Highly Regioselective [2 + 2 + 2] Cycloaddition of Terminal Alkynes Catalyzed by η^6-Arene Complexes of Titanium Supported by Dimethylsilyl-Bridged *p-tert*-Butyl Calix[4]arene Ligand

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Abstract: Two new Ti−η^6-arene complexes [(DMSC)Ti{η^6-1,2,4-$C_6H_3(SiMe_3)_3$}] (**6**) and [(DMSC)Ti{η^6-1,3,5-$C_6H_3Bu^t_3$}] (**7**) containing 1,2-alternate, Me_2Si-bridged *p-tert*-butylcalix[4]arene (DMSC) ancillary ligand have been synthesized. The solid-state structure of **6** revealed a highly folded arene ligand [with a dihedral angle of 29.7(7)°] and suggests that **6** is better described as a 7-titananorbornadiene species. Both **6** and **7** are efficient catalysts for highly regioselective [2 + 2 + 2] cycloaddition of terminal alkynes to yield 1,2,4-substituted benzenes. Kinetic studies of the catalytic [2 + 2 + 2] cycloaddition of $Me_3SiC{\equiv}CH$ revealed first-order dependence on [**6**] and [$Me_3SiC{\equiv}CH$]; and activation parameters, $\Delta H^{\ddagger} = 14$ kcal/mol, and $\Delta S^{\ddagger} = -11$ cal/mol K, that are consistent with an associative mechanism. The reaction rate is influenced by the steric requirements of both the alkyne and the η^6-arene compound. The high selectivity for 1,2,4-substituted benzene may be understood in terms of the directing influence of the DMSC ligand.

Introduction

The organometallic chemistry of the group 4 metals has been studied using mainly complexes supported by cyclopentadienyl (Cp) or substituted Cp ligands.[1] Since the electronic and steric properties of an ancillary ligand can have a pronounced effect on the reactivity of a transition metal complex, non-Cp ligand arrays such as chelating diamides,[2] aryloxides,[3] carboranes,[4] amidinates,[5] porphyrins,[6] tetradentate Schiff bases,[7] borataben-zenes,[8] and calixarenes[9,10a−f] have recently been attracting increased attention, especially with regard to Ziegler−Natta α-olefin polymerization. The use of calixarenes as ancillary ligands in organotransition metal chemistry has not been adequately explored.[9,10] The degree of steric shielding and electronic stabilization provided by a calix[4]arene ligand may be influenced by which conformation it adopts.[11] During the past few years, Floriani has been studying the use of *p-tert*-butylcalix[4]arene and its O-methylated derivatives (in cone

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(1) (a) *Metallocenes: Synthesis. Reactivity. Applications*; Togni, A., Halterman, R. L., Eds.: Wiley-VCH: Weinheim. 1998: Vol 1 and 2. (b) *Comprehensive Organometallic Chemistry II*: Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.: Pergamon: New York. 1995: Vol 4.

(2) See for example: (a) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1996**, *15*, 562. (b) Tsuie, B.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 1392. (c) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 308. (d) Guerin, F.; McConville, D. H.; Payne, N. C. *Organometallics* **1996**, *15*, 5085. (e) Guerin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *15*, 5586. (f) Horton, A. D.; de With, J. *J. Chem. Soc., Chem. Commun.* **1996**, 1375. (g) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672. (h) Scollard, J. D.; McConville, D. H., Payne, N. C.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241. (i) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008. (j) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830. (k) Mack, H.; Eisen, M. S. *J. Organomet. Chem.* **1996**, *525*, 81. (l) Gibson, V. C.; Kimberley, B. S.; White, A. J. P.; Williams, D. J.; Howard, P. *J. Chem. Soc., Chem. Commun.* **1998**, 313. (m) Jeon, Y.-M.; Park, S. J.; Heo, J.; Kim, K. *Organometallics* **1998**, *17*, 3161. (n) Schrock, R. R.; Baumann, R.; Reid, S. M.; Goodman, J. T.; Stumpf, R.; Davis, W. M. *Organometallics* **1999**, *18*, 3649. (o) Flores, M. A.; Manzoni, M. R.; Baumann, R.; Davis, W. M.; Schrock, R. R. *Organometallics* **1999**, *18*, 3220.

(3) See for example: (a) Balaich, G. J.; Hill, J. E.; Waratuke, S. A.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1995**, *14*, 656. (b) Durfee, L. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics*, **1990**, *9*, 75. (c) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1992**, *11*, 1775. (d) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1992**, *11*, 1771. (e) Hill, J. E.; Balaich, G. J.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1991**, *10*, 3428. (f) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 2211. (g) Durfee, L. D.; Hill, J. E.; Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1990**, *28*, 3095. (h) Covert, K. J.; Mayol, A. R.; Wolczanski, P. T. *Inorg. Chim. Acta* **1997**, *263*, 263. (i) Thorn, M. G.; Hill, J. E.; Waratuke, S. A.; Johnson, E. S.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 8630. (j) Johnson, E. S.; Balaich, G. J.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 11086. (k) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1991**, *30*, 145. (l) Okuda, J.; Fokken, S.; Kang, H.-C.; Massa, W. *Chem. Ber.* **1995**, *128*, 221. (m) Fokken, S.; Spaniol, T. P.; Kang, H.-C.; Massa, W.; Okuda, J. *Organometallics* **1996**, *15*, 5069. (n) Eilerts, N. W.; Heppert, J. A. *Polyhedron* **1995**, *14*, 3271. (o) Thorn, M. G.; Villardo, J. S.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Chem. Comunn.* **1998**, 2127.

(4) See for example: Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455.

(5) See for example: (a) Hagadorn, J. R.; Arnold, J. *Organometallics*, **1998**, *17*, 1355. (b) Hagadorn, J. R.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **1997**, 3087. (c) Hagadorn, J. R.; Arnold, J. *Organometallics*, **1993**, *13*, 4670. (d) Hagadorn, J. R.; Arnold, J. *J. Am. Chem. Soc.* **1996**, *118*, 893. (e) Hao, S.; Feghali, K.; Gambarotta, S. *Inorg. Chem.* **1997**, *36*, 1745. (f) Schmidt, J. A. R.; Arnold, J. J. *Chem. Soc. Chem. Commun.* **1999**, 2149.

(6) See for example: (a) Gray, S. D.; Thorman, J. L.; Adamian, V. A.; Kadish, K. M.; Woo, K. L. *Inorg. Chem.* **1998**, *37*, 1 (b) Wang, X.; Gray, S. D.; Chen, J.; Woo, K. L. *Inorg. Chem.* **1998**, *37*, 5. (c) Woo, K. L.; Hays, J. A. *Inorg. Chem.* **1993**, *32*, 2228. (d) Woo, K. L.; Hays, J. A.; Jacobson, R. A.; Day, C. L. *Organometallics* **1991**, *10*, 2102.

(7) See for example: (a) Tjaden, E. B.; Sewnson, D. C.; Jordan, R. F.; Petersen, J. L. *Organometallics*, **1995**, *14*, 371. (b) Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Dalton Trans.* **1992**, 367.

(8) See for example: Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmad, S.; Muller, C. *J. Am. Chem. Soc.* **1996**, *118*, 2291. (b) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmad, S.; Kampf, J. W. *Organometallics* **1997**, *16*, 2492. (c) Barnhart, R. W.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 1082. (d) Rogers, J. S.; Bazan, G. C.; Sperry, C. K. *J. Am. Chem. Soc.* **1997**, *119*, 9305. (e) Ashe, A. J., III; Al-Ahmad, S.; Fang, X.; Kampf, J. W. *Organometallics* **1998**, *17*, 3883.

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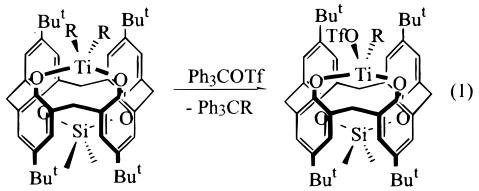
conformation) to support organometallic chemistry at early transition metal centers.[9,10g−k]

We have been investigating the potential of bis(aryloxide) ligands derived from *p-tert*-butylcalix[4]arene in early transition metal chemistry. Recently, we described the synthesis of Ti(IV) complexes supported by proximally bridged *p-tert*-butylcalix[4]arenes in 1,2-alternate conformation.[12,13] In this conformation, the calix[4]arene ligand imposes a unique stereochemical environment at titanium. For example, the two chloride ligands in (DMSC)$TiCl_2$ (**1**) (DMSC = 1,2-alternate Me_2Si-bridged *p-tert*-butylcalix[4]arene) exist in different stereochemical environments.[13] The *endo*-chloride is located inside the calix[4]arene cavity, above the centers of two aromatic rings while the *exo*-chloride is located outside of the calix[4]arene cavity. The difference between the endo and exo coordination sites is also evident in the reactivity of dialkyl derivatives (DMSC)TiR_2 (**2**, R = Me; **3**, R = CH_2Ph). Thus, **2** and **3** give alkyl-triflato complexes **4** and **5**, respectively; formed by exclusive abstraction of the more exposed *exo*-alkyl (eq 1).[12]



R = Me (**2**) or CH_2Ph (**3**) R = Me (**4**) or CH_2Ph (**5**)

We have found that (DMSC)$TiCl_2$ (**1**) catalyzed the [2 + 2 + 2] cycloaddition of terminal alkynes RC≡CH (R = Me_3Si, Ph, or *p*-tolyl) at 80 °C and in the presence of an excess of sodium (with respect to Ti) to yield the corresponding 1,2,4-substituted benzene with excellent regioselectivity (≥97%) and in excellent yield.[13] Although many transition metals catalyze [2 + 2 + 2] cycloaddition of alkynes to yield substituted benzenes,[14,15] the reaction rarely proceeds with high regioselectivity.[14d] Highly regiocontrolled synthesis of arenes is very attractive since arenes are important building blocks in organic synthesis. In this paper, we present results from our investigation of the scope and mechanism of the [2 + 2 + 2] cycloaddition of terminal alkynes mediated by titanium complexes supported by ancillary DMSC ligation.

