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N–H Group Transfer and Oxidative Addition Chemistry Promoted by Isolable Bis(cyclopentadienyl)titanium Sandwich Complexes

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Addition of propylenimine (2-methylaziridine) to the bis(cyclopentadienyl)titanium sandwich complexes, (η^5-C_5Me_4R)$_2$-Ti (R = *i*Pr, $SiMe_3$), resulted in rapid [NH] group transfer followed by C–H activation of a cyclopentadienyl methyl group to yield the corresponding cyclometalated titanocene amido compounds. Exposure of these molecules to 4 atm of H_2 at 55 °C resulted in hydrogenolysis of the metal–carbon bond to form the titanium amido hydride compounds, (η^5-C_5Me_4R)$_2$-Ti(NH_2)H. Deuteriolysis with DCl gas confirmed exclusive cyclometalation from the positions adjacent to the isopropyl and trimethylsilyl substituent. Oxidative addition of the N–H bonds of amines has also been observed. Addition of NH_3 to either (η^5-$C_5Me_4SiMe_3$)$_2$Ti or (η^5-C_5Me_4*i*Pr)$_2$Ti yielded the corresponding titanocene amido hydrides along with the titanocene(III) amides, (η^5-C_5Me_4R)$_2$TiNH_2, arising from formal deprotonation by unreacted sandwich from the putative titanocene ammonia complex.

Introduction

The synthesis of isolable, thermally stable bis(cyclopentadienyl)titanium sandwich complexes by introduction of sterically demanding ring substituents has offered the rare opportunity to explore the fundamental coordination chemistry of a well-defined divalent titanium center.[1,2] Our laboratory has discovered that several complexes of the general formula, (η^5-C_5Me_4R)$_2$Ti (R = *i*Pr, *t*Bu, $SiMe_3$, $SiMe_2Ph$) coordinate dinitrogen upon cooling in solution (Figure 1).[3] Both the maximum temperature of dinitrogen coordination[3] and the number of N_2 ligands[4] are sensitive to the nature of the ring substituents, where smaller, electron-withdrawing groups increase the azophilicity of the titanium. Unusual examples of titanocene monocarbonyl complexes have also been prepared by careful addition of CO to the

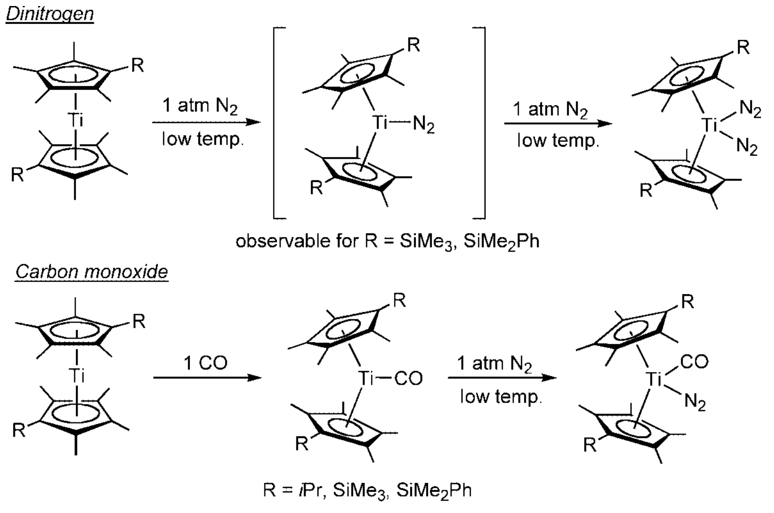

Figure 1. Unusual examples of mono(dinitrogen), bis(dinitrogen), monocarbonyl and mixed carbonyl-dinitrogen complexes of bis(cyclopentadienyl) titanium sandwich compounds.

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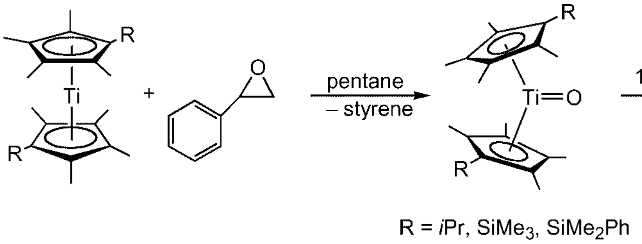


Figure 2. Synthesis and hydrogenation of bis(cyclopentadienyl)titanium oxo complexes.

corresponding sandwich (Figure 1).[4] At low temperature, these molecules coordinate N_2 to yield mixed carbonyl-dinitrogen compounds.[4]

Subsequent studies have focused on the oxidation of the isolable bis(cyclopentadienyl)titanium sandwiches with the goal of generating titanium ligand multiple bonds that do not require stabilization by coordination of additional base. Our initial studies have focused on the preparation of monomeric, base-free titanocene oxo complexes. Treatment of $(\eta^5\text{-}C_5Me_4R)_2Ti$ [R = *i*Pr (**1**), $SiMe_3$ (**2**), $SiMe_2Ph$ (**3**)] with styrene oxide induced oxygen atom abstraction affording the desired terminal oxo complexes, $(\eta^5\text{-}C_5Me_4R)_2Ti{=}O$, and free olefin (Figure 2).[5] While the isopropyl-substituted variant **1=O** is only stable in [D$_6$]benzene for hours at 23 °C, the silylated compounds **2=O** and **3=O** were isolated in the solid state and in the case of **3=O** characterized by X-ray diffraction. The relative thermal stability of these compounds contrasts $(\eta^5\text{-}C_5Me_5)_2Ti{=}O$, which requires the presence of a Lewis base such as 4-phenylpyridine for observation and isolation.[6,7]

Exposure of each of the monomeric, base-free titanocene oxo complexes to H_2 results in rapid hydrogenation of the Ti=O bond to furnish the corresponding hydroxy hydride derivatives, $(\eta^5\text{-}C_5Me_4R)_2Ti(OH)H$. This behavior highlights the benefits of the base-free species as addition of dihydrogen to $(\eta^5\text{-}C_5Me_5)_2Ti(O)L$ (L = pyridine) yields a mixture of products from which $(\eta^5\text{-}C_5Me_5)_2Ti(OH)_2$ and $(\eta^5\text{-}C_5Me_5)_2Ti(OH)H$ were identified.[8] The pressure dependence on the rate of hydrogenation of **2=O** established a first order dependence on H_2.[5] This rate law, in combination with the measurement of a normal, primary kinetic isotope effect of 2.7(3) at 23 °C, supports a 1,2-addition pathway for hydrogenation of the Ti=O bond. Similar results were obtained for hydrosilylation of **2=O** to yield the corresponding hydrido titanocene siloxide. In contrast, C–H bonds of saturated and unsaturated hydrocarbons have proven unreactive, most likely a result of the strong Ti=O π-bond.

Inspired by these observations, the synthesis of the corresponding "parent imido" complexes, $(\eta^5\text{-}C_5Me_4R)_2Ti{=}NH$, was targeted. Many isolable titanium imides have been reported and their chemistry extensively studied,[9] especially with respect to C–H activation.[10] Most of these compounds contain sterically demanding nitrogen substituents (e.g. *t*Bu, aryl, $SiMe_3$), which impart stability. Parent imido derivatives, $L_nTi{=}NH$, are by comparison relatively rare[11] despite their potential intermediacy in the preparation of titanium nitride thin films.[12] In this contribution, we describe our efforts to prepare parent titanocene imido derivatives by [NH] group transfer and also explore N–H oxidative addition of amines. The stability of the transient parent imides is also compared with isolable titanocene oxo compounds.

