Synthesis and structural characterization of [(C₅H₄)SiMe₂(N-*t*-Bu)]Ti[(*o*-C₆H₄)C(Ph)=C(Ph)], generated via an alkyne-Ti benzyne coupling reaction

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Dedicated to Professor Gerhard Erker on the occasion of his 60th birthday.

Abstract

The thermolysis of [(C₅H₄)SiMe₂(N-*t*-Bu)]TiPh₂ in the presence of diphenylacetylene proceeds at 80 °C in cyclohexane solution with the sole formation of the titanacyclic complex [(C₅H₄)SiMe₂(N-*t*-Bu)]Ti[(*o*-C₆H₄)C(Ph)=C(Ph)], which has been characterized by solution NMR measurements and X-ray crystallographic analysis. This reaction is accompanied by the elimination of benzene and presumably occurs via coupling of a titanium benzyne intermediate with diphenylacetylene. The two chemically inequivalent Ti–C bonds of 2.081(7) and 2.103(6) Å in [(C₅H₄)SiMe₂(N-*t*-Bu)]Ti[(*o*-C₆H₄)C(Ph)=C(Ph)] reflect the increased electrophilicity of the d⁰ Ti(IV) center arising from the presence of the bifunctional *ansa*-cyclopentadienyldimethylsilylamido ligand.
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Keywords: Ti-benzyne intermediate; Coupling reaction; Titanacyclic complex

1. Introduction

Transition metals have the ability to stabilize highly reactive organic fragments, such as benzyne [1]. The heating of a reaction mixture of diphenyltitanocene and diphenylacetylene leads to the elimination of benzene and concomitant formation of a titanacyclic species (Eq. (1)) [2]. Vol'pin and his co-workers [3] subsequently observed that the thermolysis of diphenyltitanocene in the presence of CO₂ produced a five-membered oxatitanacyclic complex (Eq. (2)). Both of these reactions presumably involve the participation of a titanium-benzyne intermediate.

$$Cp_2TiPh_2 + PhC{\equiv}CPh \xrightarrow[-C_6H_6]{\Delta} \quad (1)$$

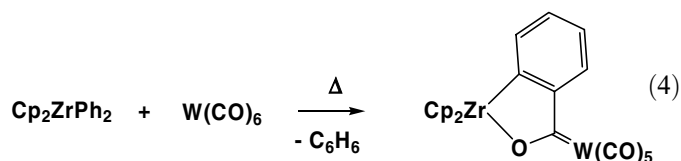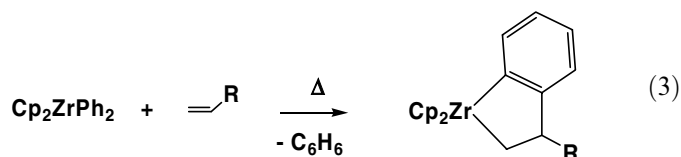$$Cp_2TiPh_2 + CO_2 \xrightarrow[-C_6H_6]{\Delta} \quad (2)$$
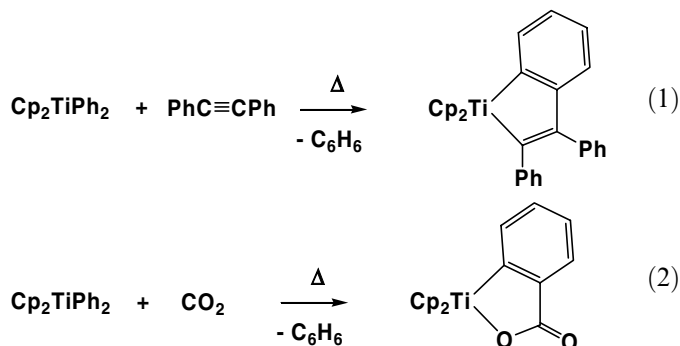
In the late 1970s, Erker [4] investigated the thermal stability of diphenyl- and ditolyl-zirconocene complexes and demonstrated the intermediacy of a benzyne complex. His classic study involved the thermolysis of various diarylzirconocenes in aromatic hydrocarbon solvents and then analyzing the biphenyls produced upon photodegradation. Thermolysis

