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Synthesis, Characterization, and Reactivity of Low-Coordinate Titanium(III) Amido Complexes

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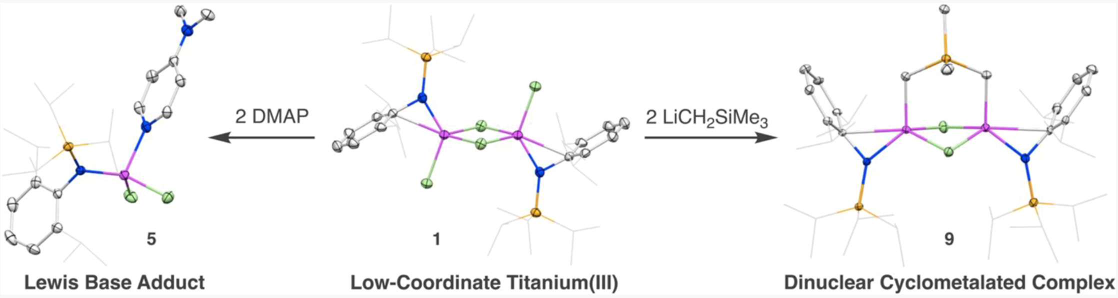

ABSTRACT: Low-coordinate titanium(III) amido complexes were readily prepared via treatment of β-$TiCl_3$ with 1 or 2 equiv of Li[N(Si^{i}Pr$_3$)DIPP] (DIPP = 2,6-di-*iso*-propylphenyl) to form dinuclear [{Ti(N(Si^{i}Pr$_3$)DIPP)Cl(μ-Cl)}$_2$] (**1**) or mononuclear Ti[N(Si^{i}Pr$_3$)DIPP]$_2$Cl (**2**), respectively. Both complexes were characterized by a variety of methods, including NMR spectroscopy, Evans method magnetic susceptibility, and single-crystal X-ray diffraction studies. Complex **1** was shown to be a versatile precursor for salt metathesis reactions to form heteroleptic complexes bearing alkoxide or silyl ligands. Alternatively, **1** formed adducts with Lewis bases such as 4-dimethylaminopyridine (DMAP) that are paramagnetic, mononuclear species. The base-stabilized complex **5** was alkylated with 1 or 2 equiv of $LiCH_2SiMe_3$ to form mono- or dialkyl products, respectively. In contrast, treatment of complex **1** in the absence of DMAP with 2 equiv of $LiCH_2SiMe_3$ results in the ultimate formation of a dinuclear cyclometalated complex **9** bearing a [$Ti_2(\mu$-$Cl)_2(\mu$:η^1-$CH_2SiMe_2CH_2$-)] core. This study demonstrates the convenient synthesis of a family of low-coordinate titanium(III) amido complexes possessing a variety of neutral and monoanionic ligands.

■ INTRODUCTION

Low-valent early transition metal complexes have gained attention due to their ability to enable difficult chemical transformations useful to organic synthesis and catalysis, as well as their applications in challenging processes like small-molecule activation, energy storage, and photoredox catalysis.[1,2] Most low-valent complexes of titanium(II) and titanium(III) that have been isolated feature cyclopentadienyl (Cp)-type ligands or are stabilized by O- and N-based Lewis bases as ancillary ligands.[1,3−6] Indeed, many of the relevant complexes used as olefin polymerization catalysts possess Cp-type ligands.[7] Titanium amido complexes offer an intriguing alternative to these classic Cp-type catalyst frameworks, as both types of ligands feature monoanionic and sterically tunable ancillary ligands, yet the former have not been extensively studied to date.[8]

In 1994, Gambarotta and co-workers demonstrated the synthesis and characterization of a four-coordinate titanium(III) complex stabilized by two amido ligands [-NCy_2 (Cy = cyclohexyl)],[9] which was of interest for its low-coordinate nature. In 1995, Cummins, Wilcox, and co-workers described the synthesis and isolation of Ti{NRAr}$_3$ [R = $C(CD_3)_2CH_3$, Ar = 3,5-$C_6H_3Me_2$] (**A**),[10] the first homoleptic three-coordinate titanium(III) amido complex structurally characterized by X-ray diffraction (Scheme 1). The X-ray crystallographic analysis showed a close interaction between the aryl rings of two of the amido ligands with the metal center, reminiscent of the η^3-bonding mode occasionally observed for benzyl ligands.[11] Soon after, Cummins and co-workers successfully synthesized an alkyl titanium(III) derivative of **A**, Ti(NRAr)$_2$[CH(SiMe$_3$)$_2$] [R = $C(CD_3)_2CH_3$, Ar = 3,5-$Me_2C_6H_3$], which also exhibited an aryl−metal interaction involving one of the amido ligands.[12] Although other examples of both amido and silylamido[13−17] complexes of titanium(III) have since been described, to the best of our knowledge, a systematic study of low-coordinate heteroleptic titanium(III) amido complexes bearing other types of anionic ligands, such as alkyls, aryls, and silyls, has not been reported.[11]

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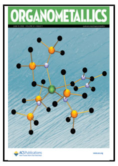

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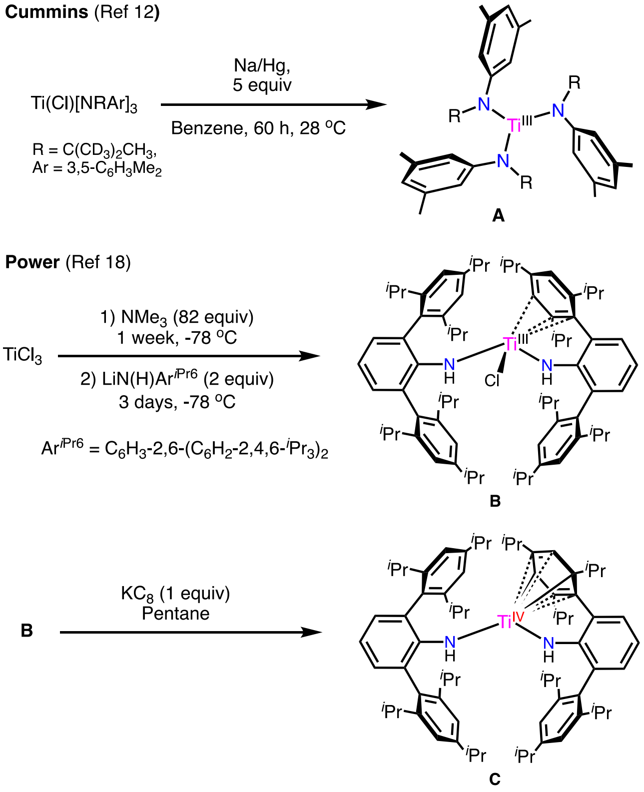
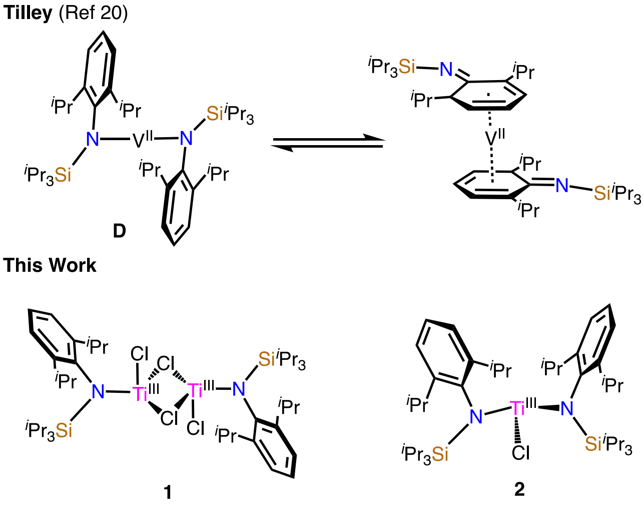
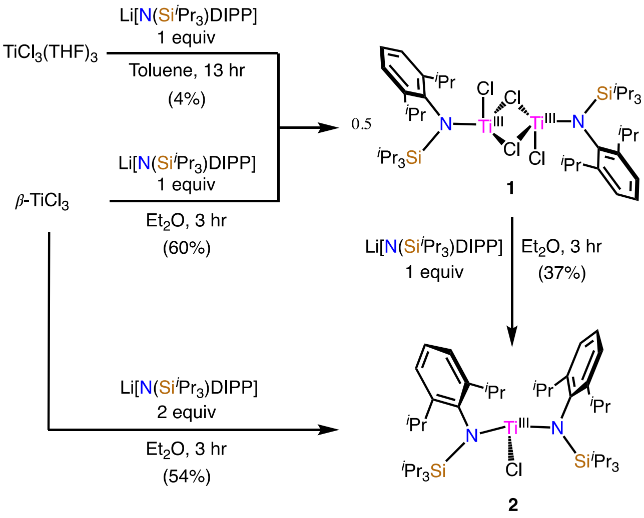
Scheme 1. Reported Examples of Low-Coordinate Titanium Amido Complexes