Experimental Section

General. All experiments were performed under dry nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. glovebox. Solvents were dried and distilled by standard methods before use. Alkynes were purchased from Aldrich or Farchan and were distilled from CaH_2 prior to use. $Mg(C_{14}H_{10})(thf)_3$[16] was prepared by modification of the reported method. ^1H (200 MHz) and ^{13}C (50.3 MHz) NMR spectra were recorded on a Varian Gemini-200 spectrometer at ∼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. HR-MS analysis was performed in the University of Kentucky Mass-Spectrometry Center. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Ithaca, NY.

[(DMSC)Ti{η^6-$C_6H_3(SiMe_3)_3$}] (6). A suspension of $C_{14}H_{10}Mg(THF)_3$[16] (1.31 g, 3.13 mmol) in 50 mL of toluene was heated under N_2 atmosphere at 90 °C for 30 min, during which time Mg* precipitated. The toluene solution was removed via suction through a glass tube equipped with a glass frit. Mg powder was washed with ether until all of the anthracene was removed. Toluene (30 mL) was added to the flask followed by Me_3SiC≡CH (1.78 mL, 12.5 mmol) and (DMSC)$TiCl_2$ (**1**)[13] (2.06 g, 2.50 mmol). THF (1 mL) was added, while the reaction mixture was vigorously stirred. The mixture quickly turned brown-yellow, it was stirred for 10 min, 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 filtrate was stripped to dryness, and the residue was treated with 15 mL of ether. The resulting suspension was stirred for 30 min and then cooled at −15 °C for 24 h. The suspension was then filtered, and the solids on the filter were washed with 15 mL of cold ether. The yellow product was dried in vacuo (1.80 g, 69%) and identified as **6** on the basis of the following data: ^1H NMR (C_6D_6) δ 7.83 (br, 2H, arom CH), 7.30 (d, J = 2.5 Hz, 1H, arom CH), 7.26 (d, J = 2.5 Hz, 1H, arom CH), 7.01 (d, J = 2.5 Hz, 1H, arom CH), 6.96 (d, J = 2.5 Hz, 1H, arom CH), 6.80 (br, 1H, arom CH), 6.60 (br, 1H, arom CH), 5.39 (br d, 1H, $C_6H_3\{SiMe_3\}_3$), 5.14 (br d, 1H, $C_6H_3\{SiMe_3\}_3$), 4.73

(9) See for example: (a) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chim. Acta* **1998**, *270*, 298. (b) Castellano, B.; Zanotti-Gerosa, A.; Solari, E.; Floriani, C. *Organometallics*, **1996**, *15*, 4894. (c) Corazza, F.; Floriani, C.; Lesueur, W.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1990**, 1083. (d) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1990**, 640. (e) Giannini, L.; Caselli, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N.; Sgamellotti, A. *J. Am. Chem. Soc.* **1997**, *119*, 9198. (f) Giannini, L.; Caselli, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N.; Sgamellotti, A. *J. Am. Chem. Soc.* **1997**, *119*, 9709. (g) Giannini, L.; Solari, E.; Zanotti-Gerosa, A.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1996**, *36*, 85. (h) Zanotti-Gerosa, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Chem. Commun.* **1997**, 183. (i) Caselli, A.; Giannini, L.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1997**, *16*, 5457. (j) Floriani, C. *Chem. Eur. J.* **1999**, *5*, 19. (k) Giannini, L.; Solari, E.; De Angelis, S.; Ward, T. R.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. A. *J. Am. Chem. Soc.* **1995**, *117*, 5801.

(10) (a) Olmstead, M. M.; Sigel, G.; Hope, H.; Xu, X.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 8087. (b) Delaigue, X.; Hosseini, M. W.; Leize, E.; Kieffer, S.; Van Doersselaer, A. *Tetrahedron Lett.* **1993**, *34*, 7561. (c) Acho, J. A.; Lippard, S. J. *Inorg. Chim. Acta* **1995**, *229*, 5. (d) Hampton, P. D.; Daitch, C. E.; Alam, T. M.; Bencze, Z.; Rosay, M. *Inorg. Chem.* **1994**, *33*, 4750. (e) Clegg, W.; Elsegood, M. R. J.; Teat, S. J.; Redshaw, C.; Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1998**, *18*, 3037. (f) Hofmeister, G. E.; Alvarado, E.; Leary, J. A.; Yoon, D. I.; Pedersen, S. F. *J. Am. Chem. Soc.* **1990**, *112*, 8843. (g) Castellano, B.; Solari, E.; Floriani, C.; Scopelliti, R.; Re, N. *Inorg. Chem.* **1999**, *38*, 3406. (h) Dovesi, S.; Solari, E.; Scopelliti, R.; Floriani, C. *Angew. Chem., Int. Ed.* **1999**, *38*, 2388. (i) Caselli, A.; Solari, E.; Scopelliti, R.; Floriani, C. *J. Am. Chem. Soc.* **1999**, *121*, 8296. (j) Giannini, L.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1999**, *38*, 1438. (k) Giannini, L.; Solari, E.; Dovesi, S.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1999**, *121*, 2784.

(11) Gutsche, C. D. *Calixarenes*; The Royal Society of Chemistry: Cambridge, U.K., 1989.

(12) Ozerov, O. V.; Ladipo, F. T.; Rath, N. P. *J. Organomet. Chem.* **1999**, *586*, 223.

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

(14) 14. See for example: (a) Ojima, I.; Tzamarioudaki, M.; Zhaoyang, L.; Donovan, R. *J. Chem. Rev.* **1996**, *96*, 635. (b) Negishi, E. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Permagon: Oxford, 1991; Vol. 5, pp 1163−1184. (c) Tamao, K.; Kobayashi, K.; Ito, Y. *Synlett* 1992, 539. (d) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (e) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1.

(15) See for example: (a) McAllister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1666. (b) Volhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (c) Strickler, J. R.; Bruck, M. A.; Wigley, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 2814. (d) Heeres, H. J.; Heeres, A.; Teuben, J. H. *Organometallics* **1990**, *9*, 1508. (e) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 2211. (f) Smith, D. P.; Strickler, J. R.; Gray, S. D.; Bruck, M. A.; Holmes, R. S.; Wigley, D. E. *Organometallics* **1992**, *11*, 1275. (g) Hill, J. E.; Balaich, G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2911. (h) van der Linden, A.; Schaverien, C. J.; Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008. (i) Sigman, M. S.; Fatland, A. W.; Eaton, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 5130. (j) Musso, F.; Solari, E.; Floriani, C.; Schenk, K. *Organometallics*, **1997**, *16*, 4889. (k) Bruck, M. A.; Copenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525. (l) Solari, E.; Floriani, C.; Schenk, K.; Chiesi-Villa, A.; Rizzoli, C.; Rosi, M.; Sgamellotti, A. *Inorg. Chem.* **1994**, *33*, 2018.

(16) (a) Bogdanovic, B.; Liao, S.; Schwickardi, M.; Sikorsky, P.; Spliethoff, B. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 818. (b) Bogdanovic, B. *Acc. Chem. Res.* **1988**, *21*, 261.

(d, 1H, $C_6H_3\{SiMe_3\}_3$), 4.41 (d, $J = 16$ Hz, 1H, calix-CH_2), 4.21 (d, $J = 17$ Hz, 1H, calix-CH_2), 4.13 (d, $J = 14$ Hz, 2H, calix-CH_2), 3.84 (d, $J = 14$ Hz, 1H, calix-CH_2), 3.79 (d, $J = 14$ Hz, 1H, calix-CH_2), 3.59 (d, $J = 17$ Hz, 1H, calix-CH_2), 3.36 (d, $J = 16$ Hz, 1H, calix-CH_2), 1.51 (s, 9H, Bu^t), 1.45 (s, 9H, Bu^t), 1.34 (s, 9H, Bu^t), 1.24 (s, 9H, Bu^t), 0.20 (s, 3H, exo-$SiCH_3$), −0.04 (s, 9H, $C_6H_3\{SiMe_3\}_3$), −0.27 (s, 9H, $C_6H_3\{SiMe_3\}_3$), −0.35 (s, 9H, $C_6H_3\{SiMe_3\}_3$), −0.77 (s, 3H, *endo*-$SiCH_3$); ^{13}C NMR (75 °C, C_6D_6) 161.2(TiO*C*), 160.1(TiO*C*), 152.0(SiO*C*), 150.7(SiO*C*), 142.8, 142.4, 142.3, 141.7, 139.2, 139.0, 136.8, 135.6, 132.8(br), 131.3, 130.9, 129.3, 129.1, 128.9, 128.3, 127.8, 127.3, 127.1, 126.9, 126.8, 126.6, 126.2, 126.0, 125.7, 125.7, 114.3-(br), 41.1 (calix-CH_2), 38.4 (calix-CH_2), 38.1 (calix-CH_2), 36.7 (calix-CH_2), 34.3 (br, $C(CH_3)_3$), 34.2 ($C(CH_3)_3$), 34.0 ($C(CH_3)_3$), 32.1 ($C(CH_3)_3$), 32.0 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$), 31.8 ($C(CH_3)_3$), 2.3 (*exo*-SiMe), 1.3 ($SiMe_3$), 0.3 ($SiMe_3$), −1.9 ($SiMe_3$), −2.0 (*endo*-SiMe). Anal. Calcd for $C_{61}H_{88}O_4Si_4Ti$: C, 70.07; H, 8.48; Cl, 0.00. Found: C, 69.76; H, 8.54; Cl, <0.005.