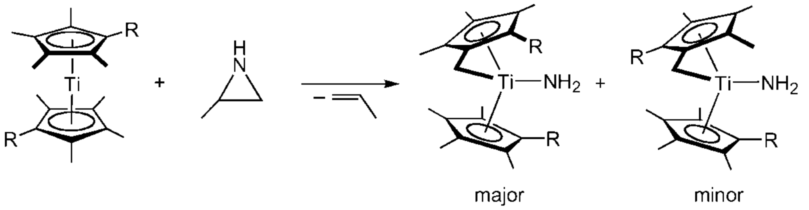
Results and Discussion

Our synthetic approach for the preparation of $(\eta^5\text{-}C_5Me_4R)_2Ti{=}NH$ compounds was inspired by the [O]-atom transfer chemistry used to prepare the corresponding oxo derivatives. Treatment of a [D$_6$]benzene solution of **1** with a stoichiometric quantity of propylenimine yielded one equivalent of propylene and an initial equimolar mixture of two new C_1-symmetric titanium products, inconsistent with formation of the desired imido compound.

Over the course of one week at 23 °C, the mixture of diastereomers (vide infra) converts to a single thermodynamic product. The major isomer exhibits two doublets centered at δ = 1.78 and 2.90 ppm, indicating cyclometalation of one of the cyclopentadienyl methyl groups. Similar resonances centered at δ = 1.94 and 2.82 ppm are observed for the minor thermodynamic isomer. In addition, both compounds exhibit N–H resonances that integrate to two protons, consistent with formation of two diastereomers of the cyclometalated amide complex **1-CM-NH$_2$** [Equation (1)].

A similar outcome was observed with the silylated titanium sandwich, **2**. Addition of one equivalent of propylenimine again resulted in rapid evolution of one equivalent of propylene and formation of two C_1-symmetric titanocene compounds. In this case, a 3:1 mixture of diastereomers of the cyclometalated titanium amide complex **2-CM-NH$_2$** was formed [Equation (1)]. No change in the ratio of the mixture of isomers was observed after standing for one week at 23 °C. Thermolysis at 65 °C over the course of days resulted in gradual decomposition.

The assignment of the stereochemistry of the observed diastereomers of **1-CM-NH$_2$** and **2-CM-NH$_2$** was accomplished by a combination of two-dimensional (NOESY, HSQC, HMBC) NMR experiments. Complete details are reported in the Supporting Information. Observation of cyclometalated titanocene amide complexes following addition of propylenimine suggests that the desired parent imido compounds, $(\eta^5\text{-}C_5Me_4R)_2Ti{=}NH$, are formed transiently but undergo rapid 1,2-addition of a C–H bond from



1: R = *i*Pr
2: R = SiMe$_3$

1-CM-NH$_2$: R = *i*Pr
2-CM-NH$_2$: R = SiMe$_3$

(1)

the diastereotopic cyclopentadienyl methyl groups adjacent to the isopropyl or trimethylsilyl substituent. The conversion of the kinetic mixture of diastereomers of **1-CM-NH$_2$** to a sole thermodynamic isomer demonstrates that the C–H activation reaction is reversible. In the case of **2-CM-NH$_2$** where the ratio of diastereomers remains constant, we are unable to distinguish between the kinetic and thermodynamic preferences for methyl group cyclometalation.

To determine whether bis(cyclopentadienyl)titanium imido complexes bearing larger nitrogen substituents would exhibit improved thermal stability, $(\eta^5\text{-}C_5Me_4SiMe_3)_2$Ti=NSiMe$_3$ (**2=NSiMe$_3$**) was prepared by addition of Me$_3$SiN$_3$ to **2** [Equation (2)]. As was observed with $[\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2]_2$Ti=NSiMe$_3$,[13] the [D$_6$]benzene ^{1}H and ^{13}C NMR spectra of **2=NSiMe$_3$** exhibit the number of resonances expected for a C_2-symmetric imide complex. It should be noted that in the solid state, $[\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2]_2$Ti=NSiMe$_3$ contains a near linear Ti=N–Si linkage.[13]

Allowing [D$_6$]benzene solutions of **2=NSiMe$_3$** to stand at 23 °C for days resulted in cyclometalation of the cyclopentadienyl methyl groups both adjacent and distal to the [SiMe$_3$] substituent. All four diastereomers were detected by NMR spectroscopy, but only two formed in appreciable quantities. The major isomer was identified as one of the diastereomers arising from distal methyl group cyclometalation while the other is one of the diastereomers from adjacent methyl group C–H activation. The two minor diastereomers account for less than 10% of the mixture. Because the presence of four isomeric C_1-symmetric titanocene compounds produces complex NMR spectra with considerable peak overlap, the stereochemistry of each diastereomer could not be reliably assigned.

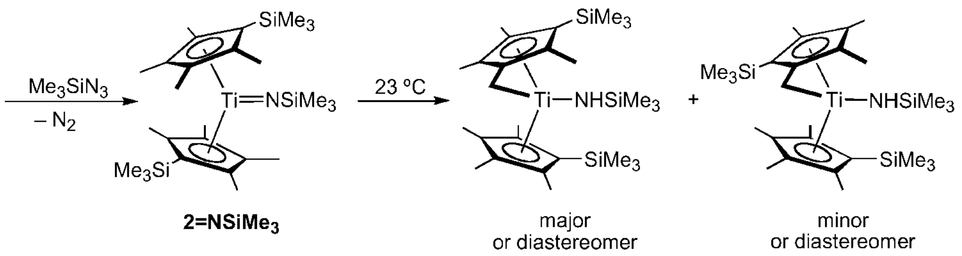
Confirmation of the regiochemistry of cyclometalation was provided by treating the mixture of products with DCl. Analysis of the resulting isotopomers of **2-Cl$_2$** established deuterium incorporation into both methyl positions. Importantly, no deuterium incorporation into the [SiMe$_3$] substituents was observed, confirming that these positions do not undergo C–H activation.

The reactivity of **1-CM-NH$_2$** and **2-CM-NH$_2$** was also explored. Exposure of the kinetic mixture of diastereomers of **1-CM-NH$_2$** to 4 atm of H$_2$ resulted in slow hydrogenation to give the hydrido titanocene amido complex $(\eta^5\text{-}C_5Me_4\textit{i}Pr)_2Ti(NH_2)H$ [**1-(NH$_2$)H**] upon heating to 55 °C for three days. Performing the experiment with D$_2$ gas yielded the deuterated isotopologue with the isotopic labels incorporated into the appropriate cyclopentadienyl methyl groups and the titanium-hydride (deuteride). Incorporation of the isotopic label was also observed in the N–H position, consistent with reversible 1,2-addition and elimination sequences. Similar hydrogenation chemistry was observed with **2-CM-NH$_2$** to yield $(\eta^5\text{-}C_5Me_4SiMe_3)_2Ti(NH_2)H$ [**2-(NH$_2$)H**] (Figure 3).