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of di-*p*-tolylzirconocene and di-*m*-tolylzirconocene in benzene produced mixed tolyl-phenyl Zr complexes with the eventual observation of diphenylzirconocene. Alternatively, thermolysis of diphenylzirconocene in toluene occurs with replacement of the phenyl ligands by tolyl groups and the concerted elimination of benzene. Erker proposed the intermediacy of a Zr-aryne species, which is formed by the abstraction of an *ortho* proton from a σ-bonded aryl ligand by the other aryl ligand. Subsequent reactivity studies revealed that this Zr-aryne intermediate is capable of reductive coupling with olefins to form zirconaindan derivatives (Eq. (3)) [5] and reacting with W(CO)$_6$ to afford a Fischer-type zirconaoxycarbene complex (Eq. (4)) [6]

$$Cp_2ZrPh_2 \ + \ {=}\!\!{-}R \xrightarrow[-\ C_6H_6]{\Delta} Cp_2Zr\ \text{(indan-R)} \qquad (3)$$

$$Cp_2ZrPh_2 \ + \ W(CO)_6 \xrightarrow[-\ C_6H_6]{\Delta} Cp_2Zr\text{–O–}W(CO)_5 \qquad (4)$$

Buchwald and his co-workers [7] extended Erker's seminal contribution by coupling an assortment of nitriles with the Zr-benzyne generated from diphenylzirconocene. More significantly, they successfully isolated the trimethylphosphine adduct of the zirconocene-benzyne intermediate and determined its molecular structure [8]. The structural data revealed that the η^2-benzyne moiety experiences little strain, with the "triple bond" length and angles at the two Zr-bound carbon atoms varying only slightly from those in benzene. In contrast to the in situ generated Zr-benzyne intermediate, its PMe$_3$ adduct reacts cleanly with ketones and nitriles to produce oxazirconacyclopentenes (Eq. (5a)) and azazirconacyclopentadienes (Eq. (5b)) [7,9], respectively
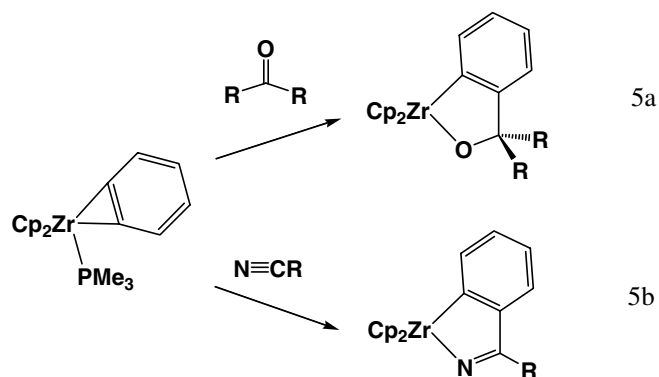
Although the reactivity of group 4 metallocene benzynes has been extensively examined, far less is known about the influence of the electrophilicity of the metal center on the stability and reactivity of the metal-stabilized benzyne. Bercaw and co-workers [10] demonstrated that the replacement of a pair of cyclopentadienyl rings with the dianionic bifunctional chelating ligand [(C$_5$Me$_4$)SiMe$_2$(N-*t*-Bu)]$^{2-}$ provides an effective means to enhance the Lewis acidity of an electrophilic metal center. The weaker π-donating character and lower steric requirement of the amido functionality increases the metal's Lewis acidity by the simultaneous reduction of the formal electron count and the steric congestion at the metal center. The incorporation of bifunctional monocyclopentadienylamido ligands on group 4 metals may be accomplished by conventional metathesis routes [10,11] or by the thermally-induced amine elimination reaction of M(NMe$_2$)$_4$ with (C$_5$R$_4$H)L(NHR′), where L is either a silyl or hydrocarbon linkage [12]. The conversion of [(C$_5$R$_4$)SiMe$_2$(NR′)]M(NMe$_2$)$_2$ to the corresponding dichloride derivatives may in some cases be accomplished by treatment with excess SiMe$_3$Cl [12d,12e].

In this paper, we wish to report the synthesis and structural characterization of [(C$_5$H$_4$)SiMe$_2$(N-*t*-Bu)]Ti[(*o*-C$_6$H$_4$)C(Ph)=C(Ph)], which was prepared by the thermolysis of [(C$_5$H$_4$)SiMe$_2$(N-*t*-Bu)]TiPh$_2$ in the presence of diphenylacetylene. The formation of this titancyclic complex presumably occurs via the coupling of the alkyne with a titanium-benzyne intermediate, reminiscent of the related zirconocene benzyne chemistry initially examined by Gerhard Erker and co-workers 30 years ago.

