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Synthesis and Characterization of Cyclohexadienyl-Based Constrained Geometry Complexes

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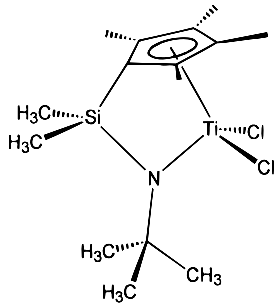
The novel constrained geometry complexes [η^5:η^1-$C_5H_4EMe_2$−$SiMe_2$−N(*t*-Bu)]TiX_2, **5a** (E = C, X = Cl), **5b** (E = C, X = Me), **6a** (E = Si, X = Cl), and **6b** (E = Si, X = Me), based on dimethylcyclohexadienyl and dimethylsilacyclohexadienyl ligands have been prepared and characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and single-crystal X-ray structure analysis (**5a** and **6a**). These complexes are the first examples of compounds containing η^5 “open” dienyl ligands (pentadienyl or cyclohexadienyl) for titanium in its highest (4+) oxidation state. The crystallographic and electrochemical analysis of these complexes demonstrate that “open” dienyl ligands can be used as a viable replacement for the cyclopentadienyl ring in complexes containing a pendant amido group.

I. Introduction

There has been enormous interest and research activity in the area of homogeneous olefin polymerization catalysis.[1] The vast majority of the catalyst systems investigated in this field have been based on the cyclopentadienyl (or its derivatives) ligand framework. Two major classes of olefin polymerization catalysts that have emerged from this research are bis(cyclopentadienyl) and mono(cyclopentadienyl) complexes of early transition metals.[1] Over the past few years a significant amount of effort has been devoted to finding new ligand systems for both early[2] and late[3] transition metals with the purpose of generating active olefin polymerization catalysts. Application of the cyclopentadienyl−silylamido ligand to group III and IV metals has led to complexes such as **1**.[4,5] Upon activation these constrained geometry complexes (CGC) exhibit high reactivity toward α-olefins and other vinyl monomers such as styrene, due in part to the sterically unencumbered ancillary ligand framework. This unique reactivity has led to a wide range of new and innovative polymers.[6]



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This paper describes an extension of this effort into a new class of non-Cp (Cp = cyclopentadienyl)-based constrained geometry complexes where the cyclopentadienyl ring has been replaced with a dimethylcyclohexadienyl or dimethylsilacyclohexadienyl fragment.

The cyclohexadienyl ring is an example of the “open metallocene” ligand family.[7] “Open” and “half-open metallocenes” have been prepared and studied for a wide range of transition metals, lanthanides, and actinides.[7] The acyclic dienyl ligands (pentadienyls) tend to form stronger metal−carbon bonds than Cp but then are generally more reactive than Cp. This increased reactivity is influenced by a number of factors, including the accessibility of a variety of bonding modes (U, W, and S), η^5-η^3-η^1 lability, a small HOMO−LUMO gap, a

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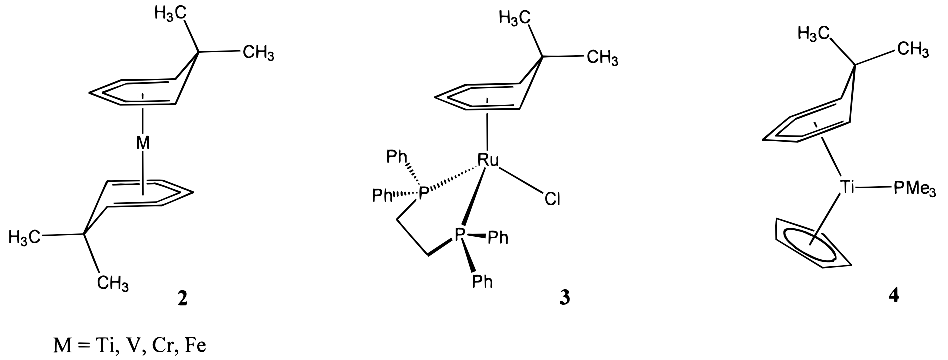

Figure 1.

tendency toward localization of the negative charge at the 1-, 3-, or 5-positions, and the lack of aromaticity.

The 6,6-dimethylcyclohexadienyl ligand (dmCh) was first utilized by Wolczanski and co-workers in the preparation of bis(6,6-dimethylcyclohexadienyl) complexes of Ti, Cr, V, and Fe (Figure 1).[8a] These investigations demonstrated that substitution on the ends of the pentadienyl ligand to form a non-Cp closed ring diminished reactivity at the 1- and 5-positions of the ligand. This feature of the dmCh ligand reduces the number of reaction pathways that are available to the open pentadienyl ligands, thus bridging the reactivity gap between the Cp and the acyclic pentadienyl ligands. However, the dimethylcyclohexadienyl fragment may still undergo unique transformations when coordinated to a metal center. For example, chloride abstraction from **3** using $TlPF_6$ forms a cationic ruthenium complex which then undergoes β-methyl elimination from the dmCh ligand, leading to the [(toluene)(diphos)Ru-Me]-PF_6 complex.[8c] Ernst and co-workers also have found that the dimethylcyclohexadienyl ligand in complex **4** couples regioselectively with 2 equiv of a variety of ketones and aldehydes.[9]

Additional cyclohexadienyl compounds that have been reported include $(C_5H_5SiMe_2)_2Fe$, $(C_5H_5SnMe_2)_2Fe$,[10] a series of mononuclear and cluster molybdenum complexes,[8b] and two uranium complexes.[11]

Since the cyclohexadienyl ligand binds to metals in a fashion similar to Cp and it possesses a steric environment similar to the Cp anion, it is potentially a good candidate for the preparation of non-Cp constrained geometry catalysts. It was anticipated that incorporation of the cyclohexadienyl fragment into the CGC ligand framework would allow for complexes that are as robust as the cyclopentadienyl ligand when coordinated to the metal center. Metal complexes containing "open" dienyl ligands have yet to be reported for the highest oxidation states of the group IV metals [Ti(IV), Zr(IV), or Hf(IV)]. The only case of a Zr(IV) "open" dienyl complex is $[(C_5H_4t\text{-Bu})_2Zr(C_5H_3\text{-}2,3,4,5\text{-}Me_4)]^+$ $[B(C_6H_4\text{-}4\text{-}F)_4]^-$, where the acyclic pentadienyl coordination "occurs via a sigma-bond and two weak unconjugated η^2-interactions with the double bonds".[12] The synthesis,

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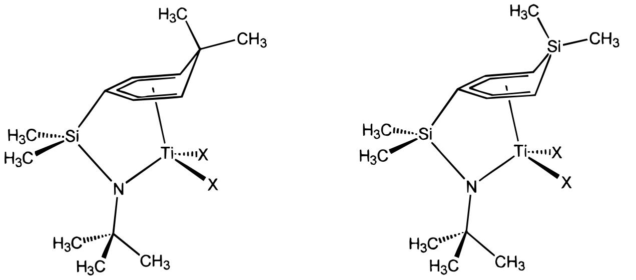

5a: X = Cl

b: X = CH3

6a: X = Cl

b: X = CH3

Figure 2.

spectroscopy, and X-ray crystal structure analysis of the new CGC complexes containing dimethylcyclohexadienyl (**5a**, **5b**) and dimethylsilacyclohexadienyl (**6a**, **6b**) fragments are the subject of this paper (Figure 2).