Intramolecular hydrogen exchange was explored with **2-(NH$_2$)H** by EXSY NMR spectroscopy. No crosspeaks indicative of exchange were observed up to temperatures of 90 °C with mixing times of 700 ms. Intermolecular exchange was probed by addition of four atmospheres of D$_2$ gas to a [D$_6$]benzene solution of **2-(NH$_2$)H** and no isotopic incorporation was observed over the course of days at 23 °C. The failure to observe isotopic exchange at ambient temperature demonstrates that the barrier for 1,2-elimination of H$_2$ is higher for **2-(NH$_2$)H** than **2-(OH)H**.[5]

The isolation of the thermally stable bis(cyclopentadienyl)titanium amido hydrides **1-(NH$_2$)H** and **2-(NH$_2$)H** suggested that these compounds could also be prepared by N–H oxidative addition of ammonia.[14,15] Addition of one equivalent of NH$_3$ gas to a [D$_6$]benzene solution of **1** yielded only small amounts (about 10%) of the desired amido hydride **1-(NH$_2$)H** (Figure 4). The major product

2



2=NSiMe$_3$

2-CM-NHSiMe$_3$

(2)

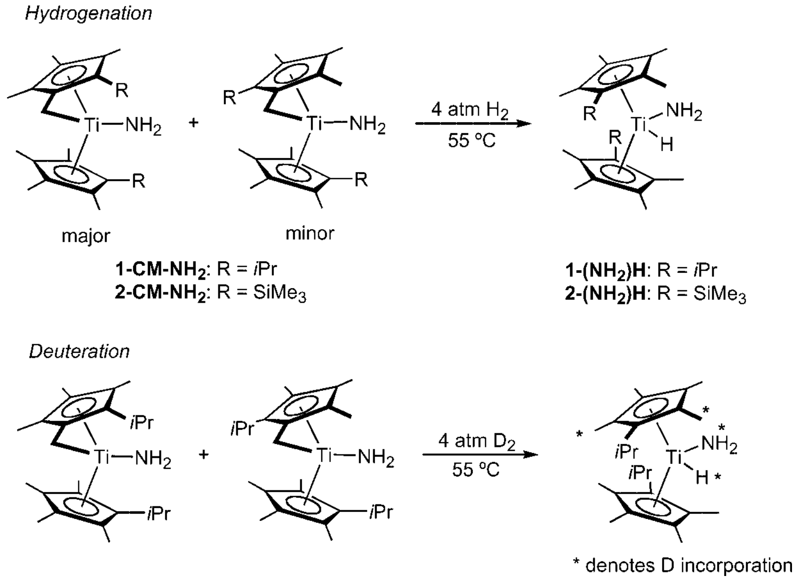


Figure 3. Hydrogenation and deuteration of bis(cyclopentadienyl)titanium cyclometalated amide complexes.

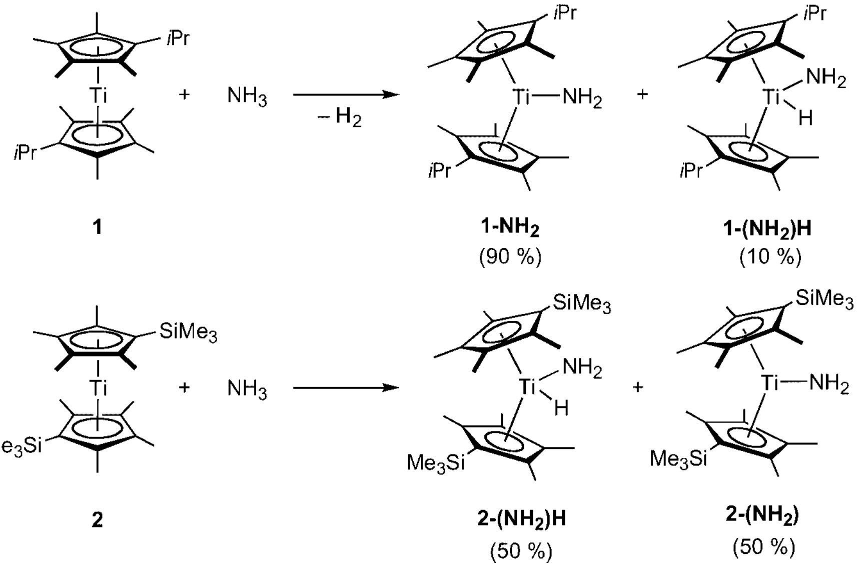


Figure 4. Ammonia addition to **1** and **2**.

was identified as the paramagnetic titanium(III) amido complex, (η^5-C_5Me_4*i*Pr)$_2$Ti(NH_2) (**1-NH$_2$**).[16]

For the silylated sandwich **2**, ammonia addition yielded approximately 50% of **2-(NH$_2$)H** along with an NMR-silent titanium compound, assigned as **2-NH$_2$**. This mixture was formed reproducibly and was unchanged when either an excess or stoichiometric quantity of NH_3 was added. The identity of **2-NH$_2$** was established by treatment with PhSSPh to yield diamagnetic (η^5-$C_5Me_4SiMe_3$)$_2$Ti(NH_2)(SPh) [**2-(NH$_2$)(SPh)**].

Several additional experiments were performed to elucidate the origin of **1-NH$_2$**. Inverting the order of addition whereby **1** was added to a saturated [D$_6$]benzene solution of ammonia increased the amount of **1-(NH$_2$)H** formed. Treatment of **1** with a slightly larger amine, $MeNH_2$, produced only the oxidative addition product, (η^5-C_5Me_4*i*Pr)$_2$Ti(NHMe)H [**1-(NHMe)H**] (Figure 5). No reaction was observed upon addition of *t*BuNH$_2$, PhNH$_2$ or Me$_2$NH.

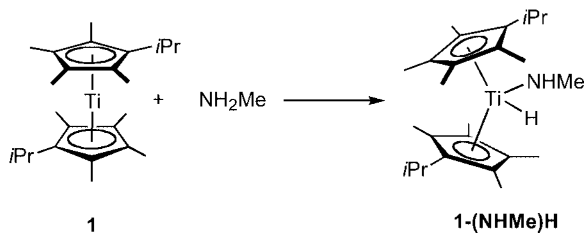


Figure 5. Methylamine addition to **1**.

Based on the experimental data, a mechanism for the formation of **1-NH$_2$** was proposed and is presented in Figure 6. Addition of ammonia to the sandwich forms the transient ammonia complex **1-NH$_3$**, which in the presence

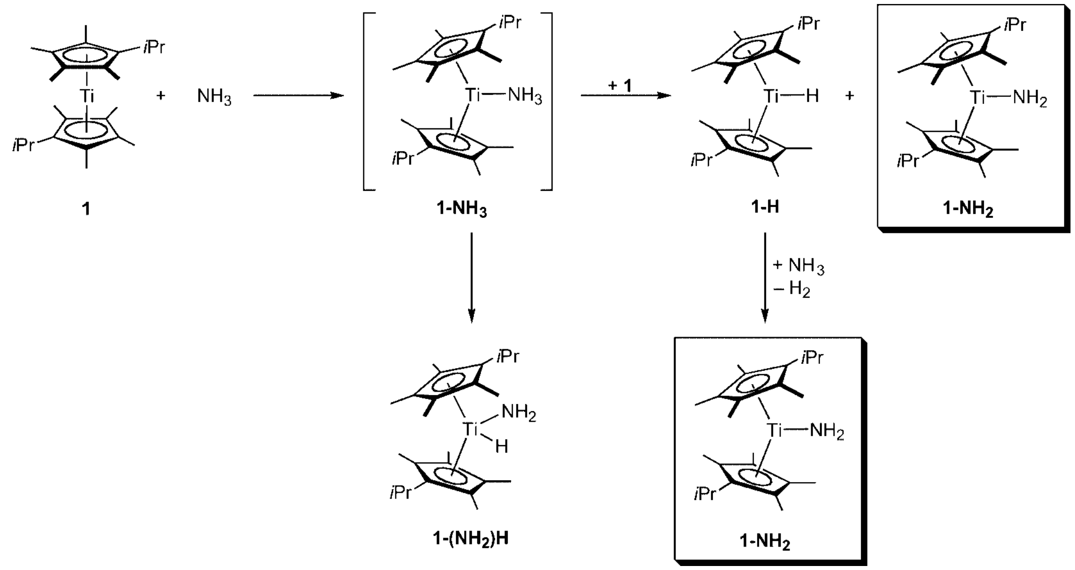


Figure 6. Proposed mechanism for the formation of **1-NH$_2$** from NH$_3$ addition to **1**.