Scheme 2. Previous and New Examples of Low-Coordinate Complexes Stabilized by the -N(Si^{i}Pr$_3$)DIPP Ligand



Scheme 3. Synthetic Routes to 1 and 2



In 2013, Power and co-workers described the synthesis and isolation of a diamagnetic titanium bis(amido) complex, Ti{N(*H*)Ar^{iPr6}}$_2$ [Ar^{iPr6} = C$_6$H$_3$−2,6-(C$_6$H$_2$−2,4,6-^{i}Pr$_3$)$_2$] (**C**), prepared from its three-coordinate titanium(III) precursor TiCl{N(*H*)Ar^{iPr6}}$_2$ (**B**) (Scheme 1).[18] The X-ray diffraction and magnetization analysis of complex **C** suggest that the electronic structure is best viewed as involving a formally reduced, dianionic aryl ring of the amido ligand coordinated to titanium(IV). The structure of monomeric complex **B** also possesses an η^3-aryl−metal interaction similar to that observed in complex **A**, and magnetic properties are consistent with an open-shell d^1 electronic configuration.

Recently, this research group demonstrated the versatility of the amido ligand [N(Si^{i}Pr$_3$)DIPP] (DIPP = 2,6-di-*iso*-propylphenyl) in supporting two-coordinate chromium complexes in the +1, +2, and +3 oxidation states,[19] as well as the two-coordinate vanadium(II) complex **D** (Scheme 2).[20] Other groups have used this amido ligand with yttrium,[21] alkaline earth metals,[22−24] and several late transition metals.[25] Further investigations of this bulky amido ligand in allowing access to low-valent early transition metal complexes are described here, involving the synthesis, characterization, and reactivity of a family of low-coordinate, heteroleptic complexes of titanium(III) supported by the [N(Si^{i}Pr$_3$)DIPP] ligand.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of 1 and 2. Reaction of a suspension of TiCl$_3$(THF)$_3$ in toluene with 1 equiv of Li[N(Si^{i}Pr$_3$)DIPP] over 13 h afforded a minor amount of dimeric {Ti[N(Si^{i}Pr$_3$)DIPP]Cl(μ-Cl)}$_2$ (**1**) as blue needles in 4% isolated yield (Scheme 3). Subsequent optimization studies demonstrated that treatment of a suspension of β-TiCl$_3$,[26] a polymorph of TiCl$_3$, in Et$_2$O with 1 equiv of Li[N(Si^{i}Pr$_3$)DIPP], followed by stirring of the reaction mixture for 3 h, afforded **1** in a much improved yield (60% isolated, Scheme 3). These results suggest that this source of titanium(III) might offer useful synthetic routes to other THF-free low-coordinate titanium(III) complexes.[27] Treatment of **1** with an additional equiv of Li[N(Si^{i}Pr$_3$)DIPP] resulted in a color change from blue to green, and after work-up, the product Ti[N(Si^{i}Pr$_3$)DIPP]$_2$Cl (**2**) was isolated in 37% yield by crystallization from cold pentane (Scheme 3). Concurrent studies demonstrated that complex **2** could be prepared directly by the treatment of β-TiCl$_3$ in Et$_2$O with 2 equiv of Li[N(Si^{i}Pr$_3$)DIPP] in 54% isolated yield. An indication of the steric demands of the amido ligand is given by the reaction of β-TiCl$_3$ with 3 equiv of Li[N(Si^{i}Pr$_3$)DIPP] in Et$_2$O, which after 30 min at room temperature afforded only complex **2** rather than the tris(amido) complex Ti[N(Si^{i}Pr$_3$)DIPP]$_3$.

Notably, preparation of bis(amido) complex **B** from TiCl$_3$(THF)$_3$ required multiple steps and stirring at −78 °C for days (Scheme 1).[18] In contrast, the three-coordinate bis(amido) titanium(III) complex **2** was prepared under mild conditions by stirring for 3 h at ambient temperature.

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The ^{1}H NMR spectrum of **1** in benzene-d_6 features slightly broadened resonances between 0.0 and +7.0 ppm. Magnetic susceptibility measurements (Evans method) confirmed that complex **1** is diamagnetic, most likely due to strong antiferromagnetic coupling between two titanium(III) centers. In contrast to complex **1**, the ^{1}H NMR spectrum of **2** in benzene-d_6 features broad resonances between −1.0 and 8.5 ppm consistent with a paramagnetic species. Accordingly, the room-temperature magnetic susceptibility measurement (Evans method) of **2** in benzene-d_6 gave a μ_{eff} value of 1.4 μ_B, consistent with a monomeric (S = 1/2) titanium(III) complex.

Solid-State Structures of 1 and 2. Single crystals of **1** were grown from a concentrated 1:1 pentane/toluene solution, and the solid-state structure was determined by X-ray crystallography. The solid-state structure of **1** consists of molecular units possessing a planar central $Ti_2(\mu\text{-}Cl)_2$ core with terminal chloride ligands oriented in a *transoid* fashion (Figure 1), a common motif for dinuclear titanium(III) species bridged by two chloride ligands.[28−31] Notably, Yélamos and co-workers isolated and characterized the analogous pentamethylcyclopentadienyltitanium(III) complex [{Ti(η^5-C_5Me_5)Cl(μ-Cl)}$_2$], which exhibits similar structural parameters, and this indicates that the [N(Si^{i}Pr$_3$)DIPP] and η^5-C_5Me_5 ligands have comparable steric profiles.[31]

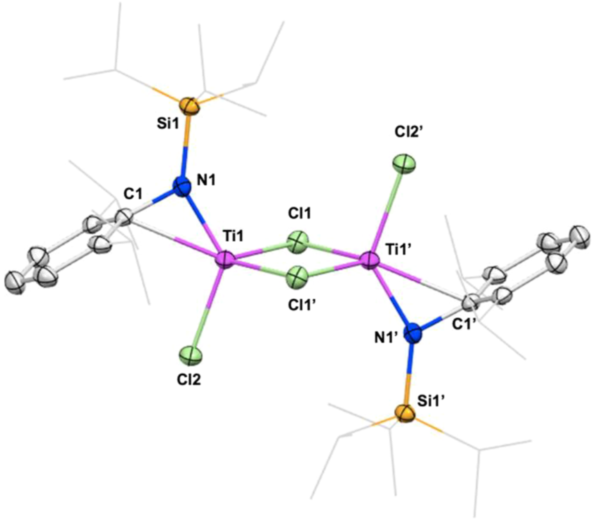


Figure 1. Solid-state molecular structure of **1** with 50% probability ellipsoids. Several carbon atoms presented as wireframe and hydrogen atoms and co-crystallized solvent omitted for clarity.