2. Experimental

2.1. General considerations

Reagent grade hydrocarbon and etheral solvents were purified using standard methods [13] and distilled under nitrogen. These solvents were then transferred to storage flasks containing either [(C$_5$H$_5$)$_2$Ti(μ-Cl)$_2$]$_2$Zn [14] or potassium benzophenone ketyl. Hexamethyldisiloxane was dried over (C$_5$H$_5$)$_2$ZrMe$_2$. The deuterated solvents, C$_6$D$_6$ (Cambridge Isotopes, 99.5%) and CDCl$_3$ (Aldrich, 99.8%), were dried over activated 4A molecular sieves prior to use, as was NH$_2$-*t*-Bu (Acros).

Starting materials such as Ti(NMe$_2$)$_4$, (C$_5$H$_5$)SiMe$_2$(N(H)-*t*-Bu), and [(C$_5$H$_4$)SiMe$_2$(N-*t*-Bu)]TiCl$_2$ were prepared by literature procedures [12d]. Other starting materials such as TiCl$_4$ (Aldrich), LiNMe$_2$ (Aldrich 95%), Na (Aldrich), dicyclopentadiene (Kodak), and phenylmagnesiumbromide (Aldrich) were used without further purification, whereas diphenylacetylene (Kodak) was purified by sublimation. SiMe$_2$Cl$_2$ (Acros) and SiMe$_3$Cl (Acros) were vacuum distilled prior to use.

The ^{1}H and ^{13}C NMR spectra were measured with either a JEOL GX-270 or a JEOL Eclipse 270 NMR spectrometer operating in the FT mode at 270 MHz (^{1}H) or 67.5 MHz (^{13}C). The ^{1}H chemical shifts are referenced to the residual proton peaks of benzene-d_6 at δ 7.15 (vs. TMS) or chloroform-d_1 at δ 7.24 (vs. TMS). The ^{13}C resonances are referenced to the central peak of benzene-d_6 at δ 128.0 (vs. TMS) or chloroform-d_1 at δ 77.0 (vs. TMS).

To minimize exposure to air and moisture, all manipulations and reactions were carried out on a high-vacuum line

or in a Vacuum Atmosphere glovebox equipped with a HE-493 Dri-Train. Reactions were typically carried out in pressure equalizing filter-frits equipped with high vacuum Teflon stopcocks. All glassware was oven-dried or flame-dried under vacuum prior to use. NMR sample tubes were sealed normally under 400–500 Torr of nitrogen pressure. Nitrogen was purified by passage over reduced BTS catalysts and activated 4A molecular sieves. Elemental analyses were performed by E&R Microanalytical Labs, Parsippany, NJ 07054.

2.2. Synthesis of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]TiPh_2$

A 1.50-g sample (4.8 mmol) of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$ was placed in a two-neck 100-mL pear-shaped flask equipped with Solv-seal joints. One neck was capped with a Suba-seal septum and the other was attached to a filter frit assembly. Diethyl ether (ca. 30 mL) was added by vacuum distillation. The reaction mixture was then cooled in a liquid N_2/2-propanol bath. While stirring the reaction mixture under a N_2 flush, 3.20-mL of a 3.0 M solution of PhMgBr in Et_2O was added dropwise via syringe over a 45 min period. The solution was slowly warmed to room temperature and stirred overnight. The solvent was transferred under reduced pressure into a liquid N_2 cooled trap and the product was washed initially with cold pentane to remove soluble impurities and then extracted with pentane to give 1.08 g of a reddish orange crude product, which upon recrystallization gave 0.98 g (51.4% yield) of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]TiPh_2$ as a yellow semi-crystalline solid. Anal. Calc. for $C_{23}H_{29}SiNTi$ (395.45): C, 69.85; H, 7.39; N, 3.54. Found: C, 69.71; H, 7.21; N, 3.63%. ^{1}H NMR (C_6D_6, $^3J_{HH}$ in Hz): δ 8.14, 7.12, 7.09 (C_6H_5, m), 6.56, 5.27 (C_5H_4, t, 2.1), 0.90 (NCMe_3, s), 0.61 (SiMe_2, s). Gated nondecoupled ^{13}C NMR (C_6D_6, $^1J_{CH}$ in Hz): δ 188.4 (*ipso*-carbon of C_6H_5, s), 133.7, 128.7, 126.7 (C_6H_5, d, 169), 118.5, 118.0 (proximal and distal carbons of C_5H_4, d, 169), 110.5 (bridgehead carbon, s), 60.5 (NCMe_3, s), 33.8 (NCMe_3, q, 124), 1.51 (SiMe_2, q, 118).