of unreacted **1** undergoes formal deprotonation to yield **1-NH$_2$** and the titanium(III) hydride **1-H**. Increased amounts of the N–H oxidative addition product **1-(NH$_2$)H** from the inverse addition experiment support this initial pathway. Furthermore, the observation of sole N–H oxidative addition chemistry upon MeNH$_2$ addition to **1** is also consistent with this proposal, as bimolecular reactions are less likely with a more hindered amine. Addition of ammonia to **1-H** liberates dihydrogen (experimentally observed) and yields additional **1-NH$_2$** (Figure 6). The feasibility of this reaction has been confirmed experimentally by treatment of isolated **1-H** (vide infra) with ammonia.[16]

The proposed intermediacy of **1-H** during formation of **1-NH$_2$** prompted exploration of the hydrogenation chemistry of **1**. Addition of four atmospheres of H$_2$ to **1** forms a bright orange [D$_6$]benzene solution signaling formation of diamagnetic **1-H$_2$**. The ^{1}H NMR spectrum of **1-H$_2$** suggests a dynamic process involving the cyclopentadienyl methyl groups in solution as these resonances are broadened while those for the isopropyl substituents remain sharp. Monitoring the addition of D$_2$ gas to **1** by ^{2}H NMR spectroscopy revealed rapid incorporation of the isotopic label into both methyl positions of **1-D$_2$** (Figure 7), consistent with reversible cyclometalation on the NMR time scale. Much like (η^5-C$_5$Me$_5$)$_2$TiH$_2$,[17] removal of the dihydrogen atmosphere from **1-H$_2$** resulted in rapid conversion to the titanium(III) monohydride **1-H**, demonstrating that the introduction of the isopropyl substituent into the cyclopentadienyl rings offers little increased stability for the corresponding titanocene dihydride.

The reactivity of the titanium sandwich **1** with heterocycles was also explored. Our laboratory has previously demonstrated that the η^9,η^5-bis(indenyl)zirconium sandwich complex, [η^9-C$_9$H$_5$-1,3-(SiMe$_3$)$_2$][η^5-C$_9$H$_5$-1,3-(SiMe$_3$)$_2$]Zr, promotes the C–H activation of 4-(dimethylamino)pyridine (DMAP) to yield the corresponding zirconium aryl hydride compound.[18] We were curious if the less reducing first row transition metal was sufficiently potent to promote C–H activation or if a stable titanium(II) ligand complex would form. If the later scenario was favored, the spin state (*S* = 0 or 1) of the resulting bent titanocene derivative was of interest. With the exception of dicarbonyl and dinitrogen derivatives, bis(cyclopentadienyl)titanium(II) ligand complexes are relatively rare. Examples include (η^5-C$_5$R$_5$)$_2$Ti(bipy) (R = H, Me; bipy = bipyridine),[19] (η^5-C$_5$H$_5$)$_2$Ti(pyrrole)$_2$,[20] (η^5-C$_5$H$_5$)$_2$Ti(PMe$_3$)$_2$[21] and (η^5-C$_5$H$_5$)$_2$Ti(PF$_3$)$_2$.[22] As expected for coordinatively saturated complexes, all of these compounds, with the exception of (η^5-C$_5$Me$_5$)$_2$Ti(bipy), are diamagnetic.

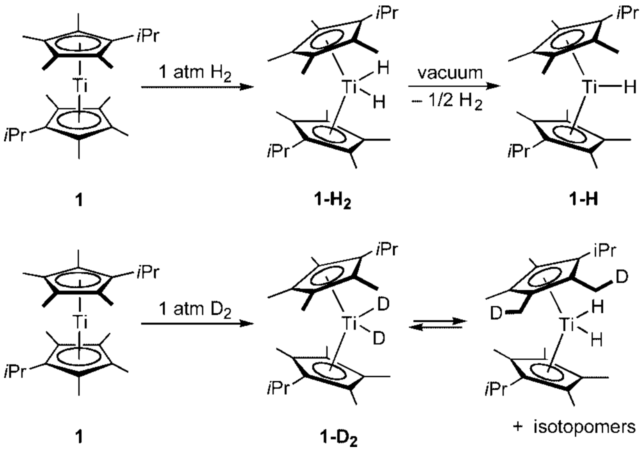
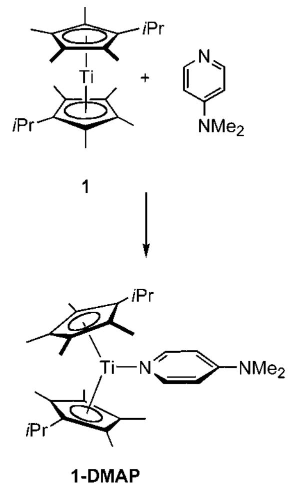


Figure 7. Addition of dihydrogen and dideuterium to **1**.

Stirring a diethyl ether solution of **1** with a stoichiometric quantity of DMAP followed by recrystallization at –35 °C furnished red rods identified as the paramagnetic DMAP complex **1-DMAP** [Equation (3)]. A solid state magnetic moment of 2.7 μ_B was determined by magnetic susceptibility balance at 23 °C and is consistent with the spin only value for two unpaired electrons. A slightly lower value of 2.3 μ_B was measured by Evans method in [D$_6$]benzene solution but is also consistent with an $S = 1$ titanium(II) center.



(3)

The solid-state structure of **1-DMAP** was determined by X-ray diffraction and a representation is presented in Figure 8. The overall molecular geometry is typical for a group 4 bent metallocene derivative with an idealized C_2 axis of molecular symmetry defined by the Ti(1)–N(1) bond. The plane of the DMAP ring lies in the titanocene wedge and is nearly coplanar with the dimethylamino group. The metrical parameters for the coordinated heterocycle are similar to free DMAP,[23] indicating little reduction by the titanium center. Attempts to induce C–H activation by thermolysis of **1-DMAP** have been unsuccessful. Warming [D$_6$]benzene solutions of the compound to 95 °C for 3 d produced no observable change by ^{1}H NMR spectroscopy.

Comparison of Ti=E Species to Promote 1,2-Addition Chemistry

Our laboratory has synthesized a family of substituted bis(cyclopentadienyl)titanium oxo,[5] imido, and transient alkylidene compounds.[13] The propensity of each class of Ti=E (E = O, NR, CR$_2$) linkage to promote the C–H activation of the cyclopentadienyl methyl groups provides insights into the relative stability of each type of titanium element (or group) multiple bond. Within the series of imides, the nitrogen substituent influences the rate of 1,2-addition as the more sterically protected [Ti=NSiMe$_3$] and [Ti=N*Ar*] (*Ar* = substituted aryl) linkages are isolable[13] while [Ti=NH] species have yet to be observed directly.

