Ti═NR vs Ti−R′ Functional Group Selectivity in Titanium Imido Alkyl Cations from an Experimental Perspective

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A study of the reactions of the titanium imido methyl cation $[Ti(N^tBu)(Me_3[9]aneN_3)X]^+$ ($\mathbf{5}^+$, X = Me) and key analogues ($\mathbf{6}^+$, X = CH_2SiMe_3; $\mathbf{7}^+$, X = Cl) with a range of unsaturated substrates provides a comprehensive evaluation of reaction site selectivity in transition-metal cations which contain both Ti═NR and Ti−R′ functional groups as potential sites for $2\pi + 2\pi$ cycloaddition and migratory insertion, respectively. Cations $\mathbf{5}^+$ and $\mathbf{6}^+$ reacted with MeCN to form Ti−R′ insertion products. Insertion reactions were also exclusively observed in their reactions with N,N′-disubstituted carbodiimides or *tert*-butyl isocyanate. In contrast, reaction of the chloride cation $\mathbf{7}^+$ with diisopropylcarbodiimide or *tert*-butyl isocyanate afforded the unusual σ adducts $[Ti(N^tBu)(Me_3[9]aneN_3)(L)Cl]^+$ (L = $^iPrNCN^iPr$, ^tBuNCO), which slowly underwent $2\pi + 2\pi$ cycloaddition. Reaction of $\mathbf{5}^+$ with the internal alkynes PhCCR (R = Ph, $SiMe_3$) also showed exclusive preference for insertion into the Ti−Me bond. In contrast, reaction with terminal alkynes RCCH (R = Ph, $SiMe_3$) yielded only the azametallacyclic products via $2\pi + 2\pi$ cycloaddition reactions. The chloride cation $\mathbf{7}^+$ also underwent a $2\pi + 2\pi$ cycloaddition with PhCCH but was unreactive toward PhCCPh, ethylene, styrene, or 1-hexene.

Introduction

This paper, in conjunction with the accompanying DFT study, presents a detailed account of the ligand reaction site preferences of the titanium imido alkyl cations $[Ti(N^tBu)(Me_3[9]aneN_3)R]^+$ (R = Me, CH_2SiMe_3) with a range of different unsaturated substrates. The development of transition-metal complexes for particular applications evidently requires a sound knowledge of the properties and reaction characteristics of the supporting ligand or ligand sets. It may also be the case that a ligand *potentially* susceptible to attack by an external reagent could appear to be *inert* when an alternative ligand or functional group offers an alternative kinetically or thermodynamically favored reactive site.[1] This has been a fundamental issue in organometallic chemistry for decades. For example, while hydride attacks the cyclopentadienyl ring in $[Co(\eta^5\text{-}C_5H_5)_2]^+$ and the arene ring in $[Re(\eta^6\text{-}C_6H_5Me)_2]^+$,[2,3] in the *non*-homoleptic cation $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^+$ it is only the six-membered ring that is attacked.[4] Ligand substitution can also alter the expected reaction outcomes: on reaction of $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]^+$ with hydride the permethylated benzene is unreactive and now only the cyclopentadienyl ring is substituted.[5] This signals a change from kinetic to thermodynamic control.[1]

Transition-metal imido compounds (L)M═NR (typically R = alkyl, aryl and L = a supporting ligand or ligand set) have been widely studied for over 20 years.[6−17] Imido ligands have become an established feature of the ligand landscape for many transition metals, and the six-electron -donor imido dianion is isolobal with cyclopentadienide.[18−21] In a significant portion of its chemistry the M═NR bond is inert to common substrates and the imido ligand plays a "supporting" role. One prominent example of this aspect is the Schrock olefin metathesis catalyst family M(NR)(CHR′)(OR″)$_2$ (M = Mo, W) widely exploited in organic and inorganic applications[22−25] and comprehensively studied computationally.[26−31] The $2\pi + 2\pi$ cycloaddition reaction site selectivity of ethylene for the Mo═CH$_2$ bond in

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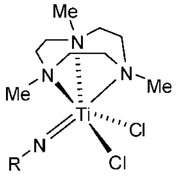
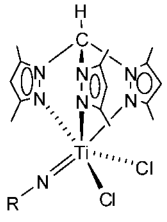
this type of system was explained by Ziegler in terms of both kinetic and thermodynamic preferences.[32] Notwithstanding the "supporting" role of the imido ligands in the Schrock metathesis catalysts, in a significant number of other compounds (especially for the group 4 metals) coupling reactions of the M═NR functional group with unsaturated organic and other substrates is found to be facile.[8,9,13,17,33]