2.3. Preparation of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]$ $Ti[(o\text{-}C_6H_4)C(Ph)=C(Ph)]$

A 0.492-g sample (1.24 mmol) of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]$-TiPh_2 was combined with 0.222 g (1.24 mmol) of diphenyl-acetylene in a 100 mL pear-shaped flask, which was attached via a Solv-seal joint to a filter-frit assembly. Cyclohexane (ca. 20 mL) was added via vacuum transfer and the reaction mixture was stirred at 80 °C overnight. The solvent was removed under reduced pressure and the red product residue was washed with hexamethyldisiloxane and then dried under vacuo to afford 0.330 g (53.5% yield). Recrystallization by slow removal of pentane from a concentrated solution yielded reddish-orange crystals of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti[(o\text{-}C_6H_4)C(Ph)=C(Ph)]$ suitable for crystallographic analysis. Anal. Calc. for $C_{31}H_{33}NSiTi$ (495.58): C, 75.12; H, 6.71; N, 2.82. Found: C, 75.69; H,

6.38; N, 2.72%. ^{1}H NMR ($CDCl_3$): δ 7.18, 7.13, 7.05, 6.83, 6.75, 6.70 (10 H, C_6H_5), 7.00, 6.96, 6.83, 6.50 (4H, $o\text{-}C_6H_4$), 7.47, 7.03, 6.20, 5.55 (4H, C_5H_4), 1.58 (9H, NCMe_3), 0.59, 0.49 (6H, SiMe_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 206.1, 193.7 (Ti–C), 147.9, 145.8 (Ti–C=C), 144.4, 138.9 (*ipso*-C(Ph)), 131.05, 129.8, 127.8, 126.2, 125.7, 123.7 (C_6H_5), 128.2, 127.4, 126.5, 124.7 ($o\text{-}C_6H_4$), 126.4, 126.0, 122.05, 121.8 (C_5H_4), 107.9 (bridgehead C), 60.1 (NCMe_3), 34.0 (NCMe_3), 1.01, 0.75 (SiMe_2). 2D HETCOR ($CDCl_3$): δ 131.05/6.70, 129.8/7.05, 127.8/7.18, 126.2/7.13, 125.7/ 6.75, 123.7/6.83 (C_6H_5), 128.2/6.96, 127.4/7.00, 126.5/6.50, 124.7/6.83 ($o\text{-}C_6H_4$), 126.4/6.20, 126.0/5.55, 122.05/7.47, 121.8/7.03 (C_5H_4), 34.0/1.58 (NCMe_3), 1.01/0.59, 0.75/ 0.49 (SiMe_3).

2.4. X-ray structural analysis of $[(C_5H_4)SiMe_2$ $(N\text{-}t\text{-}Bu)]Ti(o\text{-}C_6H_4)C(Ph)=C(Ph)]$

A crystal of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti[(o\text{-}C_6H_4)C(Ph)=C(Ph)]$ was sealed in a glass capillary tube under a N_2 atmosphere and then optically aligned on the goniostat of a Siemens P4 X-ray diffractometer. The reflections that were used for the unit cell determination were located and indexed by the automatic peak search routine provided with xscans [15]. A body-centered monoclinic cell was used for data collection and then converted to the conventional C-centered monoclinic cell prior to performing the structural analysis. The lattice parameters and other pertinent crystallographic information are summarized in Table 1.

Intensity data were measured with graphite-monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å) and variable ω scans (2–10°/min). Background counts were measured at the beginning and at the end of each scan with the crystal and counter kept stationary. The intensities of three standard reflections showed no indication of crystal decomposition or sample movement. The raw data were corrected for Lorentz-polarization effects.