II. Results and Discussion

Ligand Synthesis. The (6,6-dimethyl-1,2,3,4,5-cyclohexadienyl)potassium salt (**7a**) was prepared by a slightly modified literature procedure.[8a] The analogous (1,1-dimethylsila-2,3,4,5,6-cyclohexadienyl)potassium salt (**7b**) was generated via the reaction of 1,1-dimethyl-1-silacyclohexa-2,4-diene/1,1-dimethyl-1-silacyclohexa-2,5-diene[13] with a Lochmann−Schlosser base[14] (*n*-BuLi/KO-*t*-amylate) in hexane solution (Scheme 1).[15] Both potassium salts are insoluble in hexane and were easily isolated by filtration. Although the lithium analogue of **7b** can be formed, it does not precipitate well from hexane, making it difficult to isolate. Potassium salts **7a** and **7b** exhibit good thermal stability and can be stored in an inert atmosphere at room temperature for extended periods of time.

THF solutions of **7a** and **7b** were then added dropwise to THF solutions of $ClSiMe_2NH$-*t*-Bu at low temperature, leading to the clean formation of ligands **8a** and **8b** in high yields. The low-temperature conditions of this reaction are necessary to obtain pure product. As expected, compounds **8a** and **8b** have similar features in their ^1H and $^{13}C\{^1H\}$ NMR spectra. The ^1H NMR spectra of complexes **8a** and **8b** exhibit large singlets at 0.1 ppm for the methyl groups of the silyl bridge and at 1.0 ppm corresponding to the *tert*-butyl groups. The amine protons for both compounds appear as broad singlets at 0.5 ppm, while the protons at the bridging site of the (sila)cyclohexadienyl fragment appear as multiplets in the region of 2.3−2.8 ppm. The diastereotopic dimethyl groups of the cyclohexadienyl ring of **8a** exhibit singlets at 1.10 and 1.11 ppm, while the analogous resonances for **8b** appear upfield from that of **8a** at 0.21 and 0.23 ppm. The protons adjacent to the EMe_2 (E = C, Si) group appear as doublets at 5.44 ppm for complex **8a** and 5.85 ppm for complex **8b**. The resonances of the second vinyl pair of protons appear as a doublet of doublets at 5.68 ppm for **8a** and at 6.80 ppm for **8b** due to coupling with the proton at the bridging position and the vinyl proton adjacent to EMe_2. The $^{13}C\{^1H\}$ NMR spectra likewise are consistent with C_s symmetry of both ligands.

The free ligand **8a** was doubly deprotonated using 2 equiv of *n*-BuLi in hexane, and the resulting dilithium salt **9a** was obtained by cooling its hexane solution at −27 °C. In the case of **8b**, Schlosser−Lochmann base was used instead, leading to facile formation of dipotassium salt **9b** as a yellow precipitate in hexane solution. Similar to 1,1-dimethyl-1-silacyclohexa-2,5-diene, **8b** can be deprotonated with *n*-BuLi; however, the high solubility of the resulting dilithium salt in hexane precluded its facile isolation. The ^1H and $^{13}C\{^1H\}$ NMR spectra are consistent with the effective C_{2v} symmetry of salts **9a** and **9b**.

Complex Synthesis. Formation of the titanium complexes was problematic from two standpoints. First, although pure starting materials were employed, side reactions were observed. Second, the resulting dichloride complexes were very soluble in hexane, making them difficult to crystallize in the presence of the organic impurities. Complex **5a** was formed in low yield by the reaction of the dilithium salt **9a** with $TiCl_3(THF)_3$ followed by the oxidation of the resulting complex with $PbCl_2$. The analogous reaction using **9b** was low yielding, <50% as estimated by NMR. Acid−base reaction of **8b** with reagents such as $Ti(CH_2Ph)_4$ and $Ti(NMe_2)_4$ did not result in the formation of the desired product. The highest-yielding method for the formation of **6b** was found to be the reaction between **9b** and $TiCl_2(NMe_2)_2$, followed by the metathesis reaction to the desired dichloride **6a** with chlorotrimethylsilane. Final purification was accomplished through chromatography on a Bio-Bead[16] column using toluene as the eluent. Once the appropriate fraction was isolated and the volatiles were removed, the resulting red solid could be crystallized from hexane. Complexes **5a** and **6a** have similar ^1H and $^{13}C\{^1H\}$ NMR spectral features. The ^1H NMR spectra (C_6D_6 solvent) of both complexes exhibit large singlets in the range of −0.1−0.1 ppm for the silyl bridge methyl groups and at 1.4 ppm corresponding to the *tert*-butyl groups. For **5a**, the geminal dimethyl groups on the dmCh ring appear as singlets at 0.7 and 1.0 ppm, whereas the analogous resonances for **6a** occur at −0.15 and 0.40 ppm. The protons on the dmCh ring of **5a** coincidentally overlap, appearing as a singlet at 5.6 ppm. The same overlap is observed in CD_2Cl_2; however, two separate doublets centered at 5.73, 5.94 ppm (^3J = 8.1 Hz) are visible in THF-d_8. The corresponding resonances for **6a** appear, as expected, as a pair of doublets at 5.99 and 6.73 ppm (^3J = 13.1 Hz). Methylation of **5a** and **6a** with MeMgBr proceeded cleanly and in high yields, leading to **5b** and **6b** (Scheme 2).

X-ray Crystal Structure Analysis. Single-crystal X-ray structure analyses of complexes **5a** and **6a** have been carried out. Thermal ellipsoid drawings of complexes **5a** and **6a** are shown in Figures 3 and 4, respectively. Crystal data are presented in Table 1, while selected bond distances and angles are included in Table 2. Both complexes crystallized in the orthorhombic space group $P2_12_12_1$. Of primary interest is the