The identity of the titanium–ligand multiple bond also dictates the rate of C–H activation by 1,2-addition. Whereas the transient alkylidene, [[η^5-C$_5$H$_3$-1,3-(SiMe$_3$)$_2$]$_2$-Ti=CH(SiMe$_3$)], has proven too reactive to observe, similar imide complexes have been isolated and shown to promote C–H activation.[13] In contrast, the titanocene oxo derivatives are reluctant to activate C–H bonds. These differences are most likely a result of the strength of the Ti=E π-bond, where the Ti=O fragment is expected to be the strongest and Ti=CR$_2$ the weakest. Simply comparing O–H and C–H bond strengths of small molecules such as water and Ph$_2$CH$_2$ and assuming the overall entropy change in the 1,2-addition reaction is approximately –30 eu, the Ti=O π bond strength can be estimated as approximately 30 kcal/mol stronger than that for Ti=CR$_2$. Using the N–H bond strength of ammonia in a similar approximation places the Ti=NH π bond strength only 10 kcal/mol weaker than the oxo and accounts for the stability of certain variants of these compounds but also the ability to undergo intramolecular 1,2-addition of C–H bonds.

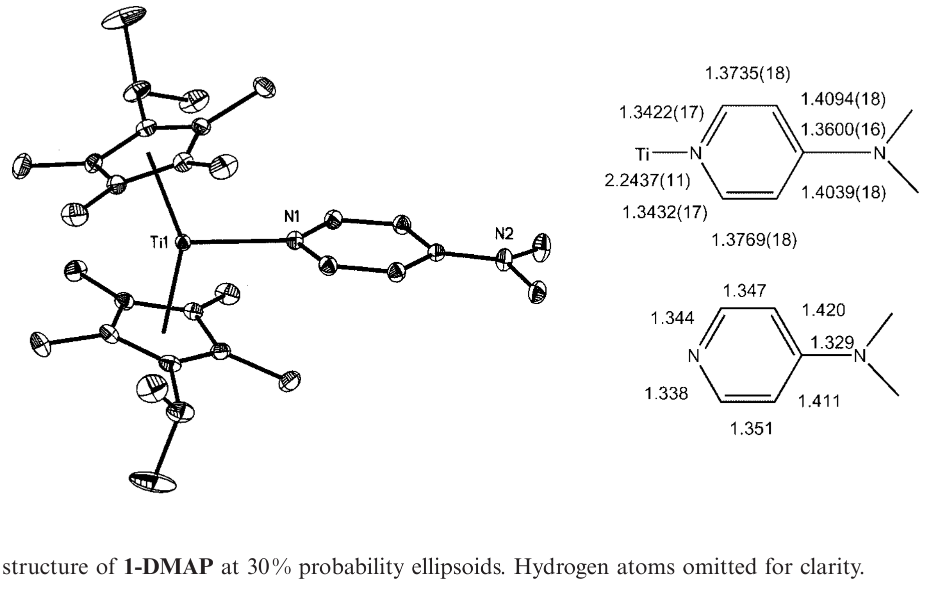


Figure 8. Molecular structure of **1-DMAP** at 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

Concluding Remarks

Treatment of isolable bis(cyclopentadienyl)titanium sandwich complexes with propylenimine resulted in [NH] group transfer followed by rapid C–H activation of a cyclopentadienyl methyl group to yield cyclometalated titanocene amido compounds. These observations suggest that the relative strength of the Ti=E π bond ($E = O > NR > CR_2$) determines the propensity of the titanium compound to participate in 1,2-addition of C–H bonds. Exposure of the resulting cyclometalated titanocene amido compounds to dihydrogen at 55 °C yielded the corresponding amido hydride complexes. For the silylated derivative, $(\eta^5\text{-}C_5Me_4SiMe_3)_2Ti(NH_2)H$, this compound was also prepared by oxidative addition of an N–H bond of ammonia along with $(\eta^5\text{-}C_5Me_4SiMe_3)_2TiNH_2$. Similar chemistry was observed with the more open titanocene sandwich, $(\eta^5\text{-}C_5Me_4\mathit{i}Pr)_2Ti$, as significant quantities of the titanium(III) amide complex, $(\eta^5\text{-}C_5Me_4\mathit{i}Pr)_2TiNH_2$, were obtained upon addition of NH_3. Subsequent experiments changing the order of addition and the size of the amine support a pathway involving deprotonation from coordinated ammonia by free bis(cyclopentadienyl)titanium sandwich.

Experimental Section

General Considerations: All air- and moisture-sensitive manipulations were carried out using standard high vacuum line, Schlenk or cannula techniques or in an M. Braun inert atmosphere drybox containing purified nitrogen. The Braun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.[24] Toluene, benzene, pentane and heptane were further dried by distillation from "titanocene".[25] Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4-Å molecular sieves. Argon and hydrogen gas were purchased from Airgas Incorporated and passed through a column containing manganese oxide on vermiculite and 4-Å molecular sieves before admission to the high vacuum line. DMAP was recrystallized from pentane and dried under vacuum. Propylenimine was initially dried with 4-Å molecular sieves and distilled immediately before use. The compounds $(\eta^5\text{-}C_5Me_4\mathit{i}Pr)_2Ti(N_2)_2$ [**1-(N$_2$)$_2$**],[3] $(\eta^5\text{-}C_5Me_4SiMe_3)_2Ti$ (**2**)[2] and $(\eta^5\text{-}C_5Me_4SiMe_2Ph)_2Ti(N_2)$ [**3-(N$_2$)**][4] were prepared according to literature procedures.

^{1}H NMR spectra were recorded on a Varian Inova 400 Spectrometer operating at 399.860 MHz. All chemical shifts are reported relative to $SiMe_4$ using ^{1}H (residual) chemical shifts of the solvent as a secondary standard. ^{2}H and ^{13}C NMR spectra were recorded on a Varian Inova 500 Spectrometer operating at 76.848 and 125.716 MHz, respectively. ^{2}H and ^{13}C chemical shifts are reported relative to $SiMe_4$ using chemical shifts of the solvent as a secondary standard.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker X8 APEX2 diffractometer equipped with a molybdenum X-ray tube (λ = 0.71073 Å). Preliminary data revealed the crystal system. A hemisphere routine was used for data collection and determination of lattice constants. The space group was identified and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved by direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures. CCDC-628974 (for **1-DMAP**) contains supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Madison, NJ.