Initial coordinates for the non-hydrogen atoms were determined by a combination of direct methods and difference Fourier calculations. The hydrogen atom positions were idealized with isotropic temperature factors set at 1.2 times that of the adjacent carbon. The positions of the methyl hydrogens were optimized by a rigid rotating group refinement with idealized tetrahedral angles. Full-matrix least-squares refinement with SHELXL-93 [16], based upon the minimization of $\sum w_i|F_o^2 - F_c^2|^2$ with weighting given by the expression $w_i^{-1} = [\sigma^2(F_o^2) + (0.0586P)^2]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$, converged to give the values of the final discrepancy indices [17] provided in Table 1.

3. Results and discussion

The stoichiometric reaction of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$ with two equivalents of PhMgBr was carried out in ether at -40 °C, affording $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]TiPh_2$ as a semi-crystalline yellow solid. Its identity was verified by solution ^{1}H and ^{13}C NMR measurements,

Table 1
X-ray data for [(C5H4)SiMe2(N-t-Bu)]Ti[(o-C6H4)C(Ph)=C(Ph)]

A. Crystal data

Empirical formula	$C_{31}H_{33}NSiTi$
Color	Red orange
Crystal dimensions (mm)	$0.15 \times 0.34 \times 0.36$
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	30.993(3)
b (Å)	11.418(2)
c (Å)	16.616(2)
β (°)	109.55(1)
Volume (Å³)	5541.1(11)
Z	8
Formula weight (amu)	495.57
Calculated density (g/cm³)	1.188
μ (cm⁻¹)	3.71
$F(000)$	2096
Temperature (°C)	22

B. Data collection and structural analyses

Scan type	ω, variable
Scan rate (°/min)	2.0–10.0
2θ Range (°)	3.0–40.0
2θ Range, centered reflections	10–25
Reflections sampled	h (−18 ⩽ h ⩽ 33),
	k (−12 ⩽ k ⩽ 1),
	l (−17 ⩽ l ⩽ 17)
Number of reflections collected	4287
Number of unique data	3558 ($R_{int} = 0.0473$)
Number of data, $I > 2\sigma(I)$	1769
R indices, $I > 2\sigma(I)$	$R_1 = 0.0636$, $wR_2 = 0.1206$
R indices, all data	$R_1 = 0.1627$, $wR_2 = 0.1896$
σ_1, GOF	1.020
Number of variables	312
Maximum difference in peak and hole	0.208, −0.221

which indicated the presence of mirror symmetry in solution. The thermally-induced reaction of diphenylacetylene with [(C5H4)SiMe2(N-t-Bu)]TiPh2 proceeds in cyclohexane with the sole formation of [(C5H4)SiMe2(N-t-Bu)]Ti[(o-C6H4)C(Ph)=C(Ph)]. This coupling reaction occurs with the intramolecular elimination of benzene to produce a benzyne intermediate. Following metal complexation of diphenylacetylene, intramolecular C–C bond formation affords the titanacyclopentadiene product (Eq. (6)).
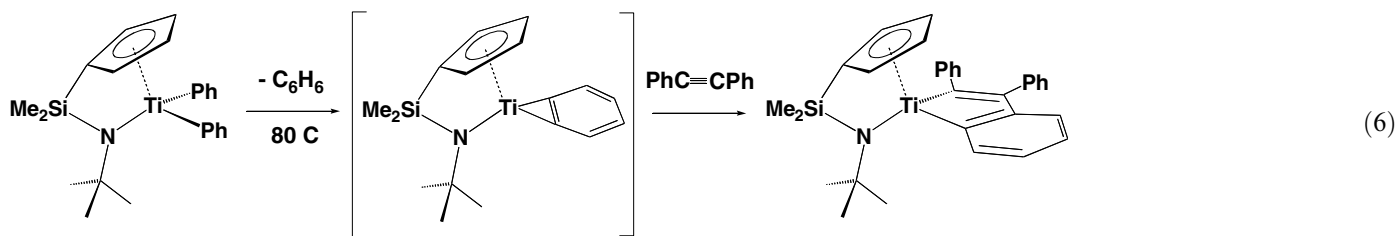
inequivalent protons on the two independent phenyl substituents of the titanacyclopentadiene ring. The four proton resonances of the o-C6H4 moiety are centered at δ 7.00, 6.96, 6.83, and 6.50, with the four chemically inequivalent protons of the cyclopentadienyl group appearing as pseudo triplets at δ 7.47, 7.03, 6.20, and 5.55. The singlet at δ 1.58 represents the nine methyl protons of the t-butyl group and the two singlets at δ 0.59 and δ 0.49 correspond to the two inequivalent methyl groups of the SiMe2 bridge.