Dark green crystals of **2** were grown from a concentrated pentane solution cooled to −30 °C, and an X-ray diffraction analysis provides an unusual example of a three-coordinate monomeric titanium(III) complex with a distorted T-shaped geometry. This geometry is likely caused by the close interaction of the ligand aryl ring (via C22 and C27) with the metal center, resulting in interatomic distances of 2.414 (1) and 2.554 (1) Å, respectively (Figure 2). Notably, the Ti−C$_{ipso}$ distance is shorter than comparable distances in complexe **1** or **B**[18] (2.428 (3) and 2.485 (2), respectively Å).

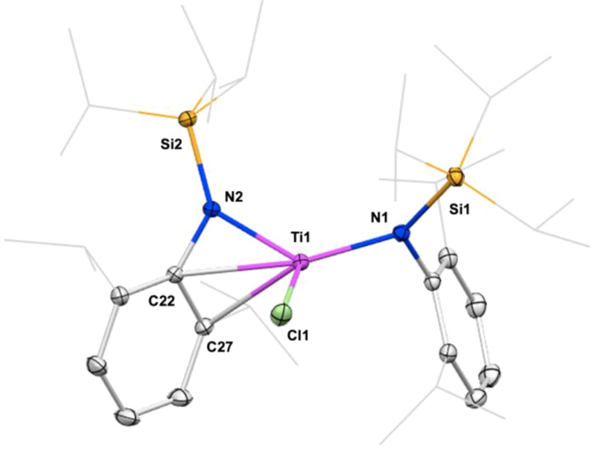
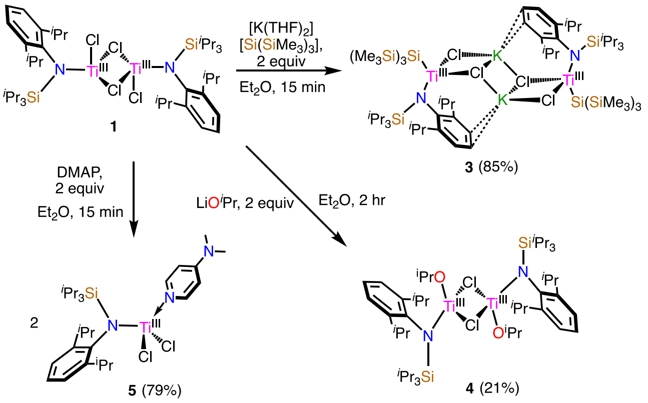


Figure 2. Solid-state molecular structure of **2** with 50% probability ellipsoids. Several carbons presented as wireframe and hydrogen atoms omitted for clarity.

Stoichiometric Reaction Chemistry of 1. Based on the low-coordinate nature of complex **1**, it was hypothesized that this complex could be a potential synthon for the preparation of Cp-free heteroleptic titanium(III) complexes. Accordingly, complex **1** was treated with a variety of silyl- and alkoxy-based alkali reagents (2.0 equiv) with the objective of producing mononuclear heteroleptic titanium(III) complexes(X)Ti[N(Si^{i}Pr$_3$)DIPP]Cl (X = SiR$_3$, OR).

Treatment of complex **1** in Et_2O with 2 equiv of [K(THF)$_2$][Si(SiMe$_3$)$_3$][32] at ambient temperature led to isolation of complex **3** as a pale orange powder in 85% isolated yield (Scheme 4). X-ray quality crystals of **3** were grown via vapor diffusion of pentane into an *ortho*-difluorobenzene solution to give orange blocks. The solid-state structure of **3** reveals an essentially planar central $Ti_2[\mu,\eta^2\text{-}(KCl)_2]$ core [torsion angle K−Cl−K−Cl = 0.00 (2)°] (Figure 3), where a slightly distorted tetrahedral geometry (τ_4 = 0.83)[33] is adopted around each titanium center with a terminal Ti−Si bond distance of 2.6938 (6).[34,35] Notably, the potassium ions are stabilized by η^2 interactions with the aromatic ring of the amido ligands, as well as by very unusual κ^1 coordination of two *ortho*-difluorobenzene molecules per potassium. In 2019, Baumgartner and co-workers isolated and characterized an anionic titanium(III) complex, (18-crown-6)·K[Cp$_2$Ti{(SiMe$_2$)H}$_2$], containing terminal Ti−Si bonds with distances of 2.664 (2) and 2.674 (3) Å,[36] that are slightly shorter than the one found in compound **3**. Also, Harrod described the preparation of several examples of non-chelating silyl complexes of titanium(III)[37−39] stabilized by Cp-type ligands. The ^{1}H NMR spectrum of **3** in THF-d_8

Scheme 4. Stoichiometric Reactivity of 1



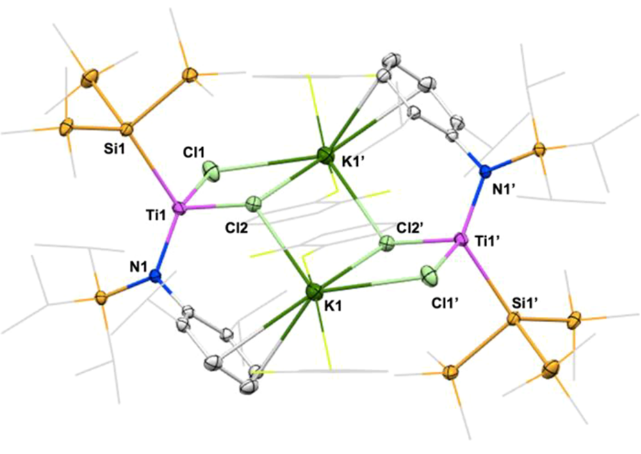


Figure 3. Solid-state molecular structure of **3** with 50% probability ellipsoids. Several carbon and fluorine atoms presented as wireframe and hydrogen atoms omitted for clarity.

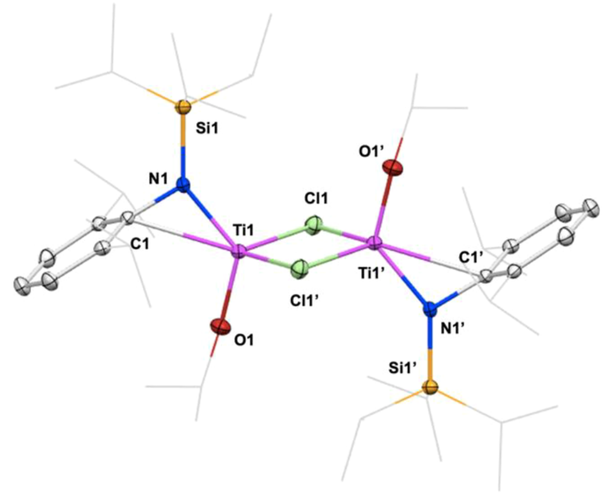


Figure 4. Solid-state molecular structure of **4** with 50% probability ellipsoids. Several carbon atoms presented as wireframe and hydrogen atoms omitted for clarity.

contains broad resonances between −7 and 10 ppm, consistent with a paramagnetic species, and an Evans method analysis gave a μ_{eff} value of 2.2 μ_B, attributable to a dinuclear structure with two magnetically isolated titanium(III) centers.