Preparation of $(\eta^5\text{-}C_5Me_4iPr)(\eta^5\text{-}C_5Me_3\text{-}\eta^1\text{-}2\text{-}CH_2\text{-}CHMe_2)TiNH_2$ (1-CM-NH$_2$): A J. Young NMR tube was charged with 0.033 g (0.077 mmol) of **1-(N$_2$)$_2$** and approximately 0.5 mL of [D$_6$]benzene were added. On the high vacuum line, the tube was degassed at liquid nitrogen temperature and 45 Torr of propylenimine (0.077 mmol) were added with a 31.6 mL calibrated gas bulb. The tube was shaken and thawed, resulting in an immediate colour change from dark red to bright red. The solvent was removed to yield **1-CM-NH$_2$** as a red oil. ^{1}H NMR ([D$_6$]benzene, major thermodynamic isomer): δ = 1.18 (d, J = 6 Hz, 3 H, C_5Me_3-η^1-2-CH_2-$CH\mathit{Me_2}$), 1.22 (d, J = 6 Hz, 3 H, C_5Me_3-η^1-2-CH_2-$CH\mathit{Me_2}$), 1.22 (d, J = 6 Hz, 6 H, $C_5Me_4CH\mathit{Me_2}$), 1.46 (s, 3 H, $C_5\mathit{Me_3}$-η^1-2-CH_2-$CHMe_2$), 1.66 (s, 3 H, $C_5\mathit{Me_3}$-η^1-2-CH_2-$CHMe_2$), 1.67 (s, 3 H, $C_5\mathit{Me_4}CHMe_2$), 1.74 (s, 3 H, $C_5\mathit{Me_4}CHMe_2$), 1.78 (d, J = 3 Hz, 1 H, C_5Me_3-η^1-2-$C\mathit{H_2}$-$CHMe_2$), 1.82 (s, 3 H, $C_5\mathit{Me_4}CHMe_2$), 1.91 (s, 3 H, $C_5\mathit{Me_3}$-η^1-2-CH_2-$CHMe_2$), 2.04 (s, 3 H, $C_5\mathit{Me_4}CHMe_2$), 2.50 (m, 1 H, C_5Me_3-η^1-2-CH_2-$C\mathit{H}Me_2$), 2.66 (m, 1 H, $C_5Me_4C\mathit{H}Me_2$), 2.90 (d, J = 3 Hz, 1 H, C_5Me_3-η^1-2-$C\mathit{H_2}$-$CHMe_2$), 4.90 (br. s, 2 H, $N\mathit{H_2}$) ppm. ^{1}H NMR ([D$_6$]benzene, minor thermodynamic isomer): δ = 1.12 (d, J = 6 Hz, 3 H, C_5Me_3-η^1-2-CH_2-$CH\mathit{Me_2}$), 1.13 (d, J = 6 Hz, 3 H, C_5Me_3-η^1-2-CH_2-$CH\mathit{Me_2}$), 1.24 (d, J = 6 Hz, 6 H, $C_5Me_4CH\mathit{Me_2}$), 1.63 (s, 3 H, $C_5\mathit{Me_3}$-η^1-2-CH_2-$CHMe_2$), 1.73 (s, 3 H, $C_5\mathit{Me_3}$-η^1-2-CH_2-$CHMe_2$), 1.75 (s, 3 H, $C_5\mathit{Me_4}CHMe_2$), 1.78 (s, 3 H, $C_5\mathit{Me_3}$-η^1-2-CH_2-$CHMe_2$), 1.80 (s, 3 H, $C_5\mathit{Me_4}CHMe_2$), 1.85 (s, 3 H, $C_5\mathit{Me_4}CHMe_2$), 1.94 (d, J = 3 Hz, 1 H, C_5Me_3-η^1-2-$C\mathit{H_2}$-$CHMe_2$), 2.10 (s, 3 H, $C_5\mathit{Me_4}CHMe_2$), 2.55 (m, 1 H, C_5Me_3-η^1-2-CH_2-$C\mathit{H}Me_2$), 2.67 (m, 1 H, $C_5Me_4C\mathit{H}Me_2$), 2.82 (d, J = 3 Hz, 1 H, C_5Me_3-η^1-2-$C\mathit{H_2}$-$CHMe_2$), 4.85 (br. s, 2 H, $N\mathit{H_2}$) ppm. ^{13}C NMR ([D$_6$]benzene): δ = 11.16, 11.21, 11.69, 11.84, 11.96, 12.06, 12.09, 12.14, 12.18, 12.26, 12.88, 13.64, 13.90 (Me), 21.01, 22.22, 23.14, 23.22, 23.26, 23.43, 26.33, 27.31, 27.37, 27.55, 27.87, 30.48 ($\mathit{C}HMe_2$/$CH\mathit{Me_2}$), 69.56, 70.05 ($\mathit{C}H_2$), 110.67, 111.25, 114.84, 115.18, 116.07, 117.42, 117.90, 117.98, 118.17, 118.42, 118.91, 119.04, 120.78, 121.24, 122.32, 123.35, 123.55, 128.45, 132.21, 137.51 (Cp) ppm. IR (KBr): $\tilde{\nu}$ = 3369, 3439 (NH_2) cm^{-1}.

Preparation of $(\eta^5\text{-}C_5Me_4SiMe_3)(\eta^5\text{-}C_5Me_3\text{-}\eta^1\text{-}2\text{-}CH_2\text{-}SiMe_3)TiNH_2$ (2-CM-NH$_2$): This compound was prepared using a similar procedure to that described for **1-CM-NH$_2$** with 0.027 g (0.0621 mmol) of **2**, 37 Torr (0.0621 mmol, 31.6 mL gas volume) of propylenimine and approximately 0.5 mL [D$_6$]benzene resulting in a colour change from dark red to bright red. The solvent was removed to yield a red oil. ^{1}H NMR ([D$_6$]benzene, major isomer): δ = 0.30 (s, 9 H, C_5Me_3-η^1-2-CH_2-$Si\mathit{Me_3}$), 0.33 (s, 9 H, $C_5Me_4Si\mathit{Me_3}$), 1.42 (s, 3 H, $C_5\mathit{Me_3}$-η^1-2-CH_2-$SiMe_3$), 1.61 (s, 3 H, $C_5\mathit{Me_4}SiMe_3$), 1.64 (s, 3 H, $C_5\mathit{Me_4}SiMe_3$), 1.67 (s, 3 H, $C_5\mathit{Me_3}$-η^1-2-CH_2-$SiMe_3$), 1.88 (s, 3 H, $C_5\mathit{Me_4}SiMe_3$), 1.92 (s, 3 H, $C_5\mathit{Me_4}SiMe_3$), 1.98 (d, J = 2 Hz, 1 H, C_5Me_3-η^1-2-$C\mathit{H_2}$-$SiMe_3$), 2.16 (s, 3 H, $C_5\mathit{Me_3}$-η^1-2-CH_2-$CHMe_2$), 2.84 (d, J = 3 Hz, 1 H, C_5Me_3-η^1-2-$C\mathit{H_2}$-$SiMe_3$), 5.40 (br. s, 2 H, $N\mathit{H_2}$) ppm. ^{1}H NMR ([D$_6$]benzene, minor isomer): δ = 0.30 (s, 9 H, C_5Me_3-η^1-2-CH_2-$Si\mathit{Me_3}$), 0.31 (s, 9 H, $C_5Me_4Si\mathit{Me_3}$), 1.56 (s, 3 H, $C_5\mathit{Me_3}$-η^1-2-CH_2-$SiMe_3$), 1.71 (s, 3 H, $C_5\mathit{Me_4}SiMe_3$), 1.75 (s, 3 H, $C_5\mathit{Me_3}$-η^1-2-CH_2-$SiMe_3$), 1.87 (d, J = 2 Hz, 1

H, C_5Me_3-η^1-2-$C\mathit{H}_2$-$SiMe_3$), 1.87 (s, 3 H, $C_5\mathit{Me}_4SiMe_3$), 1.90 (s, 3 H, $C_5\mathit{Me}_4SiMe_3$), 1.94 (s, 3 H, $C_5\mathit{Me}_3$-η^1-2-CH_2-$SiMe_3$), 2.06 (s, 3 H, $C_5\mathit{Me}_4SiMe_3$), 2.81 (d, *J* = 3 Hz, 1 H, C_5Me_3-η^1-2-$C\mathit{H}_2$-$SiMe_3$), 4.79 (br. s, 2 H, $N\mathit{H}_2$) ppm. ^{13}C NMR ($[D_6]$benzene): *δ* = 2.05, 2.49, 3.18 ($Si\mathit{Me}_3$), 10.94, 11.08, 11.18, 11.39, 11.57, 12.40, 12.52, 12.73, 14.25, 14.56, 14.78, 14.96, 15.06, 15.35 (Me), 69.89, 70.04 ($\mathit{C}H_2$), 107.11, 109.03, 114.57, 117.27, 118.50, 120.31, 120.66, 123.37, 123.93, 124.33, 125.17, 125.42, 127.62, 128.24, 128.63, 128.96, 130.29, 130.77, 131.25, 135.26 (Cp) ppm. IR (KBr): $\tilde{\nu}$ = 3377, 3453 (NH_2) cm^{-1}.