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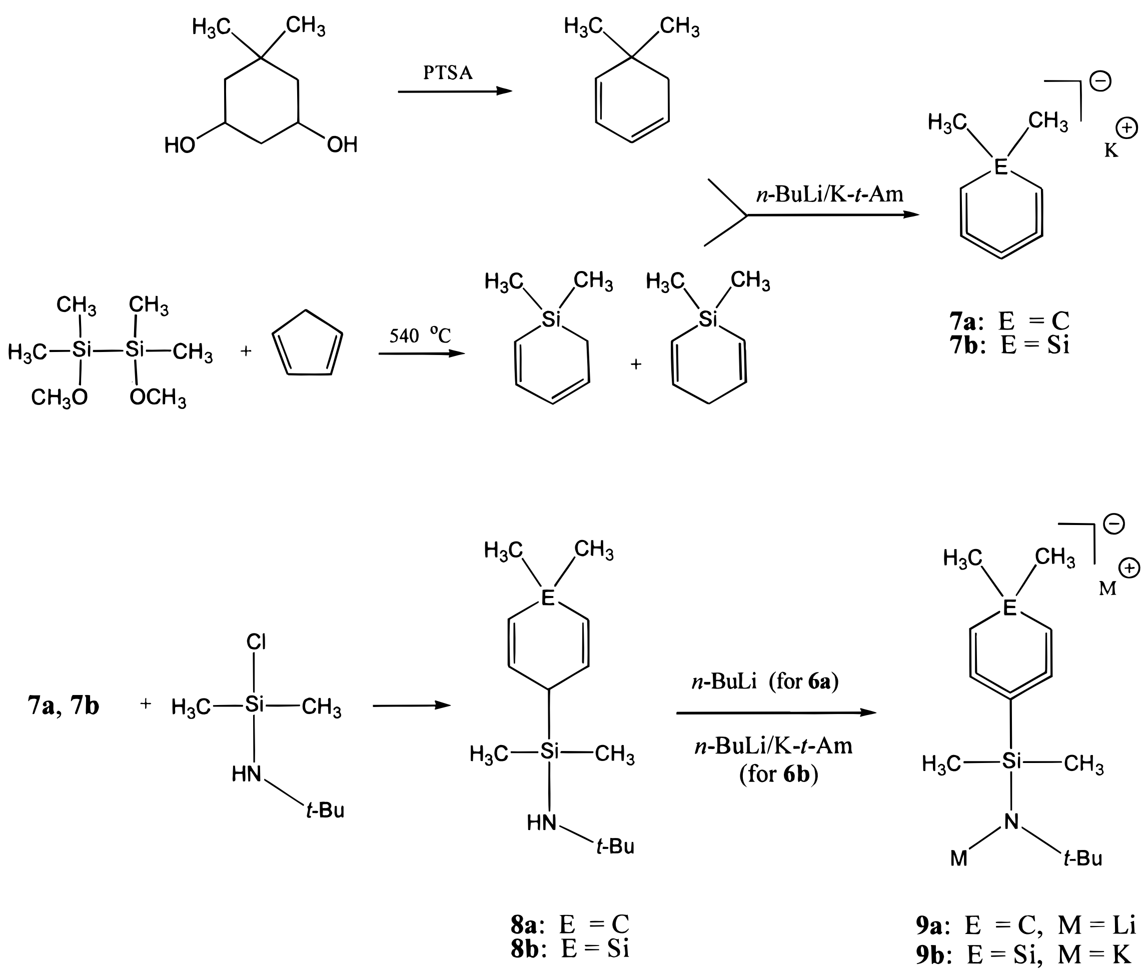
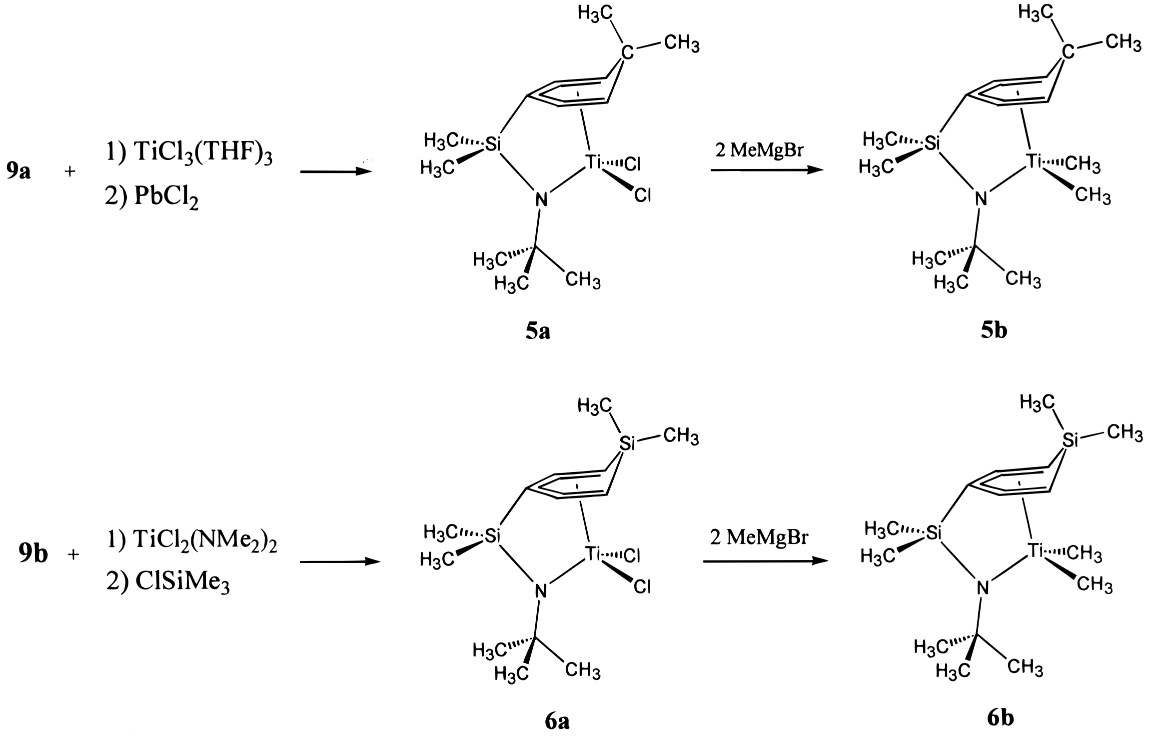
Scheme 1



Scheme 2



nature of the bonding of the cyclohexadienyl ligands to the titanium atoms. In both complexes the dimethylcyclohexadienyl or dimethylsilacyclohexadienyl rings are bonded in an η^5 fashion to the titanium atoms, similar to known cyclohexadienyl-titanium complexes.[8a] The amido nitrogen atoms have planar geometry (sum of the

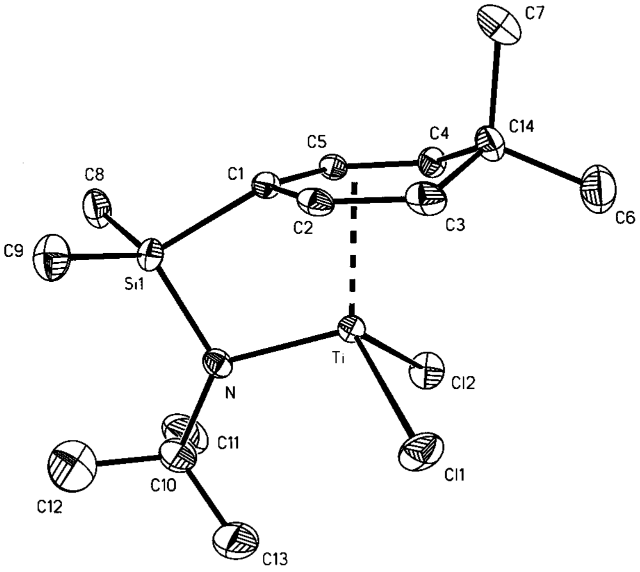


Figure 3. Molecular structure and labeling scheme for **5a** with 40% probability thermal ellipsoids.