It seemed that addition of a suitable Lewis base to complex **3** might result in the disruption of the binding to potassium cations to give a mononuclear titanium(III) species. However, no change was observed upon the addition of excess (2.1 equiv) of 4-dimethylaminopyridine (DMAP) to complex **3** in benzene-d_6 at ambient temperature. Moreover, heating the reaction mixture to 80 °C resulted only in decomposition to a complex mixture of unidentified products, as monitored by ^{1}H NMR spectroscopy.

Although a number of titanium(III) aryloxide complexes are known, alkoxide complexes of titanium(III) are more rare.[27] To probe whether alkoxide analogues of complex **1** could be accessed, complex **1** was treated with 2 equiv of LiO^{i}Pr in Et$_2$O, which resulted in a color change from blue to yellow-green. After work-up, [Ti(N(Si^{i}Pr$_3$)DIPP)O^{i}Pr(μ-Cl)]$_2$ (**4**, Scheme 3) was isolated in 21% yield as an aqua blue powder that is most soluble in coordinating solvents such as Et$_2$O and THF. The ^{1}H NMR spectrum of **4** in benzene-d_6 features slightly broad resonances consistent with a diamagnetic species due to antiferromagnetic coupling between the metal centers, as observed for complex **1**. The diamagnetism of **4** was confirmed via the Evans method.

Light blue crystals of **4** from pentane−Et$_2$O were used to determine the structure by X-ray crystallography. As with the parent complex **1**, the solid-state structure of **4** shows that the titanium coordination geometry is a distorted tetrahedron (τ_4 = 0.85) associated with a planar central Ti$_2$(μ-Cl)$_2$ core. The Ti−O bond lengths are 1.789 (4) Å (Figure 4), which are slightly shorter than those of the octahedral titanium(III) isopropoxide complex reported by Bochmann.[40]

Based on the electropositive nature of early transition metals, it was of interest to treat **1** with a variety of neutral Lewis bases (L) to form corresponding mononuclear titanium(III) adducts (L)Ti[N(Si^{i}Pr$_3$)DIPP]Cl$_2$, a class of compounds that could be suitable precursors for the preparation of low-coordinate dialkyl and diaryl titanium(III) species.

Treatment of complex **1** in Et$_2$O with 2 equiv of DMAP at ambient temperature led to isolation of the titanium(III) adduct (DMAP)TiCl$_2$[N(Si^{i}Pr$_3$)DIPP] (**5**) in 79% yield as a yellow powder (Scheme 3). The xylyl isocyanide analogue of **5** was also prepared in a similar manner (see the Supporting Information). The ^{1}H NMR spectrum of **5** in benzene-d_6 indicates a paramagnetic species, as confirmed by the Evans method (μ_{eff} = 1.7 μ_B, similar to the value for mononuclear complex **2**).

X-ray quality crystals of **5** provided a crystal structure composed of monomeric four-coordinate titanium(III) complexes with a distorted tetrahedral (τ_4 = 0.85) geometry (Figure 5). In contrast to complexes **1** and **2**, no metal−aryl interactions were observed in the solid-state structure.

Alkylation and Arylation of 5. Based on the mononuclear nature of complex **5** and the presence of two chloride ligands, it was hypothesized that **5** would be a useful platform for the preparation of well-defined dihydrocarbyl titanium(III) complexes. Arylation of complex **5** was achieved with either 2

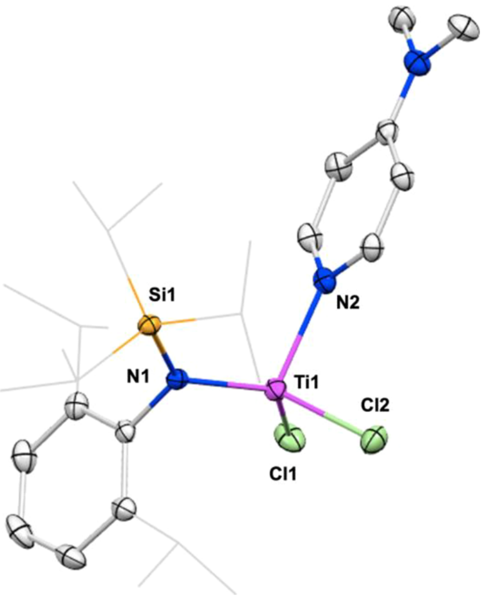
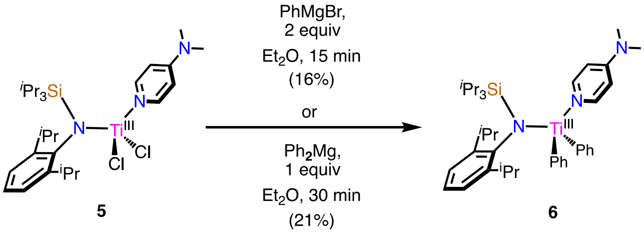


Figure 5. Solid-state molecular structure of **5** with 50% probability ellipsoids. Several carbons presented as wireframe and hydrogen atoms omitted for clarity.

equiv of PhMgBr or 1 equiv of $Ph_2Mg(THF)_2$, resulting in the formation of complex mixtures from which crude (DMAP)-$TiPh_2[N(Si^iPr_3)DIPP]$ (**6**) was isolated as maroon crystals, albeit in low yield (16% from PhMgBr; 21% from $Ph_2Mg(THF)_2$, Scheme 5). Unfortunately, **6** was not obtained in analytically pure form, and ^1H NMR spectroscopic analysis of the maroon product showed traces of additional unidentified diamagnetic impurities, possibly due to the disproportionation of the titanium(III) center.

Scheme 5. Phenylation of 5 Using Magnesium Reagents



Single crystals of **6** grown from a concentrated Et_2O solution at −30 °C were subjected to an X-ray diffraction analysis, which revealed a coordination geometry similar to that of parent complex **5** ($\tau_4 = 0.86$) (Figure 6). In 1976, Whitney and co-workers synthesized and obtained the X-ray crystal structure of the first σ-bonded aryl complex of titanium(III), $CpTi(C_6H_4CH_2NMe_2)_2$, containing only one cyclopentadienyl ligand.[41] This complex exhibits a σ Ti−C bond distance of 2.197 (6) Å, which is longer than those found in complex **6** (Ti1−C7 2.166 (2) Å, Ti1−C7 2.178 (2) Å). Both Manzer[41] and Gambarotta[42] have reported related diaryl titanium(III) complexes stabilized by neutral amine and anionic amido ligands, respectively. Otherwise, there are a few examples of aryl titanium(III) complexes not stabilized by Cp ligands.[42−44]