[(DMSC)Ti(η^6-1,3,5-$C_6H_3Bu^t_3$)] (7). (DMSC)$TiCl_2$ (1.23 g, 1.50 mmol) was treated with a solution of $Me_3SiC{\equiv}CH$ (1.28 mL, 9 mmol) in toluene (20 mL). $C_{14}H_{10}Mg(THF)_3$ (0.63 g, 1.50 mmol) was added to the resulting suspension with rapid stirring. The mixture quickly turned brown-yellow. After 10 min, the volatiles were removed in vacuo. The residue was triturated with heptane and extracted with pentane until extracts became colorless. After the suspension was filtered, all of the extracts were combined and stripped in vacuo. The resulting residue was then dissolved in pentane and filtered. $Bu^tC{\equiv}CH$ (1.0 mL, 8 mmol) was added to the filtrate, and the mixture was stirred for 72 h. After removal of the volatiles in vacuo, the solid residue was washed with pentane (10 mL) and filtered (filtrate discarded). The precipitate was extracted with toluene. After filtration, the toluene extract was concentrated to dryness under reduced pressure. The residue was washed with pentane (10 mL) and dried under vacuum to give an orange product (0.50 g, 33%) which was identified as **7** on the basis of the following data: ^{1}H NMR (C_6D_6) δ 7.84 (d, $J = 2.5$ Hz, 2H, arom CH), 7.36 (d, $J = 2.5$ Hz, 2H, arom CH), 6.88 (d, $J = 2.5$ Hz, 2H, arom CH), 6.74 (d, $J = 2.5$ Hz, 2H, arom CH), 4.87 (s, 3H, C_6H_3-Bu^t_3), 4.76 (d, $J = 15$ Hz, 1H, calix-CH_2), 4.53 (d, $J = 13$ Hz, 1H, calix-CH_2), 4.12 (d, $J = 17$ Hz, 2H, calix-CH_2), 3.87 (d, $J = 13$ Hz, 1H, calix-CH_2), 3.85 (d, $J = 17$ Hz, 2H, calix-CH_2), 3.37 (d, $J = 15$ Hz, 1H, calix-CH_2), 1.50 (s, 18H, calix-Bu^t), 1.22 (s, 18H, calix-Bu^t), 0.44 (s, 3H, exo-$SiCH_3$), 0.33 (s, 27H, $C_6H_3\{CMe_3\}3$), −0.51 (s, 3H, *endo*-$SiCH_3$); ^{13}C NMR (C_6D_6) δ 160.3(TiOC), 151.0(SiO*C*), 142.3, 141.3, 140.9, 135.7, 130.1, 129.1, 128.3, 126.9, 126.8, 126.5, 126.2, 115.5, 39.9 (calix-CH_2), 38.4 (calix-CH_2), 36.4 (calix-CH_2), 34.25 ($C(CH_3)_3$), 34.20 ($C(CH_3)_3$), 33.7 ($C(CH_3)_3$), 31.9 ($C\{CH_3\}_3$), 31.5 ($C\{CH_3\}_3$), 29.5 ($C\{CH_3\}_3$), 4.1 (exo-SiMe), −1.1 (*endo*-SiMe). Anal. Calcd for: C, 77.07; H, 8.89; Cl, 0.00. Found: C, 76.86; H, 8.51; Cl, <0.03.

General Procedure for [2 + 2 + 2] Cycloaddition of Terminal Alkynes in an NMR Tube. Catalyst (5 μmol) was dissolved in 0.6 mL of C_6D_6 in a screw-capped 5-mm NMR tube and 500 μmol of the alkyne was added to it. The course of the reaction was monitored by ^{1}H NMR until the starting alkyne was completely consumed. At this point the ^{13}C NMR spectrum of the product could be obtained. 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 to remove Ti byproducts and *p-tert*-butylcalix[4]arene. An appropriate aliquot of the solution was subjected to GC−MS analysis. Characterization data for **8**−**15** and **18** are given in the Supporting Information.

Synthesis Characterization of 1,2,4-Synthesis and Characterization of 1,2,4-$C_6H_3(CH_2OSiMe_3)_3$ (16). Compound 6 (0.157 g, 0.15 mmol) was dissolved in 30 mL of heptane. $Me_3SiOCH_2C{\equiv}CH$ (4.62 mL, 30.0 mmol) was added in 6 portions (0.77 mL every 2 min).[17] Ten minutes after addition of the last portion, the reaction mixture was treated with MeOH (2 mL). The solution was allowed to stand in air for 30 min and was then passed through a short silica column. Following removal of the volatiles in vacuo, the crude product (3.68 g, 95%) was obtained as a colorless oil that was essentially pure (a small amount of 1,2,4-$(Me_3Si)_3C_6H_3$ was present). Analytically pure product could be isolated by fractional vacuum distillation. The product is a mixture of 1,2,4- and 1,3,5-regioisomers in 95:5 ratio. Spectroscopic data for 1,2,4-$C_6H_3(CH_2OSiMe_3)3$ (**16**): ^{1}H NMR (C_6D_6) δ 7.65 (s, 1H), 7.49 (d, 1H), 7.29 (d, 1H), 4.80 (s, 2H), 4.75 (s, 2H), 4.62 (d, 2H), 0.12 (s, 9H), 0.10 (br s, 18H); ^{13}C NMR (C_6D_6) δ 140.7, 138.8, 137.3, 127.6, 125.7, 125.3, 64.7, 62.6 (br), −0.5 (br). GC−MS(EI) M^+ (384), $M^+ - CH_3$ (369). Anal. Calcd for: C, 56.19; H, 9.43. Found: C, 55.81; H, 9.20.

Characterization of Products from [2 + 2 + 2] Cycloaddition of 1-(Trimethylsilyl)-4-thiahepta-1,6-diyne. 1-(Trimethylsilyl)-4-thiahepta-1,6-diyne[18] (0.88 g, 4.84 mmol) was dissolved in 3 mL of heptane and 4 portions of **6** (21 mg, 0.02 mmol each) were added at 12 h intervals. The reaction was monitored by analyzing aliquots of the solution by ^{1}H NMR. The completion of the reaction was signaled by the absence of the starting diyne peaks. The solution was transferred onto a 15 × 1 cm SiO_2-packed column and eluted with ether. The ether solution was stripped, and the residue was poured onto a similar column of SiO_2. Pentane was used to elute 1,2,4-$C_6H_3(SiMe_3)_3$. The rest of the material was eluted from the column with ether, and the volatiles were removed in vacuo. The product (0.80 g, 91%) was obtained as a yellowish oil. The oil was somewhat cloudy due to the presence of trace amounts of *p*-Bu^t-calix[4]arene, which were removed by filtering the oil neat. ^{1}H NMR and GC−MS analysis of the resulting oil revealed a 91:9 ratio of 1,2,3,4- and 1,2,3,5-regioisomers of 1,3-dihydrobenzothiophene derivative **17** (see text). All of the above manipulations were performed in a glovebox, as **17** is susceptible to decomposition in air. Spectroscopic data for 1,2,3,4-regioisomer (**17a**): ^{1}H NMR (C_6D_6) δ 7.18 (d, $J = 8$ Hz, 1H), 6.82 (d, $J = 8$ Hz, 1H), 4.19 (br t, 2H), 3.96 (s, 2H), 3.89 (br t, 2H), 2.98 (s, 2H), 0.32 (s, 9H, $SiMe_3$), 0.19 (s, 9H, $SiMe_3$); ^{1}H NMR (CD_2Cl_2) δ 7.21 (s, 2H), 4.31 (br t, 2H), 4.15 (br t, 2H), 4.00 (s, 2H), 3.22 (s, 2H), 0.45 (s, 9H, $SiMe_3$), 0.19 (s, 9H, $SiMe_3$); ^{13}C NMR ($CDCl_3$) δ 146.8, 141.7, 139.1, 134.6, 129.2, 125.1, 101.7, 87.8, 39.4, 36.5, 36.1, 20.3, 2.8, −0.2. MS (EI-GC−MS): 364 (M^+), 349 ($M^+ - CH_3$). EI-HRMS: Measured mass (average of four scans): 364.1177 Calculated for $C_{18}H_{28}S_2Si_2$: 364.1171. 1,2,3,5-regioisomer (**17b**): ^{1}H NMR (CD_2Cl_2) δ 7.29 (br s, 1H), 7.22 (br s, 1H), 4.29 (br, 2H), 4.20 (br, 2H), 3.83 (s, 2H), 3.10 (s, 2H), 0.31 (s, 9H, $SiMe_3$), 0.20 (s, 9H, $SiMe_3$).

Synthesis of 1,3-Bis(trimethylsilyl)-6-(4-chlorophenyl)cyclohexa-1,3-diene (19). 6 (0.125 g, 0.12 mmol) was added to a mixture of 4-chlorostyrene (3.2 g, 23 mmol) and $Me_3SiC{\equiv}CH$ (1.65 mL, 11.6 mmol). The reaction mixture was stirred at ambient temperature and monitored by analyzing aliquots of the solution by ^{1}H NMR. The following additions were performed: (i) 0.04 mmol of catalyst was added after 9 h; (ii) 0.02 mmol of catalyst was added after 27 h; (iii) practically all of $Me_3SiC{\equiv}CH$ was consumed after 50 h; hence, another 1.22 mL (8.6 mmol) of $Me_3SiC{\equiv}CH$ was added; (iv) 0.02 mmol of catalyst was added after 95 h; (v) all of $Me_3SiC{\equiv}CH$ was consumed after 100 h, and the reaction was quenched with 0.5 mL of Pr^iOH. Excess 4-chlorostyrene and other volatiles were distilled off in vacuo. The residue was passed through a short SiO_2 column using pentane as eluent. The pentane solution was concentrated under reduced pressure to yield 3.0 g of a colorless oil. NMR and GC−MS analysis revealed that the oil consisted of 80% 1,3 bis(trimethylsilyl)-6-(4-chlorophenyl)-cyclohexa-1,3-diene (**19**), 12% 1,2,4-$(Me_3Si)_3C_6H_3$ and ~8% of isomers of **19**. Attempts to purify the product oil by chromatography or recrystallization were completely unsuccessful, and apparent isomerization occurred upon an attempt to distill the product oil at 0.3 Torr. **19** was therefore characterized as a part of the mixture. ^{1}H NMR (C_6D_6) δ 7.10 (pseudo d, $J = 8$ Hz, 2H, Cl−C_6H_4), 6.92 (pseudo d, $J = 8$ Hz, 2H, Cl−C_6H_4), 6.77 (s, 1H, H_A), 5.90 (dd, $J_{BD} = 2.8$ Hz, $J_{BC} = 5.8$ Hz, 1H, H_B), 3.33 (dd, $J_{CE} = 2.5$ Hz, $J_{DE} = 9.2$ Hz, 1H, H_E), 2.48 (ddd, $J_{BD} = 2.8$ Hz, $J_{DE} = 9.2$ Hz, $J_{CD} = 17.2$ Hz, 1H, H_D), 2.12 (ddd, $J_{BC} = 5.8$ Hz, $J_{CE} = 2.5$ Hz, $J_{CD} = 17.2$ Hz, 1H, H_C), 0.12 (s, 9H, $SiMe_3$), 0.02 (s, 9H, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 141.5, 139.3, 136.4, 135.6, 134.2, 132.4, 129.8, 128.5, 38.7, 32.8, −1.4, −2.0.