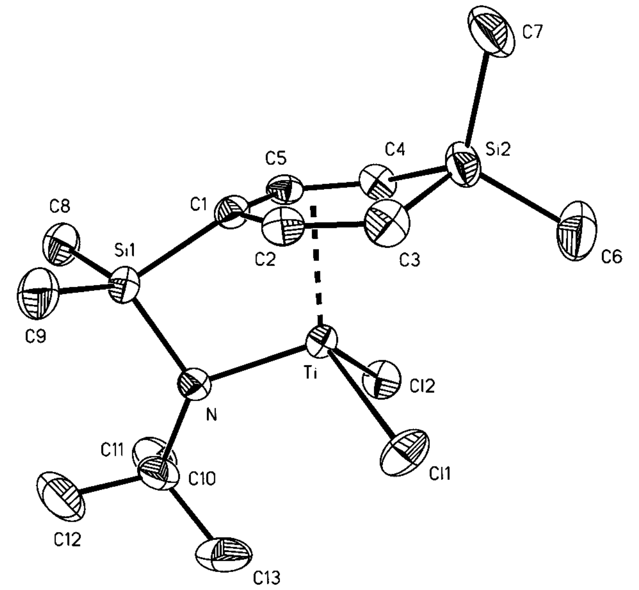


Figure 4. Molecular structure and labeling scheme for **6a** with 40% probability thermal ellipsoids.

bond angles around nitrogen is equal to 360° and 359.7° for **5a** and **6a**, respectively), in agreement with previously reported "constrained geometry" titanium complexes.[4,5g−m,17] The difference in bond angles C10−N−Ti and C10−N−Si1 for **5a** (129.9° vs 126.2°) and **6a** (130° vs 125.2°) is larger than the corresponding angles in $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti(NMe_2)_2$ (128.1° vs 127.6°),[5h] indicating a greater degree of slippage of **5a** and **6a** toward the C5−C1−C2 fragment of the cyclohexadienyl moiety. The dihedral angles between the planes defined by C1−C2−C3−C4−C5 and C3−C14(Si2)−C4 equal 150.8(6)° and 159.5(1)° for **5a** and **6a**, respectively, indicating that the silicon-based cyclohexadienyl fragment is more planar than the carbon-based analogue. The five carbon atoms (C1−C5) belonging to the six-membered ring are coplanar (maximum deviation from the least-squares plane is 0.008 Å for C5 (**5a**) and 0.013 Å for C2 (**6a**)), whereas C14 (**5a**) and Si2 (**6a**) are both 0.45 Å above this plane. The average $Ti-C_{dienyl}$ bond distances are 2.435 and 2.445 Å for **5a** and **6a**, respectively, which are slightly longer than the distances in **1**[5h] (2.357 Å). The average bond lengths Ti−C5/Ti−C1/Ti−C2 and Ti−C4/Ti−C3 are 2.328 Å/2.596 Å and 2.342 Å/2.598 Å for **5a** and **6a**, respectively, indicating an "uneven" coordination of the dimethylcyclohexadienyl and dimethylsilacyclohexadienyl ligands. These values are different than those found in **1** (2.305 Å/2.436 Å), which possesses a more symmetric coordination of the cyclopentadienyl ring. The same values in bis(cyclohexadienyl)(carbonyl)titanium were found[8a] to be 2.293 and 2.391 Å, indicating that the large "slip" of the ligands observed in **5a** and **6a** is not an inherent property of the cyclohexadienyl fragment, but rather is a result of the incorporation of those fragments into the CGC ligand framework. The Ti−Cn (Cn = centroid of the five carbons bonded to Ti) distances are 2.018, 2.018, and 1.983 Å for **1**, **5a**, and **6a**, respectively. The difference between the Ti−Cn distances in **5a** and **6a** is presumably due to the wider nature of the cyclosilahexadienyl ligand as compared to that of the cyclohexadienyl ligand (see Figure 5), allowing the titanium atom to approach the center of the ring more closely. A similar situation has been observed for the divalent $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(PEt_3)$ complex (C_7H_{11} = dimethylpentadienyl), where the average Ti−C bond distances are 2.345 Å for the cyclopentadienyl ligand and 2.240 Å for the pentadienyl ligand. However, the much greater width of the pentadienyl ligand allows a much closer approach to its plane than to that of the C_5H_5 fragment (1.563 Å vs 2.049 Å).[18] The values of the Cn−Ti−N angles of 107.3° and 105.5° for **5a** and **6a**, respectively, are comparable to that of 107.6° for **1**. The smaller angle observed for **6a** may be due to the closer proximity of the Ti atom to the cyclohexadienyl ring. The bridging Si atom is displaced from the C1−C2−C3−C4−C5 plane of the dienyl rings by 0.87, 0.89, and 0.96 Å for **1**, **5a**, and **6a**, respectively.

Electrochemical Analysis. The reduction potentials (Ti(IV) → Ti(III)) of complexes **1**, **5a**, and **6a** were determined by cyclic voltammetry measurements. More negative values are indicative of an increase in the electron density at the Ti metal center. This type of measurement has been previously used to investigate the changes in electron density of the metal center in titanocene[19] and zirconocene[20] complexes. The results demonstrate (Table 3) that the electron-donating ability of the cyclohexadienyl ring in **5a** is nearly identical to that of the tetramethylcyclopentadienyl ring in **1**. The silicon-based cyclohexadienyl ring in **6a** is, however, somewhat less electron-donating than the other two ligands.

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Table 1. Crystallographic Data for Complexes 5a and 6a

	5a	**6a**
empirical formula	$C_{14}H_{25}Cl_2NSiTi$	$C_{13}H_{25}Cl_2NSi_2Ti$
fw	354.25	370.32
temp	153(2) K	173(2) K
wavelength	0.71069 Å	0.71073 Å
diffractometer	CAD4	SMART/CCD
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
unit cell dimens	$a = 9.064(2)$ Å $b = 13.038(4)$ Å $c = 15.515(2)$ Å	$a = 9.2349(3)$ Å $b = 12.9933(4)$ Å $c = 16.0204(5)$ Å
volume, Z	1833.5(6) Å^3, 4	1922.3(1) Å^3, 4
density (calcd)	1.283 Mg/m^3	1.280 Mg/m^3
abs coeff	0.812 mm^{-1}	0.837 mm^{-1}
$F(000)$	744	776
cryst size	0.60 × 0.17 × 0.11 mm	0.30 × 0.23 × 0.19 mm
θ range for data collection	2.0−24.99°	2.02−27.50°
no. of reflns collected	1934	13126
no. of ind reflns	1878 [R(int) = 0.040]	4371 [R(int) = 0.0227]
abs corr	analytical	empirical
max. and min. transmission	0.838 and 0.921	0.888 and 0.753
refinement method	full-matrix least-squares on F	full-matrix least-squares on F^2
no. of data/restraints/params	1878/0/189	4371/0/197
goodness-of-fit on F^2	2.70	1.037
final R indices	$R = 0.04$, $R_w = 0.045$ [1555] [$I > 3\sigma(I)$]	R1 = 0.0303, wR2 = 0.0755 [3926] [$I > 2\sigma(I)$]
R indices (all data)		R1 = 0.0350, wR2 = 0.0767
extinction coefficient	0.0061(5)	0.0034(5)
largest diff peak and hole	0.78 and −0.36 e Å^{-3}	0.33 and −0.22 e Å^{-3}