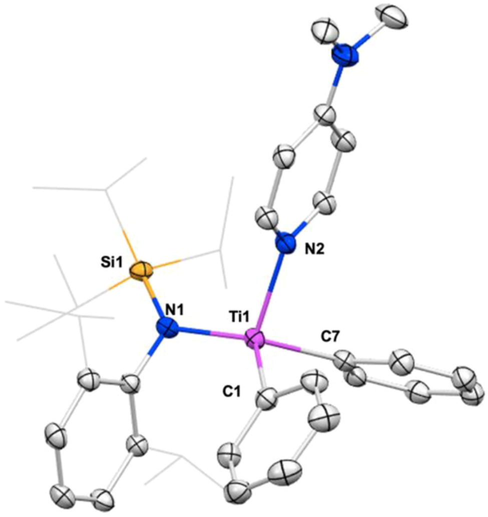
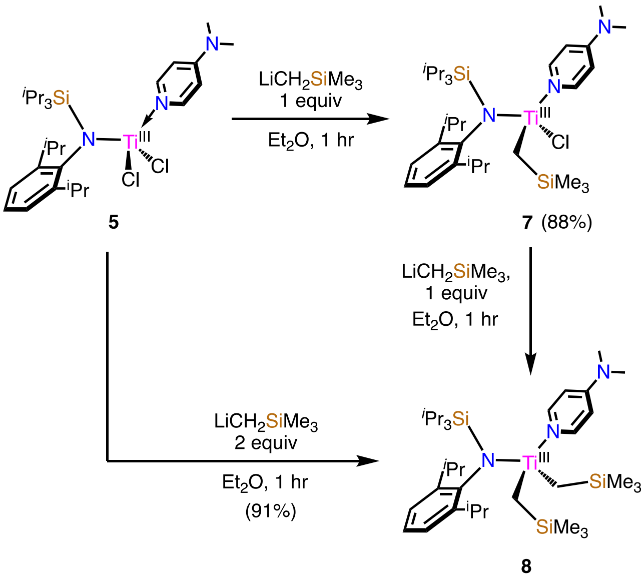


Figure 6. Solid-state molecular structure of **6** with 50% probability ellipsoids. Several carbon atoms presented as wireframe and hydrogen atoms omitted for clarity.

Analogous attempts to alkylate **5** using MeMgBr (2 equiv) resulted in dark brown mixtures of unidentified products (by ^1H NMR spectroscopy). Hypothesizing that a bulkier alkyl group might stabilize a low-coordinate organometallic product, a suspension of complex **5** in Et_2O was treated with 1 equiv of $LiCH_2SiMe_3$ at room temperature. This reaction resulted in isolation of complex **7** as a pale maroon powder in 88% isolated yield following work-up (Scheme 6). X-ray quality crystals of the monoalkyl species **7** were grown by cooling a concentrated pentane solution to −30 °C over 16 h.

Scheme 6. Alkylation of 5 Using 1 or 2 Equiv of $LiCH_2SiMe_3$



The solid-state molecular structure may be described as consisting of distorted tetrahedral metal centers ($\tau_4 = 0.86$), which, as in complex **5**, does not display any secondary aryl−metal interactions (Figure 7). Despite the steric bulk of both the CH_2SiMe_3 and amido ligands, the Ti−C bond lengths of both molecules in the asymmetric unit fall within the expected values for titanium(III)−C bonds.[18]

Gratifyingly, the dialkyl analogue of complex **7** was also readily accessed by the reaction of complex **5** with a slight excess (2.3 equiv) of $LiCH_2SiMe_3$ in Et_2O, resulting in a rapid

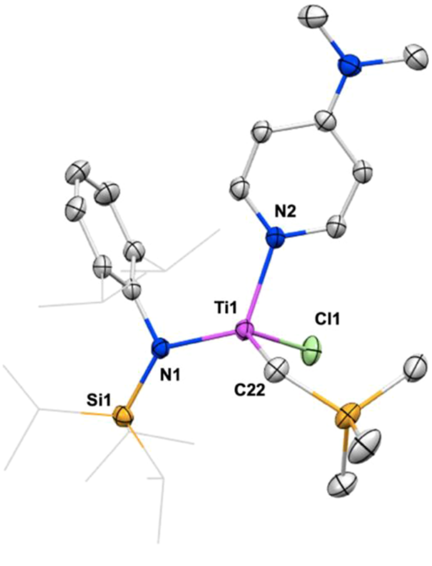


Figure 7. Solid-state molecular structure of **7** with 50% probability ellipsoids. Several carbons presented as wireframe and hydrogen atoms omitted for clarity.

color change from yellow to dark violet. After work-up, the dialkyl product (DMAP)Ti(CH$_2$SiMe$_3$)$_2$[N(Si^{i}Pr$_3$)DIPP] (**8**) was isolated in 73% yield as a dark violet powder, and an X-ray diffraction analysis revealed that the structure is generally similar to that of the monoalkyl analogue **7** (Figure 8). Related dialkyl complexes of titanium(IV) have been reported,[45−52] as well as a few examples of much rarer titanium(III) analogues.[53,54]

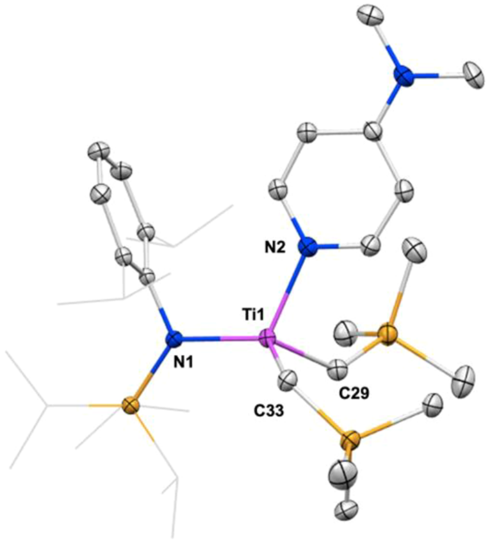
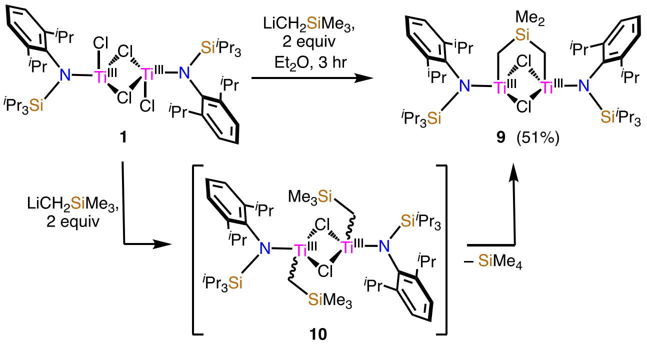


Figure 8. Solid-state molecular structure of **8** with 50% probability ellipsoids. Several carbons presented as wireframe and hydrogen atoms omitted for clarity.

Reaction of 1 with LiCH$_2$SiMe$_3$. Following the successful isolations of complexes **7** and **8**, it was of interest to explore analogous reaction chemistry in the absence of DMAP. Thus, complex **1** was exposed to LiCH$_2$SiMe$_3$ (2 equiv) in Et$_2$O solution at room temperature, giving a rapid color change to yellow. After allowing the reaction mixture to stir for 3 h, solvent was removed under reduced pressure, and the resulting residue was extracted with pentane to give a green solution. Filtration and cooling (−30 °C) this solution gave light blue X-ray quality crystals of {Ti[N(Si^{i}Pr$_3$)DIPP](μ-Cl)}$_2$[μ-CH$_2$(SiMe$_2$)CH$_2$] (**9**; Scheme 7) in 51% isolated yield.

