4SiTiCl_2$: C, 67.84; H, 7.35. Found: C, 67.64; H, 7.42.

3.3.2. (DMSHC)$TiCl_2$ (**10**)

A pentane (8.0 mL) solution of $TiCl_4$ (0.379 g, 2.00 mmol) was added dropwise into a stirred suspension of (DMSHC)H_2 (0.805 g, 1.67 mmol) in ether (50 mL) at −50 °C. The mixture turned orange-brown and was warmed gradually to room temperature and let stir for 24 h. The precipitate was filtered, washed with pentane (3 × 7 mL), and the orange product was dried in vacuo. Yield: 0.838 g, 84% based on the amount of (DMSHC)H_2. ^{1}H NMR ($CDCl_3$) δ: 6.84-7.24 (m, 12H, arom CH), 4.40 (d, $J = 14.8$ Hz, 1H, calix-CH_2), 4.34 (d, $J = 14.2$ Hz, 1H, calix-CH_2), 4.11 (d, AB, $J = 17.6$ Hz, 2H, calix-CH_2), 3.97 (d, AB, $J = 17.6$ Hz, 2H, calix-CH_2), 3.66 (d, $J = 14.2$ Hz, 1H, calix-CH_2), 3.51 (d, $J = 14.2$ Hz, 1H, calix-CH_2), 0.38 (s, 3H, *exo*-$SiCH_3$), −1.60 (s, 3H, *endo*-$SiCH_3$). Anal. Calcd. for $C_{30}H_{26}O_4SiTiCl_2$: C, 60.32; H, 4.39. Found: C, 59.97; H, 4.33.

3.3.3. (DMSMC)$TiCl_2$ (**11**)

A pentane (5.0 mL) solution of $TiCl_4$ (0.208 g, 1.09 mmol) was added dropwise into a stirred suspension of (DMSMC)H_2 (0.536 g, 1.00 mmol) in ether (30 mL) at −40 °C. The mixture turned orange-brown and was warmed slowly to room temperature and let stir for 12 h. Volatiles were then removed under vacuum, the residue was washed with pentane (3 × 10 mL), and the orange product was dried in vacuo. Yield: 0.62 g, 95%. ^{1}H NMR (C_6D_6) δ: 6.88 (d, $J = 2$ Hz, 2H, arom CH), 6.77 (d, $J = 2$ Hz, 2H, arom CH), 6.73 (d, $J = 2$ Hz, 2H, arom CH), 6.55 (d, $J = 2$ Hz, 2H, arom CH), 4.54 (d, $J = 14.4$ Hz, 1H, calix-CH_2), 4.39 (d, $J = 14.8$ Hz, 1H, calix-CH_2), 3.86 (d, AB, $J = 16.8$ Hz, 2H, calix-CH_2), 3.76 (d, AB, $J = 17.6$ Hz, 2H, calix-CH_2), 3.33 (d, $J = 14.8$ Hz, 1H, calix-CH_2), 3.24 (d, $J = 14.4$ Hz, 1H, calix-CH_2), 2.21 (s, 3H, *p-Me*-calix), 2.00 (s, 3H, *p-Me*-calix), 0.29 (s, 3H, *exo*-$SiCH_3$), -1.38 (s, 3H, *endo*-$SiCH_3$). ^{12}C NMR ($CDCl_3$): 163.3, 149.7, 138.4, 134.8, 132.1, 131.3, 131.2, 130.7, 129.7, 129.1, 128.8. 127.0, 39.3 (calix-CH_2), 36.2 (calix-CH_2), 35.8 (calix-CH_2), 21.0 (*p-Me*-calix), 4.0 (*exo*-$SiCH_3$), -2.6 (*endo*-$SiCH_3$). Anal. Calcd. for $C_{34}H_{34}O_4SiTiCl_2$: C, 62.49; H, 5.24. Found: C, 62.30; H, 5.36.