Since the early 90s the development of non-cyclopentadienyl ("post-metallocene") Ziegler-type olefin polymerization catalysts has been a topic of enormous academic and commercial significance.[34−41] Imido "supporting" ligands have been widely exploited in this regard, and a large number of compounds have been assessed for their activity.[42] The most active and also most systematically studied class of imido-supported Ziegler catalyst is of the type $\mathrm{Ti(NR)}(fac\text{-}\mathrm{N_3})\mathrm{Cl_2}$, where $fac\text{-}\mathrm{N_3}$ represents a neutral tridentate $\mathrm{N_3}$-donor ligand such as $\mathrm{Me_3[9]aneN_3}$ (1,4,7-trimethyltriazacyclononane, **1-R**[43−45]) and $\mathrm{HC(Me_2pz)_3}$ (**2-R**[46,47]). In both of these catalyst families, structure−activity relationship studies using high-throughput screening techniques found that bulky imido N substituents "R" were prerequisites for high catalytic productivities (e.g., R = ^{t}Bu, adamantyl, $\mathrm{CMe_2CH_2{}^tBu}$, 2-$\mathrm{C_6H_4{}^tBu}$, 2-$\mathrm{C_6H_4CF_3}$), especially at the commercially relevant high operating temperatures that these catalysts tolerate.



1-R



2-R

The active species in early-transition-metal Ziegler catalysts are alkyl cations $[\mathrm{(L)MR}]^+$ (L = supporting ligand or ligand set, R = initiating alkyl group or polymeryl chain).[48−50] Furthermore, the chemistry of early-transition-metal alkyl cations in general is well-understood. However, although a number of cationic imido compounds, without an additional metal−alkyl bond, have been reported,[51−57] only a handful of previous studies have looked at the question of reaction site selectivity in imido compounds (neutral or cationic) that also feature a metal−alkyl bond.[58−61]

The first well-defined experimental observation was by Legzdins, who found that neutral $\mathrm{Cp^*W(NTol)_2CH_2SiMe_3}$ (Tol = *p*-tolyl) reacted with *p*-tolyl isocyanate to form exclusively a $2\pi + 2\pi$ *cycloaddition* product via reaction of the imido ligand with the metal−alkyl bond left intact.[58] In contrast, Arnold and Bergman recently reported that $\mathrm{Ta(N^tBu)(CH_2Ph)_3}$ gave exclusively alkyl group *insertion* products with diisopropylcarbodiimide and 2,6-dimethylphenyl isocyanide.[61]

Gibson reported that the bis(imido)chromium systems $\mathrm{Cr(NR)_2X_2}$ (R = alkyl, aryl; X = Cl, $\mathrm{CH_2Ph}$) formed moderately active olefin polymerization catalysts with suitable activators and described limited in situ spectroscopic evidence for the benzyl cation $[\mathrm{Cr(N^tBu)_2(CH_2Ph)}]^+$ and a $\mathrm{PMe_3}$ adduct.[62] No reactivity studies were reported. Jensen and Børve reported DFT studies of the reaction of the model cation $[\mathrm{Cr(NH)_2Me}]^+$ with $\mathrm{C_2H_4}$ and found that, although insertion of $\mathrm{C_2H_4}$ into the Cr−Me bond was thermodynamically favored, cycloaddition to Cr═NH was kinetically the much preferred route.[63,64] However, no experimental probes of this system have been reported and the computational predictions have remained untested. In a previous attempt to address this question of reaction site selectivity in imido alkyl cations, we studied the reactions of $[\mathrm{W(NPh)\{MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2\}Me}]^+$ with polar substrates such as $\mathrm{CO_2}$ and certain heterocumulenes.[59,60] In contrast to Jensen and Børve's predictions,[63,64] DFT calculations for the tungsten cation suggested that cycloaddition to W═NPh was both kinetically *and* thermodynamically *disfavored* relative to insertion into W−Me. Unfortunately the diamide−pyridine ligand set in this case is noninnocent, and attempts to test experimentally the DFT predictions gave exclusively insertion into the $\mathrm{W{-}N_{amide}}$ bonds of the supporting ligand itself. Finally, Arnold and Bergman[61] found that the ill-defined and insoluble species

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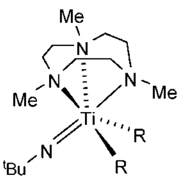
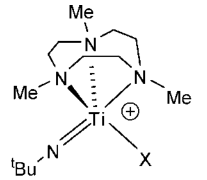
"$[\mathrm{Ta(N^tBu)(CH_2Ph)_2}][\mathrm{BAr^F_4}]$" could be generated in situ and intercepted by reaction with certain alkynes and alkenes. In these reactions Ta−$\mathrm{CH_2Ph}$ bond insertion products were exclusively formed. However, the poorly characterized nature of the highly unsaturated "$[\mathrm{Ta(N^tBu)(CH_2Ph)_2}]^+$" (which could for example contain unreactive $\mathrm{Ta(\mu\text{-}N^tBu)Ta}$ bridging imido groups) limit to some extent the insight attached to these results. Computational studies of this system have not been reported.