The solid-state structure of the light blue product demonstrated formation of a cyclometalated bimetallic titanium(III) complex, with a distorted tetrahedral geometry at each titanium center, and notably, the presence of a bridging CH$_2$SiMe$_2$CH$_2$ moiety (Figure 9). Also, each molecule features a central Ti$_2$(μ-Cl)$_2$ core with the amido ligands in a *cisoid* fashion, opposite to that observed for the parent complex **1**. It seems plausible that after alkylation of complex **1**, a subsequent C−H activation of one trimethylsilyl group occurs, resulting in the formation of **9** along with concomitant generation of tetramethylsilane (TMS). Indeed, reactions performed in a sealed NMR tube show the clear formation of TMS in the reaction mixture by ^{1}H NMR spectroscopy. This type of C−H activation of a CH$_2$SiMe$_3$ ligand has recently been observed with titanium(IV),[55] as well as with other metals like molybdenum[56] and zinc.[57] However, metallacycles such as **9** are traditionally prepared by salt metathesis routes.[58,59]

Scheme 7. Synthesis of Cyclometalated Complex 9 Prepared from 1 via Proposed Intermediate 10



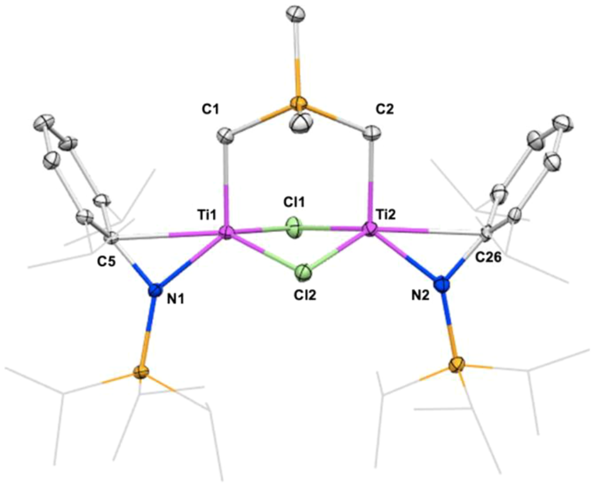


Figure 9. Solid-state molecular structure of **9** with 50% probability ellipsoids. Several carbons presented as wireframe and hydrogen atoms omitted for clarity.

It was hypothesized that the initial yellow solution observed upon alkylation of complex **1** with LiCH$_2$SiMe$_3$ in Et$_2$O could form via the dialkyl intermediate **10** (Scheme 7). Unfortunately, attempts to crystallize the yellow intermediate directly from the reaction mixture failed, invariably resulting in the formation of blue **9** instead. However, in support of the proposed structure of **10**, addition of 2 equiv of DMAP to freshly generated **10** in Et$_2$O resulted in an instant color change from yellow to maroon, and analysis by ^{1}H NMR spectroscopy reveals clean formation of the expected monoalkyl complex **7**. Further studies on related C−H activation processes with these systems are ongoing.

■ CONCLUDING REMARKS

In summary, this report details the synthesis of a family of low-coordinate titanium(III) compounds stabilized by a bulky amido ligand. These complexes are easily functionalized with a variety of salt metathesis reagents to form heteroleptic silyl, alkoxy, or alkyl complexes, which can adopt either mononuclear or dinuclear structures, depending on the nature of the anionic ligands. In certain cases, dimerization can be inhibited by the addition of DMAP, which binds to the electrophilic metal center as a Lewis base. Lastly, in the case of base-free dialkylation, C−H activation was observed, resulting in the formation of a dinuclear cyclometalated product. Overall, these complexes should be useful both as precursors to unsaturated low-coordinate complexes of titanium(III) and as catalysts for a range of useful transformations like alkene polymerization

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and hydrofunctionalization. Efforts toward exploring these applications are ongoing in our laboratory.

■ EXPERIMENTAL SECTION

General Considerations. Unless otherwise noted, all experiments were conducted with dry oxygen-free solvents using standard Schlenk techniques or in a nitrogen atmosphere glovebox. Pentane, toluene, Et$_2$O, and tetrahydrofuran were dried and deaerated using a JC Meyers Phoenix SDS solvent purification system. Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed by three freeze−pump−thaw cycles, and stored under nitrogen over activated 3 Å molecular sieves prior to use. Ph$_2$Mg(THF)$_2$,[60] β-TiCl$_3$,[26] and [K(THF)$_2$][Si(SiMe$_3$)$_3$][32] were prepared according to the literature procedures. Experimental details for the preparation of Li[N(Si^{i}Pr$_3$)DIPP] are included in the Supporting Information. All other reagents were obtained from commercial suppliers and used as received.

Analytical Method Details. Elemental analyses were performed by the College of Chemistry Microanalytical Facility at the University of California, Berkeley.

NMR Spectroscopy. All NMR spectra were collected at ambient temperature (ca. 25 °C) on Bruker AV-300, AVB-400, AVQ-400, AV-500, or AV-600 MHz spectrometers. ^{1}H NMR spectra were referenced to TMS calibrated via residual proteo solvent signals.[61] All NMR spectra were analyzed with MestReNova (v. 12.0.3). Solution-state magnetic susceptibilities for compounds **1**−**9** were determined by ^{1}H NMR spectroscopy using the Evans method, without diamagnetic corrections.[62,63]

X-ray Diffraction Experiments. Data for **1** and **2** were collected at Beamline 11.3.1/12.2.1 (Small Molecule Crystallography) of the Advanced Light Source at the Lawrence Berkeley National Laboratory (LBNL). All crystals were kept at 100(2) K throughout collection. Data collection, refinement, and reduction were performed with Bruker APEX2 or APEX3 software (v. 2013.4-0 or v. 2016.9-0). Structure solution, modeling, and refinement were performed using Olex2.[64] All structures were solved using SHELXT-2014[65] and refined with SHELXL-2018,[65] with refinement of F^2 on all data by full-matrix least squares. In all models, non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at the geometrically calculated positions and refined using a riding model, unless otherwise specified. Specific details can be found in the Supporting Information and in the crystallographic information files.

Synthesis of 1. *Method A.* To a 20 mL scintillation vial were added TiCl$_3$(THF)$_3$ (0.100 g, 0.272 mmol, 1.00 equiv) and toluene (4 mL). The resulting blue suspension was stirred, and a solution of Li[N(Si^{i}Pr$_3$)DIPP] (0.0962 g, 0.284 mmol, 1.04 equiv) in toluene (3 mL) was added dropwise, resulting in an immediate color change to dark brown. The reaction mixture was stirred at ambient temperature for 13 h. The resulting reaction mixture was concentrated under reduced pressure to a brown residue, which was dissolved with a minimal amount of a 1:1 pentane:toluene solution. The resulting solution was filtered and stored at −30 °C for 16 h to yield 4.6 mg (0.0051 mmol, 4%) of **1** as blue needles, which were isolated by decanting the supernatant and removing residual volatiles in vacuo.