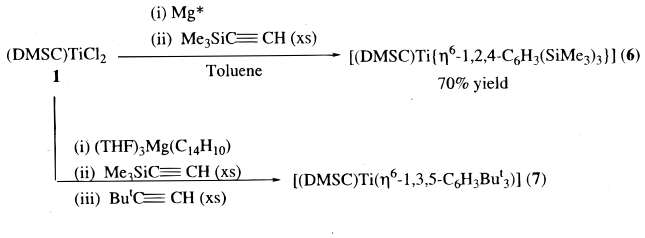
(17) The alkyne was added in portions to overcome deactivation of **6** during the reaction, due probably to oxidative cleavage of the C−O bond. For an example of [2 + 2 + 2] cycloaddition followed by C−O bond cleavage mediated by titanium−aryloxide species, see: Balaich, G. J.; Rothwell, I. P. *Tetrahedron* **1995**, *51*, 4463.

(18) The preparation is given in the Supporting Information.

Table 1. Summary of Crystal Data and Structure Refinement for [(DMSC)Ti{η^6-1,2,4-$C_6H_3(SiMe_3)_3$}] (6)

empirical formula	$C_{64}H_{95}O_4Si_4Ti$
formula weight	1088.66
temperature	173(2) K
wavelength	0.71073 Å
crystal system	triclinic
space group	*P*-1
unit cell dimensions	
	$a = 12.0956(6)$ Å $\alpha = 97.080(10)°$
	$b = 16.2223(8)$ Å $\beta = 100.920(10)°$
	$c = 17.3931(9)$ Å $\gamma = 91.990(10)°$
volume	3319.6(3) Å^3
Z	2
density (calculated)	1.089 mg/m^3
absorption coefficient	0.243 mm^{-1}
F(000)	1178
crystal size	0.47 × 0.26 × 0.105 mm
θ range for data collection	3.05 to 27.92°
index ranges	$0 \le h \le 15$, $-21 \le k \le 21$, $-22 \le l \le 22$
reflections collected	11600
independent reflections	15328 [*R*(int) = 0.0000]
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	11590/17/685
goodness-of-fit on F^2	1.125
Final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0783, wR2 = 0.1730
R indices (all data)	R1 = 0.0939, wR2 = 0.1841
extinction coefficient	0.0000(9)
largest diff. peak and hole	0.788 and −0.580 e·A^{-3}

Scheme 1



Typical Procedure for Kinetic Study of the [2 + 2 + 2] Cycloaddition of Trimethylsilylacetylene. A stock solution of [(DMSC)Ti{η^6-1,2,4-$C_6H_3(SiMe_3)_3$}] (**6**) (0.360 mL, 0.040 M) in C_6D_6 (0.0144 mmol of **6**) was added into an NMR tube, followed by 0.057 mL (0.403 mmol) of $Me_3SiC{\equiv}CH$ and then 0.183 mL of C_6D_6. This resulted in 0.600 mL of a 0.024 M solution of **6**. The tube was vigorously shaken and placed into the spectrometer at a set temperature. The first ^{1}H NMR spectrum (at time = 0) was recorded after the temperature had stabilized. Spectra were recorded at various time intervals thereafter. The time was measured with a timer. The dependence of [2 + 2 + 2] cycloaddition of $Me_3SiC{\equiv}CH$ on catalyst concentration was obtained by varying the concentration of [(DMSC)Ti{η^6-1,2,4-$C_6H_3(SiMe_3)_3$}] (**6**) while conducting each experiment in C_6D_6 at the same temperature, using an identical amount of $Me_3SiC{\equiv}CH$ (0.071 mL, 0.500 mmol) and the same total volume (0.6 mL).

Crystallographic Study. Crystal data and data collection parameters are collected in Table 1. Further details of the crystallographic study are given in the Supporting Information.

Results and Discussion

Synthesis and Characterization of η^6-Arene Complexes. The reduction of (DMSC)$TiCl_2$ (**1**) with Mg($C_{14}H_{10}$)(thf)$_3$[16] or activated Mg, in the presence of an excess of $Me_3SiC{\equiv}CH$ led to isolation of [(DMSC)Ti{η^6-1,2,4-$C_6H_3(SiMe_3)_3$}] (**6**) as a diamagnetic yellow solid (70% yield with Mg* as reductant, Scheme 1). When **1** was reduced with Mg($C_{14}H_{10}$)(thf)$_3$ in the presence of <3 equiv of $Me_3SiC{\equiv}CH$, **6** was the only detectable product. Reduction of **1** by Mg($C_{14}H_{10}$)(thf)$_3$ in the absence of alkyne did not yield a clean product. The formulation and structure of **6** were established by microanalysis, ^{1}H and ^{13}C NMR and X-ray crystallography. NMR data demonstrate that **6** is C_1-symmetric in solution, three singlets are observed in the ^{1}H NMR spectrum for the inequivalent η^6-arene $SiMe_3$ groups while the calix[4]arene Bu^t groups show as four singlets. That the calix[4]arene 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, which are observed as separate signals at δ −0.77 and 0.20, respectively (^{1}H NMR), and at δ −2.0 and 2.3, respectively (^{13}C NMR). Invariably, ^{1}H and ^{13}C NMR resonances for the *endo*-Me are strongly shielded compared to corresponding signals for the *exo*-Me, due most probably to ring current effect.[19,20] The η^6-arene ring-protons are observed as a singlet and two doublets, consistent with 1,2,4-substitution. These resonances are slightly broad at 25 °C but become sharp at < −30 °C and > 40 °C. The broad peaks could be a result of the arene oscillating or rotating about the Ti−C_6(ring) vector.

Single-crystals of [(DMSC)Ti{η^6-1,2,4-$C_6H_3(SiMe_3)_3$}] (**6**) suitable for an X-ray diffraction study were obtained by slow evaporation from heptane at ambient temperature. The molecular structure of **6** (Figure 1) confirmed that the calix[4]arene ligand exists in 1,2-alternate conformation and that the $SiMe_3$ groups are 1,2,4-substituted about the η^6-arene. Selected metrical parameters are listed in Table 2. The η^6-arene ligand is characterized by substantial folding[21] and a loss of aromatic character; the dihedral angle between the C48−C49−C50−C51 plane and the C48−C47−C52−C51 plane is 29.7(7)°. This folding suggests a strong contribution from the highly reduced cyclohexadiene dianion resonance structure (Figure 2). Although **6** may be conceived as a Ti(II)-η^6-arene complex, it possesses significant Ti(IV) character and is probably more precisely described as a 7-titananorbornadiene complex. The Ti−C bond distances are reflective of this structure, C48 and C51 approach Ti more closely (2.142(3) and 2.150(3) Å, respectively) than the other four arene carbons (2.324−2.422 Å).[22] The C−C bonds in the η^6-arene ring also reflect the apparent loss of aromaticity, having short C47−C52 and C49−C50 bonds and longer C47−C48, C48−C49, C50−C51, and C51−C52 interactions (Table 2).[23] As shown in Figure 1, the environment about the titanium center in **6** may be described as pseudo-tetrahedral (with O1, O2, C48, and C51 as vertexes of the tetrahedron, see Table 2 for bond angles). One tetrahedral face is sterically protected by the highly distorted 1,2-alternate DMSC ligand. The severe distortion of the DMSC ligand is evidently due to the steric requirements of the bulky $SiMe_3$ groups of the 1,2,4-substituted arene ring.

Arene complexes of titanium are quite rare, and two main classes of such species are known: Ti(0) sandwich complexes [(η^6-arene)$_2$Ti][24−27] and Ti(II)−η^6-arene complexes.[28−34] In

(19) Fan, M.; Zhang, H.; Lattman, M. *Organometallics* **1996**, *15*, 5216.
(20) Gunther, H. *NMR Spectroscopy: An Introduction*; Wiley: New York, 1980; pp 77−86.
(21) For a discussion of structurally folded arenes, see: Arney, D. J.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1990**, *9*, 1282.
(22) In this context, it is interesting to note that Ti−C48 and Ti−C51 distances are in the range expected for Ti(IV)−C(sp3) bonds. See for example: Chesnut, R. W.; Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *Polyhedron* **1987**, *6*, 2019.
(23) The short C−C bonds (C47−C52 and C49−C52) are slightly elongated from C(sp2)−C(sp2) bond distance of 1.34 Å, while the longer C−C bonds have lengths between those of benzene (1.395 Å) and a C(sp3)−C(sp3) bond = 1.54 Å. See: Loudon, G. M. *Organic Chemistry*, 3rd ed.; Benjamin/Cummings: Redwood City, 1995; p 717.
(24) Anthony, M. T.; Green, M. L. H.; Young, D. *J. Chem.. Soc. Dalton Trans.* **1975**, 1419.
(25) Morand, P. D.; Francis, C. G. *Inorg. Chem.* **1985**, *24*, 56.