[a] R, R1 $= \sum(||F_o| - |F_c||)/\sum|F_o|$. wR2 $= [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o{}^2) + (0.0370*p)^2 + 0.31*p]$, $p = [\max(F_o{}^2,0) + 2F_c{}^2]/3$. $R_w = [\sum[w(F_o - F_c)^2]/\sum[w(F_o)^2]]^{1/2}$ where $w = 1/\sigma^2(F_o) = 4F_o{}^2/\sigma^2(F_o{}^2)$. $S = [\sum[w(F_o{}^2 - F_c{}^2)^2]/(n - p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 5a and 6a

	5a	**6a**		**5a**	**6a**
Ti−Cl1	2.278(2)	2.2748(7)	Si2−C7		1.860(3)
Ti−Cl2	2.283(2)	2.2805(7)	C14−C6	1.529(9)	
Ti−N	1.906(5)	1.917(2)	Si2−C6		1.864(3)
Ti−C1	2.267(6)	2.267(2)	Si1−N	1.757(5)	1.763(2)
Ti−C2	2.370(7)	2.382(2)	Si1−C1	1.853(6)	1.852(2)
Ti−C3	2.586(7)	2.593(2)	Si1−C9	1.852(7)	1.861(3)
Ti−C4	2.606(7)	2.603(2)	Si1−C8	1.862(7)	1.863(3)
Ti−C5	2.346(7)	2.378(2)	N−C10	1.496(7)	1.497(3)
Ti−Si1	2.887(2)	2.9021(6)	C1−C5	1.442(9)	1.433(3)
C14−C3	1.51(1)		C1−C2	1.43(1)	1.437(3)
Si2−C3		1.848(3)	C2−C3	1.36(1)	1.379(4)
C14−C6	1.51(1)		C4−C5	1.38(1)	1.373(4)
Si2−C4		1.850(3)	Ti−Cn	2.018(9)	1.983(1)
C14−C7	1.539(8)				
N−Ti−Cl1	106.8(2)	107.02(6)	C10−N−Ti	129.7(4)	130.5(2)
C1−Ti−Cl1	129.9(2)	131.53(7)	Si1−N−Ti	103.9(2)	104.01(8)
N−Ti−Cl2	105.6(2)	104.08(6)	C5−C1−C2	113.9(5)	119.4(2)
C1−Ti−Cl2	129.1(2)	129.87(7)	C5−C1−Si1	117.5(5)	117.4(2)
Cl1−Ti−Cl2	99.08(7)	97.17(3)	C3−C2−C1	124.4(7)	125.6(2)
C3−C14−C4	104.6(5)		C3−C2−C14	121.8(7)	
C3−Si2−C4		96.06(10)	C2−C3−Si2		123.0(2)
C7−C14−C6	109.1(6)		C5−C4−C14	123.3(7)	
C7−Si2−C6		109.8(2)	C5−C4−Si2		122.8(2)
N−Si1−C1	91.6(2)	91.22(9)	C4−C5−C1	121.1(7)	126.3(2)
C9−Si2−C8	111.3(3)	111.2(2)	Cn-N−Ti	107.3(3)	105.5(1)
C10−N−Si1	126.2(4)	125.2(2)			

[a] Cn denotes the centroid of the C1−C5 fragment of the cyclohexadienyl ring.

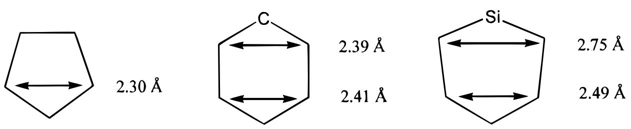

Figure 5.

Table 3. Reduction Potentials for Complexes 1, 5a, and 6a [Ti(IV) → Ti(III)]

complex	$E_{1/2}$ (V)
1	−1.98
5a	−1.95
6a	−1.82

III. Conclusions

The preparation of analogues of the constrained geometry class of complexes based on non-Cp cyclohexadienyl ligands has been demonstrated. Complex **5a** was synthesized by reaction of the dilithium ligand salt with $TiCl_3(THF)_3$ followed by oxidation with $PbCl_2$. Complex **6a** was formed by reaction of the dipotassium ligand salt with $TiCl_2(NMe_2)_2$ followed by metathesis of the product with chlorotrimethylsilane. Crystallographic as well as electrochemical analyses of these complexes demonstrate that dimethylcylohexadienyl and dimethylsilacyclohexadienyl ligands can be used as viable replacements for the cyclopentadienyl ring. Cyclohexadienyl fragments were found to be η^5-coordinated but with substantial coordination slippage. These complexes have also been shown to be active catalysts upon combination with the appropriate activator.[21] Polymerization studies will be reported in the future. Additionally, efforts to examine the structure−activity relationships of dienyl complexes are currently under way.

IV. Experimental Section

General Considerations. All syntheses were performed under dry nitrogen or argon atmospheres using a combination of glovebox and high-vacuum techniques. Tetrahydrofuran (THF), diethyl ether, toluene, and hexane were used following passage through double columns charged with activated alumina and Q-5 catalyst.[22] The ^{1}H (300 MHz) and ^{13}C NMR

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[21] (a) Wilson, D. R.; Neithamer, D. R.; Nickias, P. N.; Kruper, W. J, Jr. US 5495036 A 960227. (b) Wilson, D. R.; Neithamer, D. R.; Nickias, P. N.; Kruper, W. J, Jr. PCT Int. Appl, WO 9608498 A1 960321.

(75 MHz) spectra were recorded on a Varian XL-300 spectrometer. The ^{1}H and ^{13}C NMR spectra are referenced to the residual solvent peaks and are reported in ppm relative to tetramethylsilane. All J values are given in hertz. Mass spectra (EI, CI) were obtained on the Finnigan MAT95Q hybrid-sector mass spectrometer at the University of Florida Mass Spectrometry Facility. Elemental analysis was performed by Oneida Research Services, Whitesboro, NY. The MeMgBr and *n*-BuLi were used as purchased from Aldrich. Potassium *tert*-amylate (15 wt % in hexane) was obtained from Callery Chemical Co. The compounds $TiCl_3(THF)_3$,[23] $TiCl_2(NMe_2)_2$,[24] 5,5-dimethyl-1,3-cyclohexadiene,[8c] 1,1-dimethyl-1-silacyclohexa-2,4-diene/1,1-dimethyl-1-silacyclohexa-2,5-diene,[13] and *N*-(*tert*-butyl)-*N*-(1-chloro-1,1-dimethylsilyl)amine[25] were prepared as described in the literature.