3.3.4. (DPSC)$TiCl_2$ (**12**)

A pentane (10 mL) solution of $TiCl_4$ (0.458 g, 2.41 mmol) was added dropwise into a stirred suspension of (DPSC)H_2 (2.00 g, 2.41 mmol) in ether (50 mL) at −40 °C. The mixture turned orange-brown and was warmed slowly to room temperature and let stir for 12 h. Volatiles were then removed under vacuum, the residue was washed with pentane (3 × 5 mL), and the orange product was dried in vacuo. Yield: 1.88 g, 82%. ^{1}H NMR (C_6D_6) δ: 7.65 (m, 2H, arom CH), 7.24 (br d, 2H, arom CH), 6.99-7.13 (m, 8H, arom CH), 6.82 (br d, 2H, arom CH), 6.66 (br t, 2H, arom CH), 6.27 (d, $J = 7$ Hz, 2H, arom CH), 5.16 (d, $J = 15.4$ Hz, 1H, calix-CH_2), 4.93 (d, $J = 14.2$ Hz, 1H, calix-CH_2), 4.17 (d, AB, $J = 17.2$ Hz, 2H, calix-CH_2), 3.81 (d, AB, $J = 17.2$ Hz, 2H, calix-CH_2), 3.38 (d, $J = 15.4$ Hz, 1H, calix-CH_2), 3.12 (d, $J = 15.0$ Hz, 1H, calix-CH_2), 1.40 (s, 18H, *t-Bu*), 1.16 (s, 18H, *t-Bu*). ^{12}C NMR (C_6D_6): 163.3, 150.4, 147.2, 145.3, 138.9, 138.4, 135.4, 133.6, 133.5, 130.6, 130.5, 129.4, 129.3, 129.1. 128.2, 125.6, 125.2, 40.1 (calix-CH_2), 38.7 (calix-CH_2), 38.4 (calix-CH_2), 34.5 ($C(CH_3)_3$), 34.4 ($C(CH_3)_3$), 32.0 (s, $C(CH_3)_3$), 31.6 (s, $C(CH_3)_3$). Anal. Calcd. for $C_{56}H_{62}O_4SiTiCl_2$: C, 71.10; H, 6.60. Found: C, 70.98; H, 6.41.

3.4. Reactivity studies

3.4.1. In situ formation of titananorbornadienes $L_2Ti\{\eta^6$-1,2,4-$C_6H_3(SiMe_3)_3\}$ (L_2 = DESC, DMSMC or DPSC)

12.6 μmol of $C_{14}H_{10}Mg(THF)_3$ was charged into a screw-capped 5-mm NMR tube along with 0.8 mL of C_6D_6. The mixture was heated at 80 °C for 5 min to produce Mg* and release anthracene. The tube was transferred into a glovebox after cooling to room temperature. 106 μmol of $Me_3SiC{\equiv}CH$ was introduced followed by 10.6 μmol of the L_2TiCl_2 complex. The NMR tube was vigorously shaken and the reaction mixture turned dark brown-black. The reaction was monitored at room temperature by ^{1}H NMR spectroscopy until all of the $Me_3SiC{\equiv}CH$ was completely consumed. The formation of a titananorbornadiene complex was confirmed by the observed ^{1}H NMR data and by comparison of the data with that previously reported for structurally characterized (DMSC)Ti{η^6-$C_6H_3(SiMe_3)_3$} (**2a**) [12c].