The ¹H NMR resonances for the cyclopentadienyl and o-C6H4 fragments were further distinguished by an examination of the 2D COSY NMR spectrum. The proton resonance at δ 6.50 has three off-diagonal peaks at δ 6.83, 6.96, and 7.00 due to coupling with three nearby protons. The remaining three proton resonances of the o-C6H4 functionality exhibit three off-diagonal peaks consistent with their assignment to the o-C6H4 unit. In the case of the cyclopentadienyl group, the distal and proximal protons are diastereotopic and each exhibit the expected set of three off-diagonal peaks.

The corresponding ¹³C{¹H} NMR spectrum exhibits 25 carbon resonances. Due to a significant number of overlapping resonances, a 2D HETCOR NMR spectrum was recorded to assist with the assignment of the carbon resonances for the carbons bearing one or more hydrogen atoms. The two methyl carbons of the SiMe2 bridge appear at δ 0.75 and δ 1.01. The three methyl carbons and the quaternary carbon of the amido functionality appear at δ 34.0 and δ 60.1, respectively. The cyclopentadienyl group exhibits five resonances with the signal at δ 107.9 representing the bridgehead carbon and the four resonances at δ 121.8, 122.05, 126.0, and 126.4 corresponding to the four remaining carbon atoms of the cyclopentadienyl ring. There are six carbon resonances for the o-C6H4 moiety, with the signals at δ 124.7, 126.5, 127.4, and 128.2 corresponding to the four carbons bearing hydrogens and the two peaks at δ 145.8 and δ 193.7 representing the two quaternary carbons within the titanacyclopentadiene ring. The two phenyl substituents exhibit the expected eight carbon resonances, with the signals at δ 123.7, 125.7, 126.2, 127.8, 129.8, and 131.05 representing the *ortho-*, *meta-*,

(6)

The identity of [(C5H4)SiMe2(N-t-Bu)]Ti[(o-C6H4)C-(Ph)=C(Ph)] was initially established by solution ¹H and ¹³C NMR measurements, including 2D HETCOR and COSY experiments. The ¹H NMR spectrum contains peaks at δ 7.18, 7.13, 7.05, 6.83, 6.75, and 6.70 for the six

and *para*-carbons and the two resonances at δ 138.9 and δ 144.4 assigned to the two *ipso*-quaternary carbons. The two resonances at δ 147.9 and δ 206.1 correspond to the two remaining carbons of the titanacyclopentadiene ring.

3.1. Molecular structure of [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]Ti [(o-C$_6$H$_4$)C(Ph)=C(Ph)]

The molecular structure of [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]Ti-[(o-C$_6$H$_4$)C(Ph)=C(Ph)] was confirmed by an X-ray crystallographic analysis. A perspective view of its molecular structure is shown in Fig. 1 with the atom numbering scheme. Pertinent bond distances and angles are provided in Table 2. The molecular structure is well-behaved with no evidence of a structural disorder or excessive thermal motion.

The most prominent feature in this structure is the titanacyclopentadiene ring constructed from the direct C–C coupling of a Ti-coordinated benzyne fragment with diphenylacetylene. This titanacyclic ring is essentially planar with the mean deviation for the Ti and four carbon atoms being 0.035 Å. The three independent C–C distances of 1.404(8), 1.511(8) and 1.355(8) Å are consistent with alternating localized C=C double bonds around the ring with the longer C=C bond being associated with the o-C$_6$H$_4$ fragment. The titanacyclopentadiene and o-C$_6$H$_4$ rings are essentially coplanar, with the acute dihedral angle between their respective planes being only 3.5°. To minimize interring repulsions, the two phenyl substituents containing carbon atoms C(20)–C(25) and C(26)–C(31) are rotated by 76.8° and 41.3°, respectively, out of the plane of the titanacyclopentadiene ring.