Cyclic voltammograms were conducted in a single compartment cell inside a Vacuum Atmospheres drybox in 1,2-difluorobenzene (DFB) which was 2 mM in tetrabutylammonium tetrakisperfluorophenylborate as conducting electrolyte and 5 mM in the metal complex studied. Potentials were measured at a platinum electrode against an Ag wire reference electrode at 25 °C. All potentials are referenced against the standard potential of the ferrocene/ferrocenium couple ($E_{1/2} = +0.49$ V vs SCE in DFB).

Preparation of (6,6-Dimethyl-1,2,3,4,5-cyclohexadienyl)potassium (7a). To 11.21 g (104 mmol) of 4,4-dimethylcyclohexadiene dissolved in 200 mL of hexane was added 65 mL (104 mmol) of a 1.6 M solution of *n*-BuLi followed by addition of 111.4 mL (104 mmol) of a 0.93 M hexane solution of potassium amylate. During addition of potassium amylate, a yellow precipitate appeared. After stirring for 5 h at room temperature, the solid was collected on a frit, washed with hexane (3 × 80 mL), and dried under reduced pressure to give 14.36 g of product as a yellow powder. Yield: 95%. ^{1}H (THF-d_8): δ 0.73 (s, 6H), 3.36 (dd, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.5$ Hz, 2H), 3.72 (tt, $^3J_{HH} = 6.2$ Hz, $^4J_{HH} = 1.5$ Hz, 1H), 5.77 (dd, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 6.2$ Hz, 2H). $^{13}C\{^1H\}$ (THF-d_8): δ 33.82, 34.51 (quat), 79.79, 91.72, 127.38.

Preparation of 1-(4,4-Dimethyl-2,5-cyclohexadien-1-yl)-*N*-(1,1-dimethylethyl)-1,1-dimethylsilanamine (8a). 6,6-Dimethyl-(1,2,3,4,5-cyclohexadienyl)potassium (**7a**) (4.00 g, 27.35 mmol) was dissolved in 180 mL of THF. The resulting dark red solution was cooled (−78 °C) in a dry ice/2-propanol bath. To this flask was added 5.44 g (32.8 mmol) of *N*-(*tert*-butyl)-*N*-(1-chloro-1,1-dimethylsilyl)amine dissolved in 10 mL of THF within 5 min. During the addition, the solution changed color from deep red to yellow. After stirring 1 h at −78 °C, the reaction mixture was warmed slowly to room temperature (solution color changed to off-white). After stirring 1 h at room temperature, the solvent was removed under reduced pressure and the residue was extracted with 60 mL of hexane. Filtration through a medium frit followed by solvent removal gave 5.96 g of light yellow liquid. Yield: 92%. Proton and carbon NMR are consistent with the desired compound. ^{1}H (C_6D_6): δ 0.11 (s, 6H), 0.43 (br s, 1H), 1.06 (s, 9H), 1.10 (s, $^3J_{H-H} = 7.2$ Hz, 3H), 1.11 (s, 3H), 2.28 (m, 1H), 5.44 (dd, $^3J_{H-H} = 8.4$ Hz, $^4J_{H-H} = 1.7$ Hz, 2H), 5.68 (dd, $^3J_{H-H} = 10.5$ Hz, $^3J_{H-H} = 3.6$ Hz, 2H). $^{13}C\{^1H\}$ (C_6D_6): δ −0.55, 32.00, 32.15, 33.12, 33.72, 33.86, 49.33, 123.55, 132.48. HRMS (CI, ($M + H^+$)): calcd 238.199, found 238.195.

Preparation of (1-(((1,1-Dimethylethyl)amino)dimethylsilyl)-4,4-dimethyl-2,5-cyclohexadien-1-yl)lithium, Lithium Salt (9a). (4,4-Dimethyl-2,5-cyclohexadien-1-yl)-*N*-(1,1-dimethylethyl)dimethylsilanamine (**8a**) (3.42 g, 14.4 mmol) was dissolved in 40 mL of hexane. To this solution was added dropwise 18.9 mL (30.25 mmol) of a 1.6 M solution of *n*-BuLi followed by addition of 2 mL of diethyl ether. After the reaction mixture was stirred overnight, the flask was put aside into the freezer (−27 °C) for 20 h. Solvent was decanted, and the remaining yellow solid was dried under reduced pressure to give 1.73 g of product. The decanted solution was evaporated to dryness, and the residue was dissolved in 15 mL of hexane. After 20 h at −27 °C, a second crop of the product (1.07 g) was obtained. Combined yield: 78%. ^{1}H (C_7D_8): δ 0.384 (s, 6H), 0.92 (t, 6H, ($\mathit{CH_3}CH_2)_2O$), 1.20 (s, 6H), 1.40 (s, 9H), 3.09 (qt, 4H, $CH_3\mathit{CH_2})_2O$), 4.27 (d, 2H, $^3J_{H-H} = 7.6$ Hz, 2H), 6.38 (d, $^3J_{H-H} = 7.6$ Hz, 2H). $^{13}C\{^1H\}$ (C_7D_8): δ 6.48, 14.82 ($(\mathit{CH_3}CH_2)_2O$), 32.73, 37.25, 37.49, 51.47, 66.08 ($(CH_3\mathit{CH_2})_2O$), 80.61, 99.18, 131.01. HRMS (EI, ($M + 2H - 2Li{-}CH_3)^+$): calcd 222.168, found 222.167. HRMS (CI, ($M - 2Li + 3H)^+$): calcd 238.199, found 238.192.

Preparation of Dichloro(1-((1,2,3,5,6-η)-4,4-dimethyl-1,5-cyclohexadien-1-yl)-*N*-(1,1-dimethylethyl)-1,1-dimethylsilanaminato(2−)-*N*)titanium (5a). A suspension of 4.03 g (10.9 mmol) of $TiCl_3(THF)_3$ in 100 mL of THF was cooled to −78 °C. To this was added within 5 min 2.71 g (10.9 mmol) of (1-(((1,1-dimethylethyl)amino)dimethylsilyl)-4,4-dimethyl-2,5-cyclohexadien-1-yl)lithium, lithium salt (**9a**) dissolved in 15 mL of THF. After stirring for 0.5 h at low temperature, the reaction mixture was brought to room temperature, where it was stirred for 1.5 h. Lead dichloride was added as a solid (1.97 g, 7.1 mmol), causing a color change of the reaction mixture from dark green to dark red-brown. After 1 h, the solvent was removed under reduced pressure and the residue was extracted with 40 mL of toluene and filtered. Toluene was removed under reduced pressure, and the remaining residue was extracted with 70 mL of hexane. The hexane solution was put aside into the freezer (−27 °C) for 1 day. The solution was decanted and the remaining brown solid, washed with 10 mL of cold hexane and then dried under reduced pressure to give 0.534 g of product. The hexane solution was concentrated to 15 mL and put aside into the freezer (−27 °C) for 2 days. The solution was decanted, and the remaining solid was washed with cold hexane and then dried under reduced pressure to give 0.48 g of a second crop of product. The combined yield was 26%. ^{1}H NMR (C_6D_6): δ 0.06 (s, 6H), 0.66 (s, 3H), 1.03 (s, 3H), 1.42 (s, 9H), 5.60 (s, 4H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ −0.58, 31.17, 32.22, 32.39, 34.76, 61.26, 94.07, 126.84, 133.36. ^{1}H NMR (CD_2Cl_2): δ 0.40 (s, 6H), 1.02 (s, 3H), 1.20 (s, 3H), 1.40 (s, 9H), 5.91 (s, 4H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ −0.49, 31.24, 32.28, 32.63, 34.95, 61.63, 95.83, 127.33, 135.14. ^{1}H NMR (THF-d_8): δ 0.36 (s, 6H), 0.94 (s, 3H), 1.14 (s, 3H), 1.36 (s, 9H), 5.73 (d, $^3J_{HH} = 8.1$ Hz, 2H), 5.94 (d, $^3J_{HH} = 8.1$ Hz, 2H). $^{13}C\{^1H\}$ NMR (THF-d_8): δ −0.50, 31.33, 32.43, 32.86, 34.92, 61.81, 99.45, 127.77, 133.91. Anal. Calcd for $C_{14}H_{25}NSiTiCl_2$: C, 47.47; H, 7.11; N, 3.95. Found: C, 47.49; H, 7.03; N, 3.72. HRMS (EI, ($M - CH_3)^+$): calcd 338.038, found 338.039.