(DESC)Ti{η^6-1,2,4-$C_6H_3(SiMe_3)_3$} (***13***). ^{1}H NMR (unobstructed resonances, C_6D_6): δ 6.80 (br s, 1H, arom CH), 6.57 (br s, 1H, arom CH), 5.77 (d, J = 12.8 Hz, 1H, calix-CH_2), 5.40 (br d, 1H, $C_6H_3\{SiMe_3\}_3$), 5.06 (br d, 1H, $C_6H_3\{SiMe_3\}_3$), 4.68 (br s, 1H, $C_6H_3\{SiMe_3\}_3$), 4.48 (d, J = 15.6 Hz, 1H, calix-CH_2), 4.18 (br d, J = 16.4 Hz, 1H, calix-CH_2), 4.08 (d, J = 12.8 Hz, 1H, calix-CH_2), 3.86 (d, 1H, J = 16.4 Hz, calix-CH_2), 3.20 (d, J = 15.6 Hz, 1H, calix-CH_2), 1.52 (s, 9H, *t*-Bu), 1.48 (s, 9H, *t*-Bu), 1.35 (s, 9H, *t*-Bu), 1.25 (s, 9H, *t*-Bu), 0.82–0.92 (m, 10H, $SiEt_2$), −0.05 (s, 9H, $C_6H_3\{SiMe_3\}_3$), −0.29 (s, 9H, $C_6H_3\{SiMe_3\}_3$), −0.35 (s, 9H, $C_6H_3\{SiMe_3\}_3$). After complete consumption of $Me_3SiC{\equiv}CH$, ^{1}H NMR revealed ~3:1 ratio of 1,2,4-$C_6H_3(SiMe_3)_3$ and 1,3,5-$C_6H_3(SiMe_3)_3$, along with minor amounts unidentified Ti(IV) species.

(DMSMC)Ti{η^6-$C_6H_3(SiMe_3)_3$} (***14***). ^{1}H NMR (unobstructed resonances, C_6D_6): 6.56 (br s, 1H, arom CH), 6.39 (br s, 1H, arom CH), 6.16 (br s, 1H, arom CH), 5.78 (d, J = 12.8 Hz, 1H, calix-CH_2), 5.48 (br d, 1H, $C_6H_3\{SiMe_3\}_3$), 5.21 (br d, 1H, $C_6H_3\{SiMe_3\}_3$), 4.71 (br s, 1H, $C_6H_3\{SiMe_3\}_3$), 4.31 (d, J = 15.2 Hz, 1H, calix-CH_2), 4.11 (d, J = 16.8 Hz 1H, calix-CH_2), 3.93 (d, J = 12.8 Hz, 1H, calix-CH_2), 3.69 (m, 2H, calix-CH_2) 3.48 (d, 1H, J = 16 Hz, calix-CH_2), 3.14 (d, J = 16 Hz, 1H, calix-CH_2), 2.34 (s, 3H, calix-Me), 2.30 (s, 3H, calix-Me), 2.14 (s, 3H, calix-Me), 2.08 (s, 3H, calix-Me), −0.02 (s, 9H, $C_6H_3\{SiMe_3\}_3$), −0.23 (s, 9H, $C_6H_3\{SiMe_3\}_3$), −0.34 (s, 9H, $C_6H_3\{SiMe_3\}_3$), −0.65 (s, *endo*-SiMe). After complete consumption of $Me_3SiC{\equiv}CH$, ^{1}H NMR revealed ~2:1 ratio of 1,2,4-$C_6H_3(SiMe_3)_3$ and 1,3,5-$C_6H_3(SiMe_3)_3$, along with minor amounts of an unidentified Ti(IV) species.

(DPSC)Ti{η^6-$C_6H_3(SiMe_3)_3$} (***15***). ^{1}H NMR (unobstructed resonances, C_6D_6): δ 6.86 (br d, 1H, arom CH), 6.72 (br d, 1H, arom CH), 6.60 (br d, 1H, arom CH), 5.37 (br d, 1H, $C_6H_3\{SiMe_3\}_3$), 5.26 (d, 1H, calix-CH_2), 5.03 (br d, 1H, $C_6H_3\{SiMe_3\}_3$), 4.99 (d, J = 16.4 Hz, 1H, calix-CH_2), 4.71 (br s, 1H, $C_6H_3\{SiMe_3\}_3$), 4.43 (d, J = 17.2 Hz, 1H, calix-CH_2), 4.20 (d, J = 17.6 Hz, 1H, calix-CH_2), 4.04 (d, 1H, calix-CH_2), 4.03 (d, 1H, calix-CH_2), 3.15 (d, J = 16.4 Hz, 1H, calix-CH_2), 1.40 (s, 9H, *t*-Bu), 1.37 (s, 9H, *t*-Bu), 1.31 (s, 9H, *t*-Bu), 1.22 (s, 9H, *t*-Bu), −0.09 (s, 9H, $C_6H_3\{SiMe_3\}_3$), −0.30 (s, 9H, $C_6H_3\{SiMe_3\}_3$), −0.34 (s, 9H, $C_6H_3\{SiMe_3\}_3$). After complete consumption of $Me_3SiC{\equiv}CH$, ^{1}H NMR revealed ~3:1 ratio of 1,2,4-$C_6H_3(SiMe_3)_3$ and 1,3,5-$C_6H_3(SiMe_3)_3$, along with minor amounts unidentified Ti(IV) species.