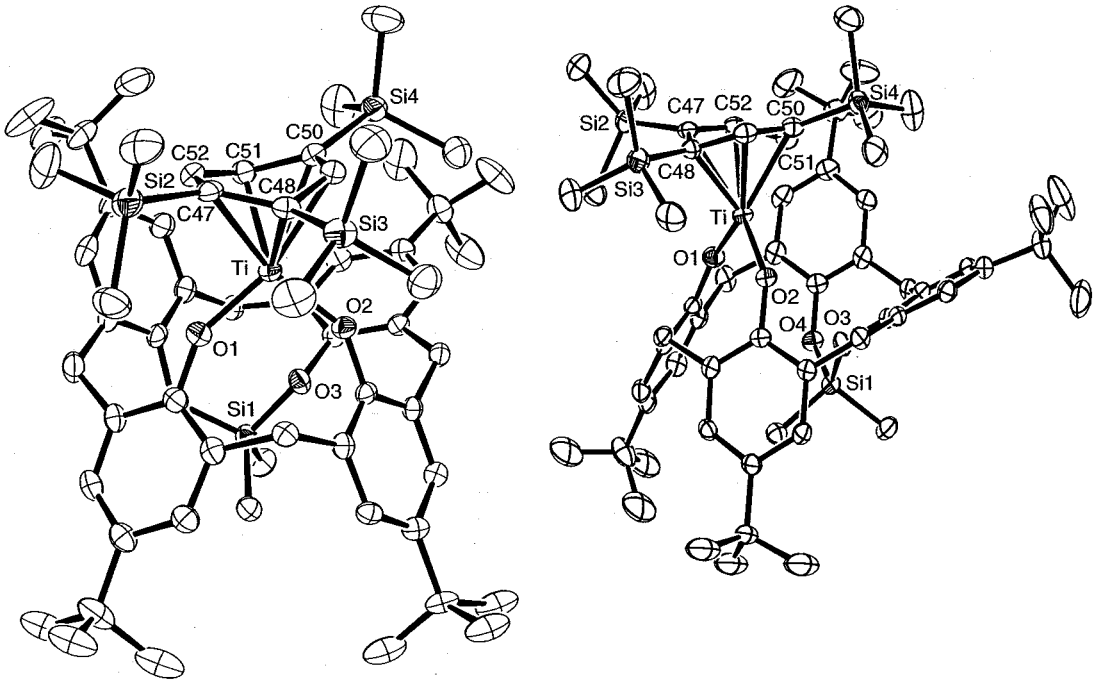


Figure 1. Molecular structure of [(DMSC)Ti{η^6-1,2,4-$C_6H_3(SiMe_3)_3$}] (**6**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **6**

Ti(1)−O(1)	1.829(2)	O(1)−Ti(1)−O(2)	100.41(11)
Ti(1)−O(2)	1.841(2)	O(1)−Ti(1)−C(48)	117.09(12)
Ti(1)−C(48)	2.142(3)	O(2)−Ti(1)−C(48)	113.53(12)
Ti(1)−C(51)	2.150(3)	O(1)−Ti(1)−C(51)	114.86(12)
Ti(1)−C(52)	2.340(3)	O(2)−Ti(1)−C(51)	127.67(12)
Ti(1)−C(49)	2.354(3)	C(48)−Ti(1)−C(51)	84.10(13)
Ti(1)−C(47)	2.379(3)		
Ti(1)−C(50)	2.422(3)		
C(47)−C(52)	1.388(5)		
C(47)−C(48)	1.490(5)		
C(48)−C(49)	1.476(5)		
C(49)−C(50)	1.365(5)		
C(50)−C(51)	1.460(5)		
C(51)−C(52)	1.447(5)		

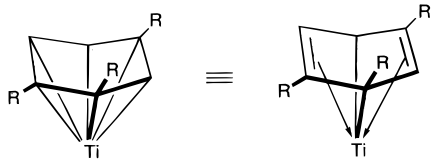


Figure 2. Cyclohexadiene dianion resonance structure of the η^6-arene ligand of **6**.

comparison with the arene ligand in **6**, Ti(II)−η^6-arene complexes generally show nearly planar arene rings with longer Ti−C bonds (∼2.50 Å).[28−34] Arnold and co-workers[35] have recently reported a Ti−η^6-toluene complex supported by a cyclohexane-linked bis(amidinate) ligand, which displayed a puckered arene structure (analogous to **6**) with a dihedral angle of 20.0°. Ti(0)−naphthalene complex [(η^6-$C_{10}H_8$)Ti{Bu^{t}Si(CH_2-PMe_2)$_3$}] was reported to have a dihedral angle of 12.4°.[27] Also, Wigley and colleagues have reported several (η^6-C_6Me_6)TaX_3 (X = O-2,6-$C_6H_3{}^iPr_2$ or Cl) complexes with dihedral angles in the range of 26−34°.[21] The folding of the arene ligand in these complexes has been attributed to a strong metal to ligand δ back-bonding interaction from a filled $d_{x^2-y^2}$ orbital into the LUMO of the arene.[21,36]

The [2 + 2 + 2] cycloaddition of Bu^{t}C≡CH by [(DMSC)-Ti{η^6-1,2,4-$C_6H_3(SiMe_3)_3$}] (**6**) gave [(DMSC)Ti{η^6-1,3,5-$C_6H_3Bu^t_3$}] (**7**) as a diamagnetic orange solid in fair yield (Scheme 1). In contrast to **6**, a significant amount of **7** was not produced when (DMSC)$TiCl_2$ (**1**) was reduced with Mg-($C_{14}H_{10}$)$(thf)_3$ in the presence of an excess of Bu^{t}C≡CH. Presumably, the formation of η^6-1,2,4-$C_6H_3Bu^t_3$ is disfavored because it results in increased steric repulsion between Bu^t groups in comparison to η^6-1,3,5-$C_6H_3Bu^t_3$.[37] In comparison with 1,2,4-$C_6H_3(SiMe_3)_3$, greater repulsive interaction between Bu^t groups should occur in 1,2,4-$C_6H_3Bu^t_3$ because the C−C bond (1.54 Å) is significantly shorter than the C−Si bond (1.85 Å).[38] Microanalysis data confirmed the formulation given for **7**. ^{1}H and ^{13}C NMR studies established that **7** is C_s-symmetric in solution. The data are consistent with a symmetrically substituted η^6-arene and a 1,2-alternate calix[4]arene ligand. Thus, the Bu^t groups of the calix[4]arene ligand are observed as two singlets, and the bridging methylene protons show as two pairs of doublets and an AB system (integrating as four protons) in the ^{1}H NMR spectrum. In the ^{13}C NMR spectrum, the bridging methylene carbons show as three peaks at δ 36.8,

(26) Hawker, P. N.; Kundig, E. P.; Timms, P. L. *J. Chem.. Soc. Chem. Commun.* **1978**, 730.
(27) Gardner, T. G.; Girolami, G. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1693.
(28) Fischer, E. O.; Rohrschied, F. *J. Organomet. Chem.* **1966**, *6*, 53.
(29) Martin, F.; Vohwinkel, F. *Chem. Ber.* **1961**, *94*, 2416.
(30) Thewalt, U.; Osterle, F. *J. Organomet. Chem.* **1979**, *172*, 317.
(31) Thewalt, U.; Stollmaier, F. *J. Organomet. Chem.* **1982**, *228*, 149.
(32) Calderazzo, F.; Ferri, I.; Pampaloni, G.; Englert, U.; Green, M. L. H. *Organometallics* **1997**, *16*, 3100.
(33) Troyanov, S. *J. Organomet. Chem.* **1994**, *475*, 139.
(34) Troyanov, S.; Polacek, J.; Antropiusova, H.; Mach, K. *J. Organomet. Chem.* **1992**, *431*, 317.
(35) Hagadorn, J. R.; Arnold, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 1729.
(36) (a) Green, J. C.; Kelly, M. R.; Grebenik, P. D.; Briant, C. E.; McEvoy, N. A.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, *228*, 239. (b) Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic Press: New York, 1973; pp 257−259.
(37) Molecular mechanics calculations (using CS Chem3D Pro version 3.2, CambridgeSoft Corporation) of the steric energies of 1,3,5- and 1,2,4-$R3C_6H_3$ (R = Bu^t, $SiMe_3$, or Ph) reveal that 1,3,5-substituted benzenes possess lower steric energy in each case [$\Delta\Delta H° = \Delta H$ (1,2,4-$R3C_6H_3$) − ΔH (1,3,5-$R3C_6H_3$)
(38) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.: Harper-Collins: New York, 1993.

38.8, and 39.9 (doubly intense), consistent with chemical shifts previously reported by us for corresponding carbons of 1,2-alternate DMSC-based titanium complexes.[12,13] Analogous to **6** and consistent with the structural characterization by Wigley et al.[15f] of a folded arene for [(η^6-1,3,5-$C_6H_3Bu^t_3$)Ta(CH_3)(O-2,6-$C_6H_3{}^iPr_2$)$_2$], the arene ligand in **7** is most likely folded. However, the NMR data does not permit such a structure to be unambiguously established. The Bu^t groups of the η^6-1,3,5-C_6H_3-Bu^t_3 ligand are observed in the ^{1}H NMR spectrum as a singlet at δ 0.33, and the ring protons resonate as a singlet at δ 4.87.[39] Also, no new peaks were observed in the spectrum down to −70 °C in toluene-d_8. The equivalence of these groups suggest that the arene ligand does not adopt a static folded structure in solution; and that interconversion among folded structures probably occurs.[40] Unfortunately, all attempts to obtain single crystals of **7** suitable for an X-ray diffraction study have thus far proven unsuccessful.