Preparation of (1-((1,2,3,5,6-η)-4,4-Dimethyl-1,5-cyclohexadien-1-yl)-*N*-(1,1-dimethylethyl)-1,1-dimethylsilanaminato(2−)-*N*)dimethyltitanium (5b). In the drybox 0.28 g (0.79 mmol) of dichloro(1-((1,2,3,5,6-η)-4,4-dimethyl-1,5-cyclohexadien-1-yl)-*N*-(1,1-dimethylethyl)-1,1-dimethylsilanaminato(2−)-*N*)titanium was dissolved in 40 mL of Et_2O. To this solution, 0.79 mL (2.37 mmol) of MeMgBr (3 M in diethyl ether) was added dropwise while stirring over a 5 min period. The solution changed color from brown to orange-red. After stirring for 1 h, the solvent was removed under reduced pressure and the residue was extracted with hexane (2 × 30 mL). The solution was filtered, and the filtrate was evaporated to dryness under reduced pressure to give 0.23 g (92% yield) of a red oil, which crystallized after a few minutes on standing. ^{1}H NMR (C_6D_6): δ 0.19 (s, 6H), 0.86 (s, 3H), 1.11 (s, 3H), 1.31 (s, 6H), 1.43 (s, 9H), 5.08 (d, $^3J_{HH} = 8.4$ Hz, 2H), 5.24 (d, $^3J_{HH} = 8.1$ Hz, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 0.32, 31.15, 31.97, 34.17, 35.00, 56.00, 56.59, 80.33, 120.91. Anal. Calcd for $C_{16}H_{31}$-

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NSiTi: C, 61.32; H, 9.97; N, 4.47. Found: C, 59.65; H, 9.21; N, 4.39. HRMS (EI, $(M - CH_3)^+$): calcd 298.147, found 298.140.

Preparation of (1,1-Dimethylsilya-2,3,4,5,6-cyclohexadienyl)potassium (7b). *n*-BuLi (4.0 mL, 2.0 M in hexane, 8.0 mmol) was added dropwise via syringe to a stirred solution of K-amylate in 30 mL of hexane (5.93 g, 15.4 wt % in cyclohexane, 8.0 mmol) at room temperature. The mixture was stirred for an additional 30 min. A mixture of 1,1-dimethylsila-2,4-cyclohexadiene and 1,1-dimethylsila-2,5-cyclohexadiene (0.99 g, 8.0 mmol) was then added dropwise to the resulting slurry. After 2 h of stirring, the resulting yellow solid was filtered by filtration, washed with 3 × 10 mL of hexane, and dried in vacuo to give 1.23 g of product (95% yield). ^{1}H NMR (THF-d_8): δ −0.14 (s, 6H), 3.97 (dd, $^3J_{H-H} = 12.9$ Hz, $^4J_{H-H} = 1$ Hz, 2H), 4.18 (tt, $^3J_{H-H} = 7.2$ Hz, $^4J_{H-H} = 1$ Hz, 1H), 6.72 (dd, $^3J_{H-H} = 12.9$ Hz, $^3J_{H-H} = 7.2$ Hz, 2H). ^{13}C{^{1}H} NMR (THF-d_8): δ 8.84, 87.29, 91.69, 141.70.

Preparation of *N*-(1,1-Dimethylethyl)-1-(1,1-dimethylsilacyclohexa-2,5-dien-4-yl)-1,1-dimethylsilanamine (8b). A solution of (1,1-dimethylsilya-2,3,4,5,6-cyclohexadienyl)potassium (**7b**) (0.97 g, 6.0 mmol) in 10 mL of THF was cannulated into a THF solution of *N*-(*tert*-butyl)-*N*-(1-chloro-1,1-dimethylsilyl)amine (0.99 g, 6.0 mmol) at −40 °C over 10 min. The mixture was allowed to warm to room temperature over 2 h and to continue to stir for 10 h. The solvent was then removed under reduced pressure, and the resulting oil was extracted with hexanes (2 × 10 mL) and filtered. Solvent removal under reduced pressure gave the product as an yellow oil (1.41 g, 90%). ^{1}H NMR (C_6D_6): δ 0.09 (s, 6H), 0.21 (s, 3H), 0.23 (s, 3H), 0.47 (br, 1H), 1.01 (s, 9H), 2.79 (t, $^3J_{H-H} = 4.5$ Hz, 1H), 5.85 (d, $^3J_{H-H} = 14.4$ Hz, 2H), 6.80 (dd, $^3J_{H-H} = 14.4$ Hz, $^3J_{H-H} = 4.5$ Hz, 2H). ^{13}C{^{1}H} NMR (C_6D_6): δ −0.34, 1.13, 33.76, 44.10, 49.40, 122.72, 147.58. HRMS (EI, M^+): calcd 253.1682, found 253.1639.

Preparation of (1-(((1,1-Dimethylethyl)amino)dimethylsilyl)-1,1-dimethylsilacyclohexa-2,5-dien-4-yl)potassium, Potassium Salt (9b). *n*-BuLi (4.0 mL, 2.0 M in hexane, 8.0 mmol) was added dropwise via syringe to a stirred solution of potassium amylate in 40 mL of hexane (5.93 g, 15.4 wt % in cyclohexane, 8.0 mmol) at room temperature. The mixture was stirred for an additional 30 min. *N*-(1,1-Dimethylethyl)-1-(1,1-dimethylsilacyclohexa-2,5-dien-4-yl)-1,1-dimethylsilanamine (1.05 g, 4.0 mmol) in 5 mL of hexane was added dropwise to the resulting slurry. After 2 h of stirring, the resulting yellow solid was filtered, washed with hexane (3 × 10 mL), and dried in vacuo to give 1.23 g of product (93% yield). ^{1}H NMR (THF-d_8): δ −0.11 (s, 6H), −0.07 (s, 6H), 1.13 (s, 9H), 4.22 (d, 2H, $^3J_{H-H} = 12.3$ Hz), 7.18 (d, 2H, $^3J_{H-H} = 10.8$ Hz). ^{13}C{^{1}H} NMR (THF-d_8): δ 6.79, 9.01, 38.98, 52.67, 90.78, 148.18. HRMS (CI, $(M + 2H - 2K - CH_3)^+$): calcd 238.1448, found 238.1408.