Preparation of (η^5-$C_5Me_4iPr)_2Ti(NH_2)(H)$ [1-(NH_2)(H)]: A J. Young NMR tube was charged with 0.033 g (0.077 mmol) of **1-CM-NH_2** and approximately 0.5 mL of $[D_6]$benzene were added. On the high vacuum line, the tube was degassed at –196 °C and 1 atm of H_2 was added. The tube was then heated to 55 °C for three days resulting in a colour change to orange. The solvent was removed in vacuo to yield 0.029 g (96.7%) of **1-(NH_2)(H)** as an orange solid. ^1H NMR ($[D_6]$benzene): *δ* = 1.32 (d, *J* = 3 Hz, 6 H, $C_5Me_4CH\mathit{Me}_2$), 1.34 (d, *J* = 3 Hz, 6 H, $C_5Me_4CH\mathit{Me}_2$), 1.78 (s, 6 H, $C_5\mathit{Me}_4CHMe_2$), 1.89 (s, 6 H, $C_5\mathit{Me}_4CHMe_2$), 1.91 (s, 6 H, $C_5\mathit{Me}_4CHMe_2$), 1.92 (s, 6 H, $C_5\mathit{Me}_4CHMe_2$), 2.13 (s, 1 H, Ti-*H*), 2.88 (m, 2 H, $C_5Me_4C\mathit{H}Me_2$), 5.88 (br. s, 2 H, $N\mathit{H}_2$) ppm. ^{13}C NMR ($[D_6]$benzene): *δ* = 11.36, 12.05, 12.38, 12.58 (Me), 23.15, 23.31, 28.29 ($\mathit{C}HMe_2$/$CH\mathit{Me}_2$), 113.24, 114.21, 114.28, 115.34, 126.71 (Cp) ppm. IR (KBr): $\tilde{\nu}$ = 1644 (Ti–H), 3361, 3435 (NH_2) cm^{-1}.

Preparation of (η^5-$C_5Me_4SiMe_3)_2Ti(NH_2)(H)$ [2-(NH_2)(H)]: This molecule was prepared in an identical manner to **1-(NH_2)(H)** with 0.027 g (0.0621 mmol) of **2-CM-NH_2**, approximately 0.5 mL of $[D_6]$benzene and one atmosphere of dihydrogen to afford **2-(NH_2)(H)** as an orange solid after 3 d of heating. $C_{24}H_{45}NSi_2Ti$ (451.63): calcd. C 63.82, H 10.04, N 3.10; found C 63.72, H 9.88, N 3.24. ^1H NMR ($[D_6]$benzene): *δ* = 0.42 (s, 18 H, $C_5Me_4\mathit{SiMe}_3$), 1.71 (s, 6 H, $C_5\mathit{Me}_4SiMe_3$), 1.73 (s, 6 H, $C_5\mathit{Me}_4SiMe_3$), 1.83 (s, 6 H, $C_5\mathit{Me}_4SiMe_3$), 1.94 (s, 6 H, $C_5\mathit{Me}_4SiMe_3$), 2.08 (s, 1 H, Ti-*H*), 5.96 (br. s, 2 H, $N\mathit{H}_2$) ppm. ^{13}C NMR ($[D_6]$benzene): *δ* = 2.56 ($SiMe_3$), 10.94, 11.58, 14.35, 14.82 (Me), 110.07, 117.04, 118.65, 119.59, 125.43 (Cp) ppm. IR (KBr): $\tilde{\nu}$ = 1610 (Ti–H), 3373, 3444 (NH_2) cm^{-1}.

Preparation of (η^5-$C_5Me_4iPr)_2Ti(NHMe)(H)$ [1-(NHMe)(H)]: A J. Young NMR tube was charged with 0.036 g (0.0836 mmol) of **1-($N_2)_2$** and approximately 0.5 mL of $[D_6]$benzene were added. On the high vacuum line, the tube was degassed at –196 °C and methylamine was admitted with a 31.6 mL gas bulb (0.0836 mmol, 49 Torr). Upon thawing, a colour change from red to bright red was observed. The solvent was removed in vacuo to yield 0.032 g (94.1%) of **1-(NHMe)(H)** as a red solid. $C_{25}H_{43}NTi$ (405.46): calcd. C 74.05, H 10.69, N 3.45; found C 73.86, H 10.86, N 3.79. ^1H NMR ($[D_6]$benzene): *δ* = 1.32 (d, *J* = 8 Hz, 12 H, $C_5Me_4CH\mathit{Me}_2$), 1.81 (s, 6 H, $C_5\mathit{Me}_4CHMe_2$), 1.96 (s, 18 H, $C_5\mathit{Me}_4CHMe_2$), 2.13 (s, 1 H, Ti-*H*), 2.86 (m, 2 H, $C_5Me_4C\mathit{H}Me_2$), 3.19 (d, *J* = 8 Hz, 3 H, NH*Me*), 6.71 (br. s, 1 H, N*H*Me) ppm. ^{13}C NMR ($[D_6]$benzene): *δ* = 11.90, 12.61, 12.79, 13.37 (Me), 23.08, 23.21, 27.82 ($\mathit{C}HMe_2$/$CH\mathit{Me}_2$), 43.71 (NH*Me*), 113.52, 114.24, 115.78, 116.67, 125.52 (Cp) ppm. IR (KBr): $\tilde{\nu}$ = 1626 (Ti–H), 3381, 3414 (N–H) cm^{-1}.

Preparation of (η^5-$C_5Me_4SiMe_3)_2Ti{=}NSiMe_3$ (2=$NSiMe_3$): A 20 mL scintillation vial was charged with 0.052 g (0.1196 mmol) of **2** and approximately 5 mL pentane were added. Azidotrimethylsilane (16.1 µL, 0.1196 mmol) was added by syringe and the solution was stirred for 10 min. An immediate colour change from red to bright red was observed, signaling formation of **2=$NSiMe_3$**. The solvent was removed in vacuo to yield a red oil which was then dissolved in benzene and lyophilized to yield 0.042 g (67.7%) of **2=$NSiMe_3$** as a red solid. $C_{27}H_{51}NSi_3Ti$ (521.80): calcd. C 62.14, H 9.85, N 2.68; found C 61.77, H 9.87, N 2.28. ^1H NMR ($[D_6]$benzene): *δ* = 0.17 (s, 18 H, $C_5Me_4Si\mathit{Me}_3$), 0.37 (s, 9 H, $NSi\mathit{Me}_3$), 1.80 (s, 12 H, $C_5\mathit{Me}_4SiMe_3$), 2.52 (s, 12 H, $C_5\mathit{Me}_4SiMe_3$) ppm. ^{13}C NMR ($[D_6]$benzene): *δ* = 1.95 ($SiMe_3$), 6.08 ($NSi\mathit{Me}_3$), 12.36, 17.66 (Me), 121.06, 125.28, 137.13 (Cp) ppm.