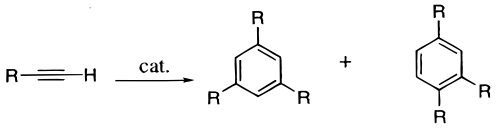
The η^6-arene complexes **6** and **7** are extremely sensitive to oxidation and hydrolysis. Both compounds are soluble in hydrocarbon solvents, especially aromatic hydrocarbon solvents (although **7** is not as soluble as **6**). The compounds are unstable in halogenated organic solvents: **6** is somewhat stable in CH_2Cl_2 with a half-life of several hours, while **7** undergoes fast decomposition in CH_2Cl_2. The decomposition of **7** in $CDCl_3$ is extremely fast, yielding (DMSC)$TiCl_2$ (**1**) and 1,3,5-$C_6H_3Bu^t_3$ quantitatively. **7** is generally less stable than **6**. Thus, **6** is thermally more stable than **7**; decomposing slowly at 80 °C in C_6D_6 ($t_{1/2} \approx 6$ days) with release of 1,2,4-$C_6H_3(SiMe_3)_3$. The decomposition rate was not affected by addition of either PMe_3 or THF. Neither **6** nor **7** undergo arene ligand exchange with C_6D_6 or toluene. Furthermore, **6** was not produced when **1** was reduced with $Mg(C_{14}H_{10})(thf)_3$ in the presence of 1,2,4-C_6H_3-$(SiMe_3)_3$.

Catalytic [2 + 2 + 2] Cycloaddition of Terminal Alkynes. The formation of η^6-arene complexes by [2 + 2 + 2] cycloaddition of alkynes is known;[15f,k,21] and η^6-arene species have been implicated in cyclotrimerization of alkynes.[15] Both **6** and **7** are highly efficient catalysts for [2 + 2 + 2] cycloaddition of terminal alkynes at 25 °C, producing 1,2,4-substituted benzenes with excellent regioselectivity and in excellent yield (Table 3). Even though **7** likely possesses less Ti(IV) character than **6**,[41] it is generally less reactive toward alkynes than **6** for steric reasons (vide infra) The catalytic [2 + 2 + 2] cycloaddition of various alkynes by **6** was investigated. Typically, a mixture of **6** (5 μmol) and alkyne (100 equiv) in C_6D_6 was monitored at 25 °C by ^{1}H NMR. Generally, aliphatic and aromatic terminal alkynes are cyclotrimerized in rapid and exothermic fashion by **6**. However, the reaction occurred more slowly for $Me_3SiC{\equiv}CH$ (200 equiv), proceeding to 98% conversion after 13 h; no decrease in the intensity of the signals of **6** was observed during the course of the catalysis. ^{1}H NMR and GC−MS analysis of the reaction mixture revealed formation of 1,2,4-$C_6H_3(SiMe_3)_3$ (**8a**) and 1,3,5-$C_6H_3(SiMe_3)_3$ (**8b**) in 99:1 ratio. Terminal diynes generally undergo [2 + 2 + 2] cycloaddition at a faster rate than monoynes. For example, catalytic [2 + 2 + 2] cycloaddition of 1,6-heptadiyne (100 equiv) by **6** (5 μmol) is extremely exothermic and was complete in <5 min with **12** as the sole product (eq 2).

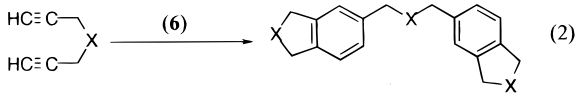
Table 3. Catalytic [2 + 2 + 2] Cycloaddition of Terminal Alkynes

entry no.	alkyne	yield(%)[c] 1,2,4−isomer	1,3,5-isomer
1	trimethylsilylacetylene[a or b]	99 (98)[d]	1
2	1-pentyne[a or b]	96	4
3	Phenylacetylene[a or b]	99 (95)[d]	1
4	*p*-tolylacetylene[a]	99	1
5	1,6-heptadiyne[a]	100	
6	propargyl ether[a]	100	
7	propargyl sulfide[a]	100	
8	*N*,*N*-dimethylpropargylamine[a]	90	10
9	*O*-trimethylsilylpropargyl alcohol[a]	>95 (70)[d]	<5
10	1-(trimethylsilyl)-4-thiahepta-1,6-diyne[a or b]	91 (**17a**)	9 (**17b**)
11	trimethylsilylacetylene[e]	95	5

[a] Catalyzed by [(DMSC)Ti{η^6-1,2,4-$C_6H_3(SiMe_3)_3$}] (**6**) in C_6D_6. [b] Catalyzed by [(DMSC)Ti{η^6-1,3,5-$C_6H_3Bu^t_3$}] (**7**) in C_6D_6;. [c] Ratios determined from GC−MS and ^{1}H NMR data. [d] Isolated yield. [e] Catalyzed by [(DMSC)Ti{η^6-1,2,4-$C_6H_3(SiMe_3)_3$}] (**6**) in C_6D_6 in the presence of THF.



The rate and regioselectivity of the cyclotrimerization reactions are influenced by the steric properties of the alkyne substituent, although modest variation in the steric size of the substituent does not adversely affect the regioselectivity (Table 3). The influence of the steric size of the alkyne substituent on rate and regioselectivity is demonstrated by the reaction of **6** with an excess of $Bu^tC{\equiv}CH$, which gave [(DMSC)Ti{η^6-1,3,5-$C_6H_6Bu^t_3$}] (**7**) and no evidence of catalytic [2 + 2 + 2] cycloaddition of $Bu^tC{\equiv}CH$ over 14 days at 25 °C. Also, no reaction occurred between **6** and more bulky $Pr^i_3SiC{\equiv}CH$ over several hours at 80 °C. Furthermore, internal alkynes are rarely cyclotrimerized, even at elevated temperatures. For instance, 93 h was required for 94% conversion of 65 equiv of 2-butyne into C_6Me_6 at 25 °C, with 21% of the original catalyst (**6**) remaining intact (by ^{1}H NMR). This suggests that the rate-determining step of this cycloaddition proceeds at a faster rate than the reaction between **6** and 2-butyne[42] and that the

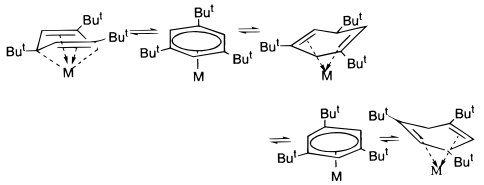


(2)

X = CH_2, **12**; X = O, **13**; X = S, **14**

(39) Arene protons of [(η^6-1,3,5-$C_6H_3Bu^t_3$)Ta(CH_3)(O-2,6-$C_6H_3{}^iPr_2$)$_2$] also show at δ 4.87 in C_6D_6.[15f]

(40) Rapid ring rotation alone cannot account for the equivalence of these groups in a static, folded structure. Wigley et al. have proposed interconversion among folded structures, via planar η^6-arene intermediates, to account for the equivalence of the arene protons in [(η^6-1,3,5-$C_6H_3Bu^t_3$)-Ta(CH_3)(O-2,6-$C_6H_3{}^iPr_2$)$_2$]:[15f,k]

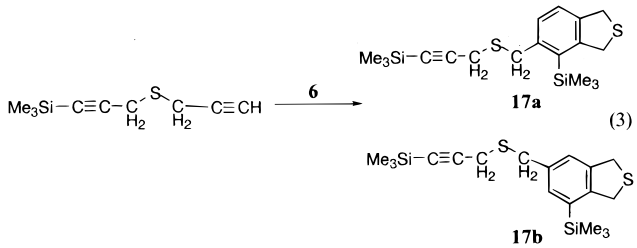


(41) The greater electron-releasing character of the Bu^t group (in comparison with $SiMe_3$) should result in reduced metal-to-ligand σ back-bonding.

(42) We have isolated a product tentatively identified as [(DMSC)TiC_4-Me_4Ti(DMSC)] from the reaction between **6** and 2-butyne. Complete characterization and the role of this product in [2 + 2 + 2] cycloaddition of 2-butyne are under investigation. For related compounds, see: Veldman, M. E. E.; Van der Wal, H. R.; Veenstra, S. J.; De Liefde Meijer, H. J. *J. Organomet. Chem.* **1980**, *197*, 59.

unisolated intermediate [(DMSC)Ti(η^6-1,2,4-C_6Me_6)] reacts faster with 2-butyne than **6**. More bulky internal alkynes such as EtC≡CEt, and Me_3SiC≡CMe did not react with **6** at 80 °C in benzene, nor did any reaction occur between **6** and $MeOCH_2C$≡CCH_2OMe, or Me_3SiC≡$C(CH_2)_3C$≡$CSiMe_3$ at 25 °C over several days. Similarly, catalytic [2 + 2 + 2] cycloaddition was not observed when the reduction of (DMSC)-$TiCl_2$ (**1**) with $Mg(C_{14}H_{10})(thf)_3$ was carried out in the presence of an excess of any of these internal alkynes.

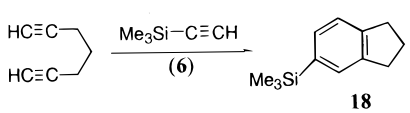
[(DMSC)Ti{η^6-1,2,4-$C_6H_3(SiMe_3)_3$}] (**6**) exhibits modest functional group tolerance. For instance, **6** catalyzed [2 + 2 + 2] cycloaddition of propargylic compounds, bearing oxygen, nitrogen, or sulfur functionality HC≡CCH_2R (R = NMe_2, $OSiMe_3$, SCH_2C≡CH, OCH_2C≡CH, or SCH_2C≡$CSiMe_3$), with high regioselectivity (Table 3). The reaction of **6** with HC≡CCH_2NMe_2 (250 equiv) was complete in <3 min, giving a 90:10 ratio of 1,2,4-$C_6H_3(CH_2NMe_2)_3$ (**15a**) and 1,3,5-$C_6H_3(CH_2NMe_2)_3$ (**15b**). The reduced regioselectivity is probably due to coordination of the amine moiety to titanium, altering the stereochemical environment at titanium (vide infra). Similarly, the cyclotrimerization of HC≡CCH_2OSiMe_3 by **6** gave 1,2,4-$C_6H_3(CH_2OSiMe_3)_3$ (**16**) in 95% yield. It is worth noting that HC≡CCH_2OSiMe_3 is similar to 1-pentyne in terms of its steric influence on the course of the reaction since the Me groups are three atoms away from the C≡C bond; the $SiMe_3$ group thus serves mainly to protect the oxygen atom. The reaction of **6** with Me_3SiC≡CCH_2SCH_2C≡CH in heptane gave the 1,3-dihydrobenzothiophene derivative **17** as 1,2,3,4- and 1,2,3,5-substitutional isomers (**17a** and **17b**, respectively; eq 3) in 91:9 ratio and in 91% yield. The formation of **17b** is likely due to prior coordination of the sulfur atom to titanium (vide infra) or the flexible three-atom linker group which permitted the required orientation of the C≡C bond.