3.4.2. Typical alkyne cyclotrimerization procedure using $[L_2TiCl_2]/Mg^*$ (L_2 = DESC, DPSC, DMSMC or DMSHC) as catalyst

Method 1: 10.6 μmol of (DPSC)$TiCl_2$ (**12**), 12.6 μmol of $C_{14}H_{10}Mg(THF)_3$, and 106 μmol of 2-pentyne were charged into a screw-capped 5-mm NMR tube along with 0.8 mL of C_6D_6. The reaction mixture was heated at 75 °C and the course of the reaction was monitored by ^{1}H NMR until the alkyne was completely consumed. At this point, the C_6D_6 solution was poured into pentane (15 mL) and treated with MeOH (0.5 mL). This solution was allowed to stand for 20 min in the air and was then passed through a plug of silica gel. An appropriate aliquot of the solution was subjected to GC-MS analysis.

Method 2: 12.6 μmol of $C_{14}H_{10}Mg(THF)_3$ was decomposed into Mg* and anthracene in C_6D_6 (0.8 mL) in a screw-capped 5-mm NMR tube at 80 °C. After cooling to ambient temperature, 10.6 μmol of L_2TiCl_2 and 106 μmol of alkyne were then charged into the NMR tube. The reaction was monitored by ^{1}H NMR and worked-up as described in method 1.

The substituted benzene products were characterized by ^{1}H NMR and MS data, as well as by comparison to literature data (see Supplementary Material).

3.5. Crystallographic study

The crystal data for $(ClPh_2Si)_2$Calix-H_2 (**7**), (DPSC)$TiCl_2$ (**12**), and the titanacyclopentene derivative **16** · 1.5(C_5H_{12}) are collected in Table 1. Further details of the crystallographic study are given in the supplementary material.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 215560–215562 for **7**, **12**, and

16 · 1.5(C_5H_{12}), respectively. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.Ccdc.cam.ac.uk).

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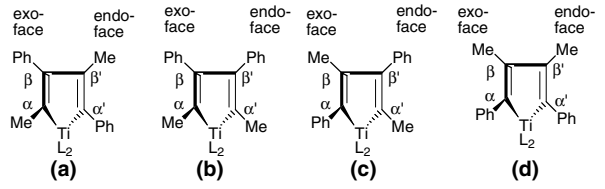
[28] A reaction proceeding via a statistical distribution of the four possible titanacyclopentadiene intermediates (**A**–**D**, below) with identical rates would yield a 3:1 ratio of 1,2,4- and 1,3,5-substitutional isomers. For relevant mechanistic discussion, see Ref. [12b] and J.E. Hill, G. Balaich, P.E. Fanwick, I.P. Rothwell, Organometallics 12 (1993) 2911.



[29] The black mixture obtained on reaction of 1.20 g (1.27 mmol) of $(DPSC)TiCl_2$ (**12**) with 0.950 mg (2.26 mmol) of Mg* and 0.646 mL (5.16 mmol) of PhC≡CMe in toluene/THF at room temperature was concentrated to dryness and then the volatiles were removed in vacuo. The remaining solids were triturated with heptane, extracted with pentane until the washings were colorless and then filtered. The pentane extract was concentrated and the residue was treated with ~5 mL of ether. Crystals of the titanacyclopent-2-ene derivative **16** were obtained from the resulting solution at −15 °C..

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