In pursuit of a better understanding of the catalyst families $\mathrm{Ti(NR)}$(*fac*-$\mathrm{N_3}$)$\mathrm{Cl_2}$,[43−46] we recently reported that the thermally stable alkyls $\mathrm{Ti(N^tBu)(Me_3[9]aneN_3)R_2}$ (**3**, R = Me; **4**, R = $\mathrm{CH_2SiMe_3}$) are cleanly and quantitatively converted to the well-defined cations $[\mathrm{Ti(N^tBu)(Me_3[9]aneN_3)R}]^+$ (**5**$^+$, R = Me; **6**$^+$, R = $\mathrm{CH_2SiMe_3}$) by treatment with $[\mathrm{CPh_3}][\mathrm{BAr^F_4}]$ ($\mathrm{Ar^F}$ = $\mathrm{C_6F_5}$).[65,66] The chloride cation $[\mathrm{Ti(N^tBu)(Me_3[9]aneN_3)Cl}]^+$ (**7**$^+$) was also readily accessed from $\mathrm{Ti(N^tBu)(Me_3[9]aneN_3)(Me)Cl}$.[66] The electronic structures of the alkyl cations **5**$^+$ and **6**$^+$ (isolobal analogues of the metallocenium alkyls $[\mathrm{Cp_2MR}]^+$) have been comprehensively studied using DFT and spectroscopic methods.[66] The base-free alkyl cations $[\mathrm{Ti(N^tBu)(Me_3[9]aneN_3)R}]^+$ therefore provide an excellent platform for stoichiometric reactivity studies. For example, they underwent a range of well-characterized reactions, including single and double C−H bond activation processes and formation of a number of main -group and transition-metal alkyl adducts.[45,66,67]



R = Me (**3**) or $\mathrm{CH_2SiMe_3}$ (**4**)



R = Me (**5**$^+$), $\mathrm{CH_2SiMe_3}$ (**6**$^+$) or Cl (**7**$^+$)

In this contribution we describe experimental studies of the reactions of $[\mathrm{Ti(N^tBu)(Me_3[9]aneN_3)X}]^+$(**5**$^+$−**7**$^+$) with a series of polar and nonpolar unsaturated organic substrates. In the subsequent paper we report detailed complementary investigations using DFT. These combined studies provide for the first time a unique and comprehensive insight into the reaction site selectivity in polymerization-active transition-metal cations which contain both M=NR and M−R′ functional groups as potential sites for $2\pi + 2\pi$ cycloaddition and migratory insertion, respectively. A part of this work has been communicated.[65]

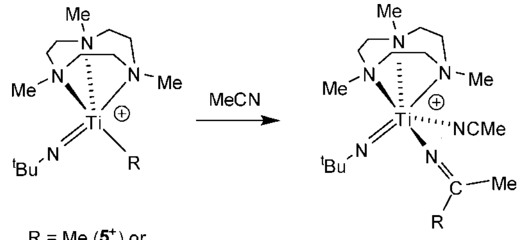
Results and Discussion

Reactions with MeCN. As a benchmark probe of the migratory insertion aptitudes of the Ti−alkyl bonds in $[\mathrm{Ti(N^tBu)(Me_3[9]aneN_3)R}]^+$ (**5**$^+$, R = Me; **6**$^+$, $\mathrm{CH_2SiMe_3}$) we first examined their reactions with MeCN (and also $\mathrm{CD_3CN}$ in the case of **5**$^+$). MeCN and other organonitriles are well-known to insert into the metal−alkyl bonds of main-group, transition-metal and f-element organometallics to form ketimido products.[68] Of particular relevance to our work are Bochmann's[69] and Jordan's[48,70] studies of the nitrile insertion reactions of group 4 metallocenium and cyclopentadienyl−dicarbollide[71] alkyls, with which the cations $[\mathrm{Ti(N^tBu)(Me_3[9]aneN_3)R}]^+$ are isolobal. In contrast, only one example is known of the cycloaddition reactions of organonitriles with a transition-metal−imido linkage.[72]