(3)

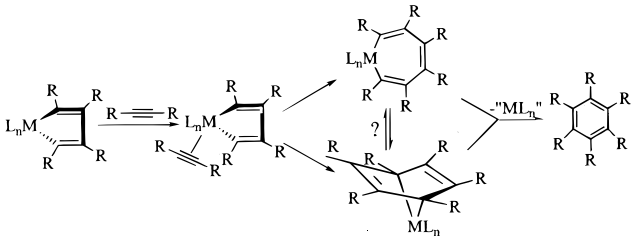
Interestingly, added Et_2O, Et_3N, Bu^tNH_2, PCy_3, PPh_3, Bu^tC≡N, Bu^tMe_2SiC≡N, $SiMe_3Cl$, or $SiMe_3I$ did not affect the rate or regioselectivity of [2 + 2 + 2] cycloaddition of Me_3SiC≡CH catalyzed by **6**. Perhaps in part, because of the relatively crowded environment at titanium. Added THF or TMEDA decreased the selectivity for 1,2,4-$C_6H_3(SiMe_3)_3$ during catalytic cyclotrimerization of Me_3SiC≡CH by **6** (Table 3, entry 11), although neither THF nor TMEDA independently react with **6**. This suggests that THF and TMEDA influence alkyne cyclotrimerization by reacting with coordinatively unsaturated intermediates generated from **6**.

Catalytic Cross-Coupling Reactions. The catalytic [2 + 2 + 2] cycloaddition of Me_3SiC≡CH with a variety of terminal alkynes was investigated. The reaction of **6** (2 μmol) with 1,6-heptadiyne (250 equiv) and Me_3SiC≡CH (250 equiv) at 25 °C in benzene was found to be exothermic, producing the benzocyclopentene derivative **18** almost quantitatively (eq 4). The

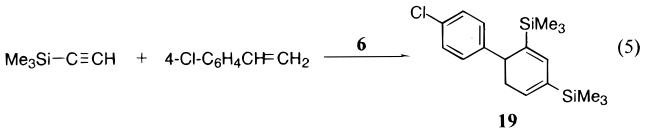


(4)

Scheme 2



selectivity for **18** probably reflects the fact that Me_3SiC≡CH is a better dienophile than 1,6-heptadiyne and effectively participates in reactions after rate-limiting displacement of arene despite its steric bulk. However, analogous reactions with other terminal alkynes generally yielded a distribution of products. We also investigated cross-coupling reactions between Me_3SiC≡CH and olefins. At 25 °C, [(DMSC)Ti{η^6-1,2,4-$C_6H_3(SiMe_3)_3$}] (**6**) catalyzed [2 + 2 + 2] cycloaddition of 4-chlorostyrene with Me_3SiC≡CH to give the 1,3-cyclohexadiene **19** as the major product (80%, GC−MS). Minor isomeric cyclohexadiene products (~8%, GC−MS) and 1,2,4-$C_6H_3(SiMe_3)_3$ (~12%) were also formed (eq 5). Cyclohexadiene isomers can differ by



(5)

double bond positions as well as substitution pattern.[43,44] Hence some of the minor cyclohexadiene isomers may have substituents that are positioned "1,2,4" relative to one another but possess different double bond positions. In this regard, several studies have demonstrated that titanium aryloxide species can isomerize 1,3-cyclohexadienes.[44] Attempts to purify and isolate **19** (see Experimental Section) were unsuccessful. Similar investigation of the cross-coupling reaction between Me_3SiC≡CH and ethylene catalyzed by **6** produced a mixture of products.[45] Only cyclotrimerization of Me_3SiC≡CH occurred in the presence of more bulky terminal or disubstituted olefins including Me_3SiCH=CH_2, Ph_2C=CH_2, Cl_2C=CCl_2, and H_2C=CMe-CMe=CH_2.

Mechanistic Considerations. Much discussion has centered on the nature of the intermediates involved in the [2 + 2 + 2] cycloaddition reaction. Many studies have implicated metallacyclopentadiene[14,15] or η^6-arene[15] intermediates in the reaction. Two pathways have been proposed to account for the reaction of a metallacyclopentadiene intermediate with 1 equiv of alkyne to produce the free arene product (Scheme 2): (i) the two new C−C bonds are formed in a stepwise manner via a metallacycloheptatriene intermediate and (ii) the two new C−C bonds are formed in a concerted fashion (as in the Diels−Alder reaction) via a metallanorbornadiene intermediate. Although the

(43) For a discussion of the NMR of 1,3-cyclohexadienes, see: *The Conformational Analysis of Cyclohexenes, Cyclohexadienes, and Related Hydroaromatic Compounds*; Rabideau, P. W., Ed.; VCH Publishers: New York, 1989; Chapter 3.

(44) See for example: (a) Johnson, E. S.; Balaich, G. J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 7685. (b) Warantuke, S. A.; Johnson, E. S.; Thorn, M. G.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc. Chem. Commun.* **1996**, 2617. (c) Balaich, G. J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1993**, *115*, 1581. (d) Warantuke, S. A.; Thorn, M. G.; Fanwick, P. E.; Rothwell, A. P.; Rothwell, I. P. *J. Am. Chem. Soc.* **1999**, *121*, 9111.

(45) GC−MS analysis of the reaction mixture following protonolysis revealed isomeric mixtures of cyclohexadiene products as well as products of cross-coupling between ethylene and cyclohexadiene species, and among cyclohexadienes. See ref 44d for similar results.

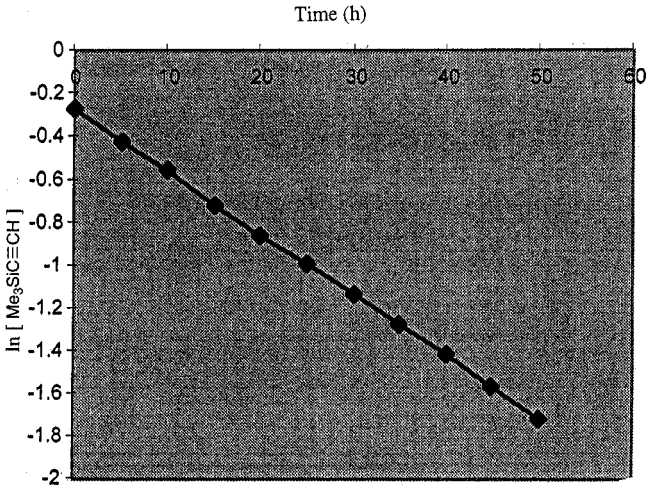
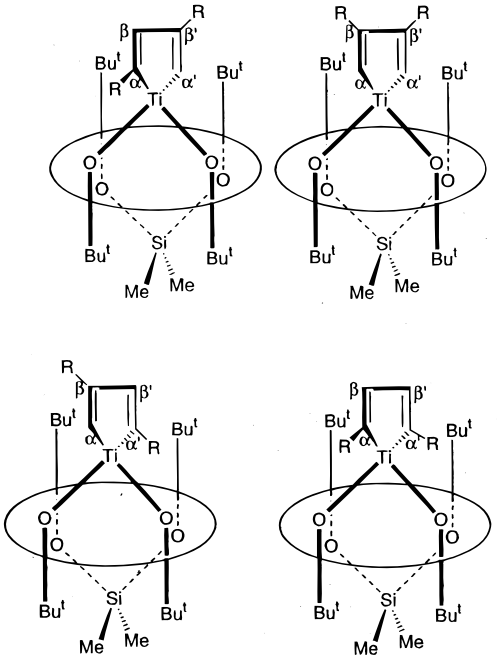


Figure 3. Plot showing the disappearance of $Me_3SiC{\equiv}CH$ with time during [2 + 2 + 2+] cycloaddition.

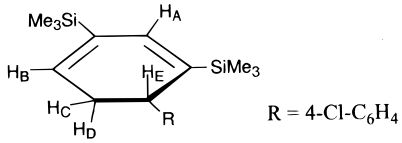
steps in each mechanism have precedence, neither pathway has been unambiguously established. Rothwell et al. have extensively studied reactions of aryloxide-based titanacyclopentadienes with alkynes and olefins;[15g,44] and their results are best interpreted in terms of a concerted pathway for the reactions. Studies by Wigley et al. also suggest a concerted addition pathway for the reactions of tantalacyclopentadiene and tantalanorbornadiene complexes supported by aryloxide ligation.[15c,f] Bianchini and Caulton et al.[46] also favored a concerted pathway for the [2 + 2 + 2] cycloaddition of acetylene at iridium centers. Recently, a theoretical study of the mechanism of the cyclotrimerization of acetylene by $CpCoL_2$ (L = CO, PR_3, olefin) concluded that the intermediacy of a cobaltocycloheptatriene was energetically prohibitive and favored a concerted addition pathway.[47]

In the present work, we found that [(DMSC)Ti{η^6-1,2,4-C_6H_3-$(SiMe_3)_3$}] (**6**) is the resting state of the catalyst in the [2 + 2 + 2] cycloaddition of $Me_3SiC{\equiv}CH$. The catalysis occurs at a convenient rate over a broad temperature range and yields 1,2,4-$C_6H_3(SiMe_3)_3$ almost exclusively (vide supra). Kinetic studies were conducted by adding an excess of $Me_3SiC{\equiv}CH$ to a C_6D_6 solution of **6**, and monitoring the reactions at various intervals by ^1H NMR spectroscopy. The reaction showed first-order dependence on both [**6**] and [$Me_3SiC{\equiv}CH$], confirming that the rate-limiting step is the displacement of 1,2,4-$C_6H_3(SiMe_3)_3$ from **6**. A plot of the disappearance of $Me_3SiC{\equiv}CH$ with time is shown in Figure 3. Analysis of the kinetic data gave activation parameters, $\Delta H^{\ddagger} = 14$ kcal/mol, and $\Delta S^{\ddagger} = -11$ cal/mol K, consistent with an associative mechanism. That **6** did not react with bulky terminal alkynes such as $Pr^i_3SiC{\equiv}CH$, and most internal alkynes may therefore be explained by the inability of the substrates to displace the η^6-arene ligand. In fact, the reaction rate is influenced by the steric requirements of both the alkyne and the η^6-arene compound. Thus, [(DMSC)Ti{η^6-1,3,5-C_6H_3-Bu^t_3}] (**7**) did not cyclotrimerize $Bu^tC{\equiv}CH$ but acts as a catalyst precursor for [2 + 2 + 2] cycloaddition of less bulky alkynes such as phenylacetylene and 1-pentyne, resulting in identical regioselectivities as **6** (Table 3, entries 2 and 3). **7** apparently reacts with these substrates to generate the corresponding η^6-arene complex which does the catalysis. To the best of our knowledge, this study presents the first unambiguous demonstration of the involvement of an η^6-arene (7-titananorbornadiene) species in the rate-limiting step of [2 + 2 + 2] cycloaddition of alkynes.