The asymmetric pseudo-tetrahedral Ti coordination sphere consists of the π-bonded cyclopentadienyl ring and its appended amido functionality and two chemically inequivalent Ti–C bonds of 2.081(7) and 2.103(6) Å. These two distances are considerably shorter than the two independent Ti–C bonds of 2.172(5) and 2.141(5) Å reported by Atwood and co-workers [18] for the related planar titanacyclopentadiene ring of (C$_5$H$_5$)$_2$Ti(C$_4$Ph$_4$), which was prepared by the photolysis of (C$_5$H$_5$)$_2$TiMe$_2$ in the

Table 2
Interatomic distances (Å) and bond angles (°) for [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]Ti[(o-C$_6$H$_4$)C(Ph)=C(Ph)][a]

A. Interatomic distances

Ti–N	1.915(5)	Ti–Cp(c)	2.025
Ti–C(12)	2.081(7)	Ti–C(15)	2.103(6)
Ti–C(1)	2.299(6)	Ti–C(2)	2.332(2)
Ti–C(3)	2.379(7)	Ti–C(4)	2.410(7)
Ti–C(5)	2.332(7)	N–C(8)	1.489(7)
Si–N	1.744(5)	Si–C(1)	1.855(8)
Si–C(6)	1.850(8)	Si–C(7)	1.845(7)
C(1)–C(2)	1.416(9)	C(2)–C(3)	1.380(9)
C(3)–C(4)	1.383(10)	C(4)–C(5)	1.391(9)
C(5)–C(1)	1.411(9)	C(8)–C(9)	1.516(8)
C(8)–C(10)	1.530(9)	C(8)–C(11)	1.548(8)
C(12)–C(13)	1.404(8)	C(13)–C(14)	1.511(8)
C(14)–C(15)	1.355(8)	C(12)–C(16)	1.390(8)
C(13)–C(19)	1.381(8)	C(14)–C(20)	1.511(8)
C(15)–C(26)	1.469(8)	C(16)–C(17)	1.381(8)
C(17)–C(18)	1.363(8)	C(18)–C(19)	1.386(9)

B. Bond angles

Cp(c)–Ti–N	108.4	Cp(c)–Ti–C(12)	115.3
Cp(c)–Ti–C(15)	118.2	N–Ti–C(12)	110.8(2)
N–Ti–C(15)	117.5(2)	C(12)–Ti–C(15)	85.1(3)
C(12)–Ti–Si	129.8(2)	C(15)–Ti–Si	137.8(2)
N–Si–C(1)	93.4(3)	N–Si–C(7)	116.0(3)
N–Si–C(6)	113.4(3)	C(1)–Si–C(6)	110.1(4)
C(1)–N–C(7)	111.8(4)	C(6)–Si–C(7)	111.0(4)
Si–N–Ti	103.4(2)	C(8)–N–Si	126.4(4)
C(8)–N–Ti	129.7(4)	C(2)–C(1)–C(5)	104.2(6)
C(2)–C(1)–Si	121.8(6)	C(5)–C(1)–Si	121.5(6)
C(1)–C(2)–C(3)	109.4(7)	C(2)–C(3)–C(4)	109.2(8)
C(3)–C(4)–C(5)	106.5(8)	C(4)–C(5)–C(1)	110.7(8)
C(13)–C(12)–Ti	108.4(5)	C(16)–C(12)–Ti	133.2(5)
C(13)–C(12)–C(16)	118.2(6)	C(12)–C(13)–C(14)	118.1(6)
C(12)–C(13)–C(19)	120.3(6)	C(14)–C(13)–C(19)	121.7(6)
C(13)–C(14)–C(15)	119.0(6)	C(13)–C(14)–C(20)	116.2(5)
C(15)–C(14)–C(20)	124.9(6)	C(14)–C(15)–C(26)	124.9(6)
C(14)–C(15)–Ti	109.0(5)	C(26)–C(15)–Ti	125.9(5)