Method B. To a 20 mL scintillation vial were added β-TiCl$_3$ (0.100 g, 0.648 mmol, 1.00 equiv) and Et$_2$O (4 mL). The resulting maroon suspension was stirred, and a solution of Li[N(Si^{i}Pr$_3$)DIPP] (0.225 g, 0.663 mmol, 1.02 equiv) in Et$_2$O (4 mL) was added dropwise. The reaction mixture was stirred at ambient temperature for 3 h. The resulting reaction mixture was concentrated under reduced pressure to a brown residue, which was triturated with pentane (2 mL). The resulting blue residue was dissolved with a minimal amount of a 1:1 pentane:toluene solution. The resulting deep blue solution was filtered and stored at −30 °C for 16 h to yield 0.176 g (0.195 mmol, 60%) of **1** as blue X-ray quality needles, which were isolated by decanting the supernatant and drying in vacuo. ^{1}H NMR (400 MHz, benzene-d_6) δ 6.92 (t, J = 7.7 Hz, 2H, Ar-para-*H*), 6.75 (d, J = 7.7 Hz, 4H, Ar-meta-*H*), 4.17 (br s, 4H, Me$_2$C*H*), 2.92 (br s, 6H, Si(C*H*Me$_2$)$_3$), 1.59 (d, J = 5.2 Hz, 36H, Si(CH(C*H*$_3$)$_2$)$_3$), 1.25 (br s, 12H, HC(C*H*$_3$)$_2$), 0.21 (br s, 12H, HC(C*H*$_3$)$_2$). Anal. Calcd for $C_{42}H_{76}Cl_4N_2Si_2Ti_2$: C, 55.88; H, 8.49; N, 3.10. Found: C, 55.59; H, 8.56; N, 3.02.

Synthesis of 2. *Method A.* To a 20 mL scintillation vial were added **1** (0.0300 g, 0.033 mmol, 1.00 equiv) and Et$_2$O (2 mL). The resulting blue suspension was stirred, and a solution of Li[N(Si^{i}Pr$_3$)-DIPP] (0.0321 g, 0.0945 mmol, 2.86 equiv) in Et$_2$O (3 mL) was added dropwise. The reaction mixture was stirred at ambient temperature for 3 h. The resulting dark brown reaction mixture was concentrated under reduced pressure to a brown residue, which was washed with minimal pentane (2 mL). The resulting green residue was extracted with pentane, filtered through a glass fiber, and stored at −30 °C for 16 h to yield 9.1 mg (0.0122 mmol, 37%) of **2** as green crystals, which were isolated by decanting the supernatant and drying in vacuo.

Method B. To a 20 mL scintillation vial were added β-TiCl$_3$ (0.100 g, 0.648 mmol, 1.00 equiv) and Et$_2$O (4 mL). The resulting maroon suspension was stirred, and a solution of Li[N(Si^{i}Pr$_3$)DIPP] (0.450 g, 1.33 mmol, 2.05 equiv) in Et$_2$O (8 mL) was added dropwise. The reaction mixture was stirred at ambient temperature for 3 h. The resulting reaction mixture was concentrated under reduced pressure to a brown residue, which was washed with minimal pentane (2 mL). The resulting green foam was dissolved with a minimal amount of pentane. The resulting solution was filtered through a glass fiber and stored at −30 °C for 16 h to yield 0.260 g (0.347 mmol, 54%) of **2** as X-ray quality green crystals, which were isolated by decanting the supernatant and drying in vacuo. Effective magnetic moment (Evans method, 500 MHz, benzene-d_6, 25 °C): μ_{eff} = 1.4 μ_{B}. Anal. Calcd for $C_{42}H_{76}N_2TiClSi_2$: C, 67.39; H, 10.23; N, 3.74. Found: C, 67.10; H, 10.37; N, 3.62.

Synthesis of 3. To a 150 mL Erlenmeyer flask equipped with a stir bar were added **1** (0.300 g, 0.332 mmol, 1.00 equiv) and Et$_2$O (12 mL). The resulting suspension was stirred, and a solution of K(THF)$_2$Si(SiMe$_3$)$_3$ (0.289 g, 0.674 mmol, 2.03 equiv) in Et$_2$O (4 mL) was added dropwise. The reaction mixture was stirred at ambient temperature for 15 min and then pentane was added (30 mL). After 15 min, the precipitate was collected by filtration, washed with pentane (2 × 2 mL), and dried in vacuo to yield 418 mg (0.283 mmol, 85%) of **3** as an orange powder. Crystals of **3** were grown via vapor diffusion, from a concentrated 1,2-difluorobenzene solution and using pentane as the antisolvent, and stored at −30 °C for 2 weeks, thus yielding orange blocks. Effective magnetic moment (Evans method, 400 MHz, THF-d_8, 25 °C): μ_{eff} = 2.2 μ_{B}. Anal. Calcd. for $C_{60}H_{130}Cl_4K_2N_2Si_{10}Ti_2$: C, 48.82; H, 8.88; N, 1.90. Found: C, 48.87; H, 8.63; N, 1.76.

Synthesis of 4. To a 20 mL scintillation vial were added **1** (20.0 mg, 0.0222 mmol, 1.00 equiv) and Et$_2$O (5 mL). The resulting blue suspension was stirred, and a solution of LiO^{i}Pr (3.0 mg, 0.0454 mmol, 2.05 equiv) in Et$_2$O (4 mL) was added dropwise, resulting in an immediate color change to yellow-green. The resulting reaction mixture was stirred at ambient temperature for 2 h. The resulting reaction mixture was concentrated under reduced pressure to a blue solid residue, which was washed with pentane (2 mL). The resulting suspension was filtered to yield 4.4 mg (0.046 mmol, 21%) of **4** as a blue powder. X-ray quality crystals of **4** were grown by cooling an Et$_2$O and pentane solution of **4** to −30 °C for 2 days, yielding light blue crystals. ^{1}H NMR (500 MHz, benzene-d_6) δ 6.85 (br s, 6H, Ar-*H*), 4.22 (br s, 2H, Me$_2$C*H*), 3.44 (br s, 4H, Me$_2$C*H*), 2.26 (br s, 6H, Si(C*H*Me$_2$)$_3$), 1.46 (d, J = 5.6 Hz, 36H, Si(CH(C*H*$_3$)$_2$)$_3$, 1.24 (d, J = 6.6 Hz, 12H, (CH(C*H*$_3$)$_2$), 1.14 (d, J = 6.5 Hz, 12H, (CH(C*H*$_3$)$_2$), 0.66 (br s, 12H, HC(C*H*$_3$)$_2$). Anal. Calcd for $C_{48}H_{90}Cl_2N_2O_2Si_2Ti_2$: C, 60.68; H, 9.55; N, 2.95. Found: C, 59.30; H, 9.66; N, 2.84. Although satisfactory elemental analyses could not be obtained after repeated attempts, the data here are included to demonstrate our best results.

Synthesis of 5. To a 20 mL vial equipped with a stir bar were added **1** (0.103 g, 0.114 mmol, 1.00 equiv) and Et$_2$O (5 mL). The resulting blue suspension was stirred, and a solution of DMAP (0.0499 g, 0.408 mmol, 3.58 equiv) in Et$_2$O (5 mL) was added dropwise. The orange reaction mixture was allowed to stir at ambient temperature for 15 min. The resulting reaction mixture was then concentrated to one-third of its volume. Pentane was then added (10 mL), and the reaction mixture was left to stir. After 15 min, the resulting precipitate was collected by filtration, washed with pentane (2 × 2 mL), and dried in vacuo to yield 104 mg (0.181 mmol, 79%) of **5** as a yellow powder. X-ray quality crystals of **5** were grown by cooling an Et_2O and pentane solution of **5** to −30 °C for 2 days, yielding yellow crystals. Effective magnetic moment (Evans' method, 400 MHz, benzene-d_6, 25 °C): μ_{eff} = 1.7 μ_B. Anal. Calcd for $C_{28}H_{48}Cl_2N_3SiTi$: C, 58.63; H, 8.44; N, 7.33. Found: C, 58.47; H, 8.69; N, 7.41.