Preparation of Dichloro(*N*-(1,1-dimethylethyl)-1-((2,3,4,5,6-*η*)-1,1-dimethylsilacyclohexa-2,4-dien-4-yl)-1,1-dimethylsilanaminato(2−)-*N*)titanium (6a). (1-(((1,1-Dimethylethyl)amino)dimethylsilyl)-1,1-dimethylsilacyclohexa-2,5-dien-4-yl)potassium, potassium salt (2.87 g, 8.71 mmol) in diethyl ether (30 mL) was added dropwise to a solution of $TiCl_2(NMe_2)_2$ (1.80 g, 8.71 mmol) in diethyl ether (100 mL) at 0 °C. This mixture was then allowed to stir for 2 h at room temperature. $ClSiMe_3$ (9.46 g, 87.1 mmol) was then added, and the mixture was then allowed to stir overnight. After the reaction period, the volatiles were removed and the residue was extracted and filtered using hexane. Removal of the hexane resulted in the isolation of a dark residue. Bio-Beads (S-X3 Beads) from BIO RAD (200−400 mesh) were swelled in a solution of toluene with $ClSiMe_3$ (0.30 g) overnight and then loaded onto a column, resulting in a stationary phase of 6 in. × 0.8 in. The dark residue (∼0.4 g/application) was then applied to the column and slowly eluted using toluene. A discrete dark red-brown band eluted slower than the yellow-colored band(s). This dark band was collected and the volatiles were removed under vacuum, resulting in a red-brown residue. The column treatment was then repeated using a larger column (11 in. × 1 in.), again collecting the red-brown band immediately, following a yellow band. Removal of the volatiles resulted in the isolation of a red-brown solid. This solid was found to be >95% pure on the basis of the ^{1}H NMR. This now solid residue was redissolved in hexane and recrystallized at −10 °C over a 48 h period of time, resulting in the formation of red crystals (about 0.07 g for 0.4 g of the crude material applied to the column) (0.30 g, 9%). ^{1}H NMR (C_6D_6): δ −0.15 (s, 3H), −0.075 (s, 6H), 0.40 (s, 3H), 1.39 (s, 9H), 5.99 (d, $^3J_{H-H} = 13.1$ Hz, 2H), 6.73 (d, $^3J_{H-H} = 13.2$ Hz, 2H). ^{13}C{^{1}H} NMR (C_6D_6): δ −0.75, 0.47, 4.94, 21.43, 32.00, 62.69, 99.65, 129.01, 143.63. Anal. Calcd for $C_{13}H_{25}NSiTiCl_2$: C, 42.17; H, 6.80; N, 3.78. Found: C, 43.16; H, 6.86; N, 3.70. HRMS (EI, $(M - CH_3)^+$): calcd 354.015, found 354.012.

Preparation of (*N*-(1,1-Dimethylethyl)-1-((2,3,4,5,6-*η*)-1,1-dimethylsilacyclohexa-2,4-dien-4-yl)-1,1-dimethylsilanaminato(2−)-*N*)dimethyltitanium (6b). Dichloro(*N*-(1,1-dimethylethyl)-1-((2,3,4,5,6-*η*)-1,1-dimethylsilacyclohexa-2,4-dien-4-yl)-1,1-dimethylsilanaminato(2−)-*N*)titanium (0.1 g, 0.27 mmol) was stirred in diethyl ether (50 mL) as MeMgBr (0.53 mmol, 0.18 mL of a 3.0 M solution in diethyl ether) was added dropwise. The mixture immediately turned from red to yellow. The mixture was allowed to stir for 45 min. After the reaction period the volatiles were removed and the residue was extracted and filtered using hexane. Removal of the hexane resulted in the isolation of the desired product as a dark yellow oil (0.07 g, 81%). ^{1}H NMR (C_6D_6) δ 0.04 (s, 3H), 0.21 (s, 6H), 0.40 (s, 3H), 1.36 (s, 6H), 1.42 (s, 9H), 5.40 (d, $^3J_{H-H} = 13.1$ Hz, 2H), 6.40 (d, $^3J_{H-H} = 13.0$ Hz, 2H).^{13}C{^{1}H} NMR (C_6D_6): δ 0.28, 0.63, 6.34, 34.03, 57.65, 57.78, 87.79, 116.42, 144.91. HRMS (CI, M^+): calcd 329.1474, found 329.1414.

X-ray Crystal Structure Analysis of 5a and 6a. Complex **5a**: Data were collected at 153 K on a CAD4 diffractometer equipped with a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.710\ 69$ A). A total of 25 reflections with 22.0° ≤ 2θ ≤ 24.0° were used to refine the cell parameters. The $\omega-\theta$ scan method was used for data collection. Three reflections were measured every 90 min to monitor instrument and crystal stability (no decay correction was applied). Compound **6a**: Data were collected at 173 K on a Bruker SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Cell parameters were refined using the entire data set. A hemisphere of data (1341 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1%). Psi scan absorption corrections were applied on both data sets.

The structures of **5a** and **6a** were solved by direct methods in SHELX86[26] and SHELXTL5,[27] respectively, and refined using full-matrix least squares. Compound **5a** was refined using F values in TEXAN,[28] while **6a** was refined using F^2 values in SHELXTL5.[16] The non-H atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the ring of **5a** were refined isotropically, the rest (methyl hydrogens) were included in fixed positions. All of the H atoms of **6a**, except those of C8 and C9, were placed in idealized positions and were refined riding on their parent atoms. Those of C8 and C9 were rotated by 120° from their ideal positions and were refined without constraints. For compound **5a**, 189 parameters were refined in the final cycle of refinement using

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(26) Sheldrick, G. M. *SHELX86*. Program for the Structure Solution of Crystal Structures; University of Gottingen, Germany, 1986.

(27) Sheldrick, G. M. *SHELXTL5*. Crystallographic Software package; Bruker AXS, Inc.: Madison, WI, 1995.

(28) *TEXAN*: Crystal Structure Analysis Package; Molecular Structure Corporation: 1985 & 1992.

1555 reflections with $I > 3\sigma(I)$ to yield R and R_w of 4.0% and 4.5%, respectively. For compound **6a**, 197 parameters were refined in the final cycle of refinement using 3926 reflections with $I > 2\sigma(I)$ to yield R1 and wR2 of 3.03 and 7.55, respectively.

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Supporting Information Available: Tables of atomic positions, anisotropic thermal parameters for non-hydrogen atoms, and comprehensive bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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