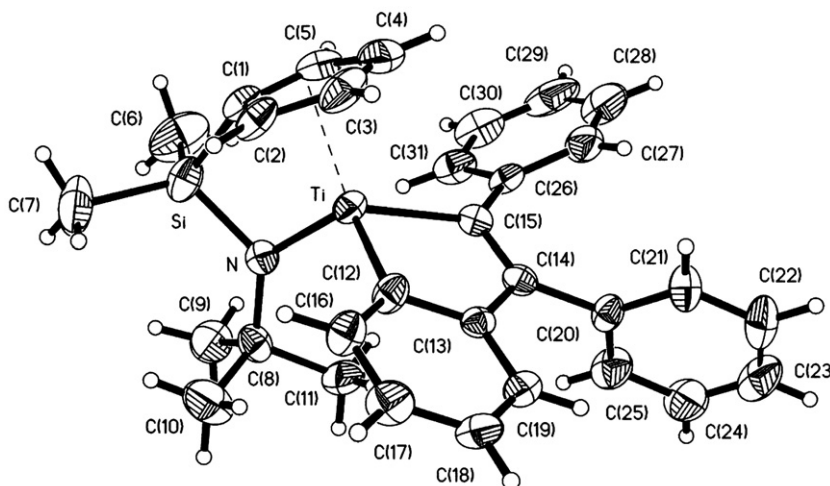[a] Cp(c) corresponds to the centroid of the five-membered cyclopentadienyl ring.

Fig. 1. The molecular structure of [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]Ti[(o-C$_6$H$_4$)C(Ph)=C(Ph)] with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

presence of diphenylacetylene. Comparable Ti–C distances ranging from 2.14 to 2.18 Å have been reported for several titanacyclopentadiene complexes, including $(C_5H_5)_2Ti$-$[C(SiMe_3)C(Ph)C(Ph)C(SiMe_3)]$, $[SiMe_2(C_5H_4)_2]Ti(C_4Ph_4)$, and $(C_5H_5)Ti(N=P(t\text{-}Bu)_3)(C_4Ph_4)$ [19]. The substantial decrease observed for the two Ti–C bond distances in $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti[(o\text{-}C_6H_4)C(Ph)=C(Ph)]$ reflects the increased electrophilicity of the electron deficient d^0 Ti(IV) center arising from the presence of the bifunctional *ansa*-cyclopentadienyldimethysilylamido ligand. The C(12)–Ti–C(15) bond angle of 85.1(3)° within the titanacyclopentadiene ring of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti[(o\text{-}C_6H_4)$-$C(Ph)=C(Ph)]$ is ca. 5° larger than the corresponding C–Ti–C angle in $(C_5H_5)_2Ti(C_4Ph_4)$. This increase is accompanied by a ca. 3° decrease in the Ti–C_α–C_β bond angles.

The presence of the $SiMe_2$ linkage between the cyclopentadienyl and amido functionalities of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti[(o\text{-}C_6H_4)C(Ph)=C(Ph)]$ produces a Cp(c)–Ti–N angle of 108.4°, which is only modestly larger than its corresponding value of 107.0° in $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$ [12d]. The similarity of the respective Ti–N(amido) (1.915(5) and 1.901(3) Å) and Ti–Cp(c) (2.025 and 2.019 Å) for these two complexes indicates that these distances are relatively insensitive to the presence of the titanacyclopentadiene ring.

Although our study is limited in scope, Sinnema and Teuben [20] have shown that thermolysis of the corresponding C_2-bridged *ansa*-cyclopentadienylamido titanium diphenyl complex, $[C_5H_4(CH_2)_2(N\text{-}t\text{-}Bu)]TiPh_2$, provides access to the corresponding titanium-benzyne intermediate, which they successfully trapped and structurally characterized as the PMe_3 adduct. Their reactivity studies revealed that $[C_5H_4(CH_2)_2(N\text{-}t\text{-}Bu)]Ti(C_6H_4)(PMe_3)$ readily inserts olefins, alkynes, nitriles, and ketones to produce the corresponding titanacyclic products. In the course of their investigation, they observed that the insertion of phenylacetylene primarily occurs with the larger phenyl substituent positioned on the α-carbon of the titancyclopentadiene ring.

Acknowledgements

Appendix A. Supplementary materials

CCDC 642293 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.06.019.

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[17] The discrepancy indices were calculated from the expressions $R1 = \sum \|F_o| - |F_c\| / \sum |F_o|$ and $wR_2 = [\sum [w_i(F_o^2 - F_c^2)^2)] / [\sum [w_i F_o^2]^2]^{1/2}$ and the standard deviation of an observation of unit weight (GOF) is equal to $[\sum (w_i(F_o^2 - F_c^2)^2) / (n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters varied during the last refinement cycle.

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