Synthesis of 6. *Method A.* To a 20 mL vial equipped with a stir bar were added **5** (50.0 mg, 0.0872 mmol, 1.00 equiv) and Et_2O (5 mL). The resulting yellow solution was stirred, and a solution of PhMgBr (3 M in Et_2O, 59.0 μL, 0.177 mmol, 2.03 equiv) in Et_2O (3 mL) was added dropwise. The reaction mixture was allowed to stir at ambient temperature for 1 h. The resulting reaction mixture was concentrated under reduced pressure to a maroon solid residue, which was triturated with pentane (2 mL). The resulting maroon residue was dissolved with a minimal amount of toluene, filtered, and stored overnight at −30 °C to yield 6.4 mg (0.0097 mmol, 11%) of **6** as X-ray quality, maroon crystals, which were isolated by decanting the supernatant and drying in vacuo. Effective magnetic moment (Evans method, 400 MHz, benzene-d_6, 25 °C): μ_{eff} = 1.3 μ_B.

Method B. To a 20-mL vial equipped with a stir bar were added **5** (31.8 mg, 0.0554 mmol, 1.00 equiv) and Et_2O (4 mL). The yellow solution was stirred, and a solution of $Ph_2Mg(THF)_2$ (18.9 mg, 0.0589 mmol, 1.07 equiv) in Et_2O (2 mL) was added dropwise, resulting in an immediate color change to maroon. The reaction mixture was allowed to stir at ambient temperature for 1 h. The resulting reaction mixture was concentrated under reduced pressure to a maroon residue, which was washed with pentane (2 mL). The resulting maroon residue was extracted with toluene, filtered through a glass fiber, and stored at −30 °C to yield 6.4 mg (0.0097 mmol, 18%) of **6** as maroon crystals, which were isolated by decanting the supernatant and removing residual volatile compounds in vacuo.

Synthesis of 7. To a 20 mL vial equipped with a stir bar were added **5** (34.1 mg, 0.0595 mmol, 1.00 equiv) and Et_2O (4 mL). The resulting yellow suspension was stirred, and a solution of $LiCH_2SiMe_3$ (5.9 mg, 0.0627 mmol, 1.05 equiv) in Et_2O (3 mL) was added dropwise, resulting in an immediate color change to maroon. The mixture was allowed to stir at ambient temperature for 1 h. The resulting maroon reaction mixture was concentrated under reduced pressure to a maroon residue, which was triturated with pentane (3 × 2 mL). The resulting maroon residue was dissolved with a minimal amount of pentane and then filtered. The volatiles were then removed in vacuo to yield 32.8 mg (0.0525 mmol, 88%) of **7** as a pale maroon powder. Crystals suitable for single-crystal X-ray diffraction studies were obtained by dissolving the resulting pale maroon powder with a minimal amount of pentane, filtering through a glass fiber, and storing the maroon solution at −30 °C to yield maroon crystals. Effective magnetic moment (Evans method, 400 MHz, benzene-d_6, 25 °C): μ_{eff} = 1.8 μ_B. Anal. Calcd for $C_{32}H_{59}ClN_3Si_2Ti$: C, 61.46; H, 9.51; N, 6.72. Found: C, 61.17; H, 9.29; N, 6.60.

Synthesis of 8. To a 20 mL vial equipped with a stir bar were added **5** (19.0 mg, 0.0332 mmol, 1.00 equiv) and Et_2O (4 mL). The resulting yellow suspension was stirred, and a solution of $LiCH_2SiMe_3$ (6.4 mg, 0.0681 mmol, 2.1 equiv) in Et_2O (3 mL) was added dropwise, resulting in an immediate change to dark violet. The mixture was allowed to stir at ambient temperature for 1 h. The resulting dark violet reaction mixture was concentrated under reduced pressure to a violet residue, which was triturated with pentane (3 × 2 mL). The resulting violet residue was extracted with pentane (blue-violet solution) and then filtered through a glass fiber. The volatiles were then removed in vacuo to yield 20.5 mg (0.0303 mmol, 91% yield) of **8** as a dark violet powder. Dark violet crystals suitable for single-crystal X-ray diffraction studies were obtained by dissolving the resulting dark violet powder with a minimal amount of pentane, filtering the solution through glass fiber, and storing the blue-violet solution overnight at −30 °C. Effective magnetic moment (Evans method, 400 MHz, toluene, 25 °C): μ_{eff} = 1.6 μ_B. Anal. Calcd for $C_{36}H_{70}N_3Si_3Ti$: C, 68.86; H, 10.42; N, 6.21. Found: C, 64.53; H, 9.31; N, 5.68. Although satisfactory elemental analyses could not be obtained after repeated attempts, the data here are included to demonstrate our best results.

Synthesis of 9. To a 20 mL scintillation vial were added **1** (0.100 g, 0.111 mmol, 1.00 equiv) and Et_2O (5 mL). The resulting suspension was stirred, and a solution of $LiCH_2SiMe_3$ (21.2 mg, 0.225 mmol, 2.03 equiv) in Et_2O (3 mL) was added dropwise, resulting in an immediate color change to yellow. The reaction mixture was stirred at ambient temperature for 3 h. The resulting yellow reaction mixture was concentrated under reduced pressure to a yellow residue, which was triturated with pentane (2 × 2 mL) and filtered through a glass fiber, and the volatiles were then removed in vacuo to a dark green residue. The resulting green residue was dissolved in pentane (4 mL). The resulting deep green solution was let to stir, and after 30 min, pentane was removed under reduced pressure. This process was repeated three times, during which the color of the solution and dried residue changed from green to blue. The volatiles from the resulting blue solution were then removed in vacuo to an aqua blue powder. The resulting aqua blue powder was suspended in hexamethyldisiloxane (3 mL) and let to stir. After 15 min, the blue solid was collected by filtration, washed with a minimal amount of hexamethyldisiloxane, and dried in vacuo to yield 52.3 mg (0.0570 mmol, 51%) of **9** as an aqua blue powder. Crystals suitable for single-crystal X-ray diffraction studies were obtained by dissolving the resulting blue solid residue with a minimal amount of pentane. The resulting solution was filtered through a glass fiber and stored overnight at −30 °C to yield X-ray quality blue needles. ^{1}H NMR (400 MHz, benzene-d_6) δ 7.07 (d, J = 7.6 Hz, 2H, Ar-para-H), 6.94 (t, J = 6.9 Hz, 4H, Ar-meta-H), 3.83 (br s, 4H, Me_2CH), 1.85 (br s, 6H, $Si(CHMe_2)_3$), 1.40 (d, J = 6.0 Hz, 36H, $Si(CH(CH_3)_2)_3$), 1.21 (br s, 12H, $HC(CH_3)_2$), 0.46 (br s, 12H, $HC(CH_3)_2$), 0.37 (s, 12H, $Si(CH_3)_2$), 0.12 (s, 4H, $Ti(CH_2)Si(CH_2)Ti$). Anal. Calcd for $C_{46}H_{86}Cl_2N_2Si_3Ti_2$: C, 60.18; H, 9.44; N, 3.05. Found: C, 59.47; H, 9.60; N, 2.92. Although satisfactory elemental analyses could not be obtained after repeated attempts, the data here are included to demonstrate our best results.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.2c00162.

NMR spectra and details of X-ray crystallography (PDF)

Accession Codes

CCDC 2160604−2160613 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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