Preparation of (η^5-$C_5Me_4SiMe_3$)(η^5-C_5Me_3-η^1-3-CH_2-$SiMe_3$)Ti-$NHSiMe_3$ and (η^5-$C_5Me_4SiMe_3$)(η^5-C_5Me_3-η^1-2-CH_2-$SiMe_3$)Ti-$NHSiMe_3$ (2-CM-$NHSiMe_3$): A J. Young NMR tube was charged with 0.030 g (0.057 mmol) of **2=$NSiMe_3$** and approximately 0.5 mL of $[D_6]$benzene were added. The solution was heated to 45 °C over the course of one week, resulting in a colour change from red to dark red/brown. The solvent was removed in vacuo to yield a dark oil. ^1H NMR ($[D_6]$benzene, major isomer): *δ* = 0.22 (s, 9 H, $NHSi\mathit{Me}_3$), 0.31 (s, 9 H, $C_5Me_4Si\mathit{Me}_3$), 0.34 (s, 9 H, C_5Me_3-η^1-3-CH_2-$Si\mathit{Me}_3$), 1.30 (s, 3 H, $C_5\mathit{Me}_3$-η^1-3-CH_2-$SiMe_3$), 1.58 (s, 3 H, $C_5\mathit{Me}_4SiMe_3$), 1.66 (s, 3 H, $C_5\mathit{Me}_4SiMe_3$), 1.93 (s, 3 H, $C_5\mathit{Me}_3$-η^1-3-CH_2-$SiMe_3$), 1.97 (s, 3 H, $C_5\mathit{Me}_3$-η^1-3-CH_2-$CHMe_2$), 1.99 (d, *J* = 5 Hz, 1 H, C_5Me_3-η^1-3-$C\mathit{H}_2$-$SiMe_3$), 2.10 (s, 3 H, $C_5\mathit{Me}_4SiMe_3$), 2.33 (s, 3 H, $C_5\mathit{Me}_4SiMe_3$), 2.56 (d, *J* = 5 Hz, 1 H, C_5Me_3-η^1-3-$C\mathit{H}_2$-$SiMe_3$), 3.70 (br. s, 1 H, $N\mathit{H}SiMe_3$) ppm. ^1H NMR ($[D_6]$benzene, minor isomer): *δ* = 0.19 (s, 9 H, $NHSi\mathit{Me}_3$), 0.22 (s, 9 H, C_5Me_3-η^1-2-CH_2-$Si\mathit{Me}_3$), 0.31 (s, 9 H, $C_5Me_4Si\mathit{Me}_3$), 1.65 (s, 3 H, $C_5\mathit{Me}_4SiMe_3$), 1.85 (s, 3 H, $C_5\mathit{Me}_4SiMe_3$), 1.87 (d, *J* = 5 Hz, 1 H, C_5Me_3-η^1-2-$C\mathit{H}_2$-$SiMe_3$), 1.88 (s, 3 H, $C_5\mathit{Me}_3$-η^1-2-CH_2-$SiMe_3$), 1.90 (s, 3 H, $C_5\mathit{Me}_3$-η^1-2-CH_2-$SiMe_3$), 1.95 (s, 3 H, $C_5\mathit{Me}_3$-η^1-2-CH_2-$CHMe_2$), 1.95 (s, 3 H, $C_5\mathit{Me}_4SiMe_3$), 2.11 (s, 3 H, $C_5\mathit{Me}_4SiMe_3$), 2.82 (d, *J* = 5 Hz, 1 H, C_5Me_3-η^1-2-$C\mathit{H}_2$-$SiMe_3$), 3.10 (br. s, 1 H, $N\mathit{H}SiMe_3$) ppm. ^{13}C NMR ($[D_6]$benzene): *δ* = 2.17, 2.47, 2.92, 3.49, 6.45, 6.84 ($Si\mathit{Me}_3$), 11.72, 12.35, 12.42, 12.73, 12.91, 13.05, 14.53, 15.29, 15.43, 16.91, 17.33, 18.02, 18.33 (Me), 71.05, 74.93 ($\mathit{C}H_2$), 104.68, 108.42, 117.71, 118.88, 119.44, 120.83, 122.89, 123.67, 124.46, 127.24, 129.14, 129.19, 130.72, 130.68, 131.61, 131.82, 132.54, 136.16, 139.68, 140.57 (Cp) ppm.

Generation of (η^5-$C_5Me_4iPr)_2TiH_2$ (1-H_2): A J. Young NMR tube was charged with 0.016 g (0.037 mmol) of **1-($N_2)_2$** and approximately 0.5 mL $[D_8]$toluene were added. On the high vacuum line, the tube was cooled to –196 °C, degassed and one atmosphere of dihydrogen was added. Upon thawing, the colour changed from red to bright orange. Cooling the solution to –75 °C under an atmosphere of dihydrogen revealed formation of **1-H_2**. ^1H NMR ($[D_8]$toluene, –75 °C): *δ* = 1.32 (d, *J* = 7 Hz, 12 H, $C_5Me_4CH\mathit{Me}_2$), 1.52 (s, 12 H, $C_5\mathit{Me}_4CHMe_2$), 2.08 (s, 12 H, $C_5\mathit{Me}_4CHMe_2$), 3.25 (s, 2 H, Ti-*H*), 3.41 (m, 2 H, $C_5Me_4C\mathit{H}Me_2$) ppm. ^{13}C NMR ($[D_8]$toluene, –75 °C): *δ* = 11.73, 14.25 (Me), 24.10, 30.47 ($\mathit{C}HMe_2$/$CH\mathit{Me}_2$), 118.00, 119.42, 134.69 (Cp) ppm.

Preparation of (η^5-$C_5Me_4iPr)_2Ti$(DMAP) (1-DMAP): A 20 mL scintillation vial was charged with 0.102 g (0.237 mmol) of **1-($N_2)_2$**, 0.029 g (0.237 mmol) of 4-(dimethylamino)pyridine (DMAP) and approximately 5 mL diethyl ether. The reaction was stirred for one hour at ambient temperature and the solvent was removed in vacuo, yielding a red/brown solid. The compound was washed with pentane and recrystallized from diethyl ether at –35 °C to yield 0.084 g (71.2%) of **1-DMAP** as red rods. $C_{31}H_{48}N_2Ti$ (496.56): calcd. C 74.98, H 9.74, N 5.64; found C 74.93, H 9.23, N 5.17. ^1H NMR ($[D_6]$benzene): *δ* = 3.74 ($\Delta\nu_{1/2}$ = 129 Hz). $\mu_{eff} = 2.7\ \mu_B$ (solid state), 2.3 μ_B (Evans) ppm.

Observation of (η^5-$C_5Me_4SiMe_3)_2Ti(NH_2)(SPh)$ [2-(NH_2)(SPh)]: A J. Young NMR tube was charged with 0.018 g (0.040 mmol) of **2-NH_2**, 0.005 g (0.040 mmol) of Ph_2S_2 and approximately 0.5 mL $[D_6]$benzene. The tube was placed in a 45 °C oil bath for approximately 18 h, leading to a colour change from orange to bright red.

^{1}H NMR ([D$_6$]benzene): δ = 0.33 (s, 18 H, $C_5Me_4SiMe_3$), 1.67 (s, 6 H, $C_5Me_4SiMe_3$), 1.79 (s, 6 H, $C_5Me_4SiMe_3$), 1.98 (s, 6 H, $C_5Me_4SiMe_3$), 2.04 (s, 6 H, $C_5Me_4SiMe_3$), 6.86 (m, 1 H, Ph), 7.10 (t, 2 H, Ph), 7.50 (d, J = 7 Hz, 2 H, Ph), 7.75 (br. s, 2 H, NH_2) ppm. ^{13}C NMR ([D$_6$]benzene): δ = 2.60 ($SiMe_3$), 11.58, 13.01, 15.03, 15.91 (Me), 120.29, 122.05, 126.26, 127.31, 128.62, 129.80, 131.96, 133.87, 148.16 (Cp/Ph) ppm. IR (KBr): $\tilde{\nu}$ = 3368, 3452 (N–H) cm^{-1}.

Supporting Information (see also the footnote on the first page of this article): Selected ^{1}H NMR spectra, isomer assignments, and checkcif results.

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