Scheme 3



The product regiochemistry can be accounted for by a mechanistic pathway in which the stereochemical environment imposed at titanium by the DMSC ligand plays an important role. Four different disubstituted titanacyclopentadiene intermediates are possible (α,α′, α′,β, α,β′, β,β′) each possessing different steric properties (Scheme 3). Both the α,α′- and α′,β-substituted species would probably be disfavored because incorporation of a bulky substituent in the *endo*-α′-position would likely lead to unfavorable steric interactions with nearby aromatic rings and the attached Bu^t groups. Wigley and colleagues[15f] have shown in a related tantalacyclopentadiene system that the thermodynamic stability and kinetic accessibility of the α,α′-substituted regioisomer is lost as steric congestion at the metal center increases. We believe that the 1,2-alternate, DMSC ligand promotes predominant (or quite possibly exclusive) formation of α,β′-substituted titanacyclopentadiene. This belief finds strong support in the cross-coupling reaction of trimethylsilylacetylene with 4-chlorostyrene, which gave **19** as the major cyclohexadiene product (~91% of the cyclohexadiene products). ^1H NMR data established that the $SiMe_3$ groups in **19** are arranged in 1,3-fashion about the cyclohexadiene ring.[43]



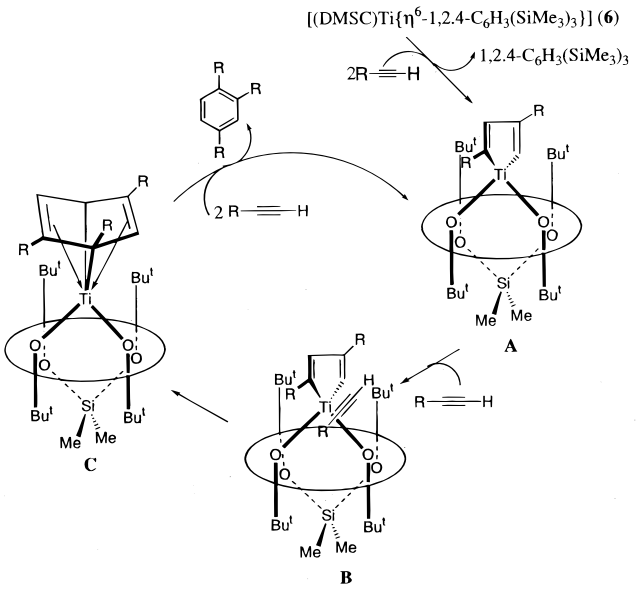
The $SiMe_3$ groups show as different singlets at δ 0.02 and 0.12, and H_A shows as a singlet at δ 6.77. H_B and H_E each show as doublet of doublets at δ 5.90 and 3.33, respectively, while H_D and H_C each show as a doublet of doublets of doublets at δ 2.48 and 2.12, respectively. This product can only be derived from reaction of an α,β′-substituted titanacyclopentadiene with 4-chlorostyrene.

Unlike β,β′-substituted titanacyclopentadiene, which would exclusively yield 1,2,4-substituted benzene regardless of the

(46) Bianchini, C.; Caulton, K. G.; Chardon, C.; Eisenstein, O.; Folting, K.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Rauscher, D. J.; Streib, W. E.; Vizza, F. *J. Am. Chem. Soc.* **1991**, *113*, 5127.

(47) Hardesty, J. H.; Koerner, J. B.; Albright, T. A.; Lee, G.-Y. *J. Am. Chem. Soc.* **1999**, *121*, 6055.

Scheme 4



approach of the third alkyne molecule, α,*β*′-substituted titanacyclopentadiene could give either 1,2,4- or 1,3,5-substituted benzene.[48] The very high regioselectivity for 1,2,4-substituted benzene presented in this report for catalytic [2 + 2 + 2] cycloaddition of terminal alkynes suggests that the DMSC ligand directs the reaction through the stereochemical environment it imposes at titanium. For instance, the related titanium aryloxide, $[(2,6\text{-}Ph_2C_6H_3O)_2Ti(C_4H_2Bu^t_2)]$, was shown to catalyze [2 + 2 + 2] cycloaddition of $Me_3SiC{\equiv}CH$ to yield 1,3,5- and 1,2,4-$C_6H_3(SiMe_3)_3$ in ∼95:5 ratio; and aliphatic alkynes such as 1-pentyne and 1-hexyne, were cyclotrimerized to 1,3,5- and 1,2,4-substituted arene products in ∼1:3 ratio.[15g] We believe the DMSC ligand promotes regioselective formation of 1,2,4-substituted benzenes by exerting steric control over the approach of the third alkyne molecule to the titanacyclopentadiene intermediate. Thus, the preferred orientation for the third alkyne molecule is one in which the bulky R group is pointing out of the calix[4]arene cavity. The product distribution obtained from catalytic [2 + 2 + 2] cycloaddition of $Me_3SiC{\equiv}CCH_2SCH_2C{\equiv}CH$ by **6** is consistent with this proposal. As previously mentioned, **17a** and **17b** were produced in 91:9 ratio and in excellent yield. This result clearly demonstrates that the reaction of $Me_3SiC{\equiv}CCH_2SCH_2C{\equiv}CH$ with the titanacyclopentadiene intermediate selectively occurs through the less-hindered terminal alkyne end (Scheme 4, R = $CH_2SCH_2C{\equiv}CSiMe_3$).

It is important to note that the regiochemistry of the arene product is in fact determined by (at least) two competing effects: (i) the directing influence of the DMSC ligand, and (ii) the steric interaction that would result from ortho-substitution in the arene product. When the arene substituents are Bu^t groups, the second effect apparently wins out, resulting in the formation 1,3,5-substituted arene as in **7**. As indicated earlier, a loss of regioselectivity was noted when alkyne cyclotrimerization reactions were catalyzed by **6** in the presence of a donor ligand such as THF (vide supra). This is presumably due to attenuation of the stereochemical influence of the DMSC ligand on the reactivity of the intermediates generated from **6**, as coordination of THF (or other donor molecule) distorts the environment about titanium from pseudo-tetrahedral. Finally, a concerted pathway best accounts for products of [2 + 2 + 2] cycloaddition catalyzed by **6** and **7**. Support for a concerted pathway can be found in the results of the cross-coupling reaction of 4-chlorostyrene with $Me_3SiC{\equiv}CH$. We did not observe products that can be attributed to *β*-H migration in a titanacyclohepta-2,4-diene intermediate.[49] In contrast, the related complex $[(2,6\text{-}Ph_2C_6H_3O)_2Ti(CH_2CMe{=}CMeCH_2)]$ has been shown to catalyze cross-coupling of 2,3-dimethyl-1,3-butadiene and ethylene via *β*-H elimination from an isolable titanacyclohept-3-ene.[3e]

Table 10

R	1,3,5- $R3C_6H_3$ kcal/mol	1,2,4- $R3C_6H_3$ kcal/mol	$\Delta\Delta H°$
Bu^t	11.0	33.2	22.5
$SiMe_3$	−16.5	−8.3	8.2
Ph	−18.0	−16.0	2

Conclusions

The effect of the DMSC ligand on the mechanism of Ti-catalyzed [2 + 2 + 2] cycloaddition of alkynes is remarkable: DMSC ligation resulted in isolation of Ti-η^6-arene complexes (**6** and **7**) from [2 + 2 + 2] cycloaddition of terminal alkynes; and **6** was the resting state of the catalyst in the [2 + 2 + 2] cycloaddition of $Me_3SiC{\equiv}CH$. Furthermore, 1,2,4-substituted benzenes are formed with excellent regioselectivity. These results represent a sharp departure from those previously observed for related titanium−aryloxide systems, where titanacyclopentadienes are usually formed as stable species and high regioselectivity is rare. In 1,2-alternate conformation, the DMSC ligand sterically defines the reaction sites at titanium; the formation of α,*β*′-substituted titanacyclopentadiene intermediate is apparently favored. The DMSC ligand also exerts steric control over approach of a substrate to the α,*β*′-substituted titanacyclopentadiene; the less hindered end of an olefin or alkyne is directed into the calixarene cavity. Thus, the DMSC ligand results in a dramatic change in the reaction mechanism and regioselectivity in comparison with that previously observed for Ti−aryloxide systems. Further reactivity studies of these and related complexes 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 **6**. Experimental and characterization data for **8**−**15** and **18**, as well as 1-(trimethylsilyl)-4-thia-1,6-heptadiyne (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA994543O

(48) See for example: Wielstra, Y.; Gambarotta, S.; Meetsma, A.; de Boer, J. L.; Chiang, M. Y. *Organometallics* **1989**, *8*, 2696.

(49) This pathway would have to be a very minor one even if one allowed that the mixture of isomeric cyclohexadiene products (∼8% by GC−MS) also contained a product derived a titanacyclohepta-2,4-diene intermediate.