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[\mathrm{Ti(N^tBu)(Me_3[9]aneN_3)(NCMe_2)(NCMe)}]^+$ (8$^+$)

Ti(1)−N(1)	2.366(2)	Ti(1)−N(6)	2.227(2)
Ti(1)−N(2)	2.329(2)	N(4)−C(10)	1.405(3)
Ti(1)−N(3)	2.251(2)	N(5)−C(14)	1.296(4)
Ti(1)−N(4)	1.755(2)	N(6)−C(17)	1.144(3)
Ti(1)−N(5)	1.860(2)		
Ti(1)−N(4)−C(10)	168.43(19)	Ti(1)−N(5)−C(14)	170.93(19)
Ti(1)−N(6)−C(17)	159.1(2)	N(5)−C(14)−C(15)	123.5(3)
N(5)−C(14)−C(16)	119.9(3)		

Reaction of $\mathrm{Ti(N^tBu)(Me_3[9]aneN_3)Me_2}$ (**3**) with $[\mathrm{CPh_3}][\mathrm{BAr^F_4}]$ in $\mathrm{CH_2Cl_2}$ (generating **5**$^+$ in situ[66]) in the presence of 2 equiv of MeCN afforded the imido−ketimido species $[\mathrm{Ti(N^tBu)(Me_3[9]aneN_3)(NCMe_2)(NCMe)}][\mathrm{BAr^F_4}]$ (**8-BAr$^F_4$**) in 77% isolated yield as a yellow crystalline solid (eq 1). The NMR and IR data for **8**$^+$ are consistent with the proposed structure, which has been confirmed by X-ray crystallography (Table 1, Figure 1). The methyl groups of the $\mathrm{NCMe_2}$ ligand were equivalent at room temperature, but cooling a sample to −60 °C resulted in decoalescence into two resonances of equal intensity. This is consistent with the expected multiple-bond character in the $\mathrm{Ti{-}N_{ketimide}}$ linkage.[68] The IR spectrum of **8-BAr$^F_4$** showed the expected bands for coordinated MeCN and a $\mathrm{NCMe_2}$ ligand. In a similar fashion, sequential reaction of $\mathrm{Ti(N^tBu)(Me_3[9]aneN_3)(CH_2SiMe_3)_2}$ with $[\mathrm{CPh_3}][\mathrm{BAr^F_4}]$ and 2 equiv of MeCN in $\mathrm{CD_2Cl_2}$ gave $[\mathrm{Ti(N^tBu)(Me_3[9]aneN_3)\{NCMe(CH_2SiMe_3)\}(NCMe)}][\mathrm{BAr^F_4}]$ (**9-BAr$^F_4$**) in 60% isolated yield after ca. 1 h at room temperature. The IR and NMR data for **9-BAr$^F_4$** are analogous to those for **8-BAr$^F_4$**. In neither case was evidence for reaction at the $\mathrm{Ti{=}N^tBu}$ linkage observed.



(1)

R = Me (**5**$^+$) or $\mathrm{CH_2SiMe_3}$ (**6**$^+$)

R = Me (**8**$^+$) or $\mathrm{CH_2SiMe_3}$ (**9**$^+$)

The structure of the cation **8**$^+$ is shown in Figure 1, and selected distances and angles are given in Table 1. The cation contains an approximately octahedral Ti center supported by a *fac*-κ^3-coordinated $\mathrm{Me_3[9]aneN_3}$ group along with MeCN, $\mathrm{Me_2CN}$, and $\mathrm{Me_3CN}$ ligands. This is the second structurally authenticated compound containing both a terminal imido and a ketimido ligand and is the first for titanium. Uniquely, it contains, at the same metal center, the full family of ligands

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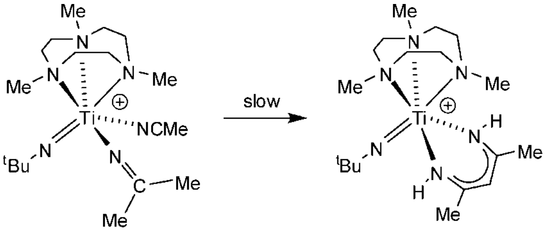
having the formula $NCMe_n$, where $n = 1$ (neutral ligand), 2 (monoanionic), 3 (dianionic).

As expected, the Ti−$NCMe_n$ distances in $\mathbf{8}^+$ increase with decreasing bond order. The Ti−$NCMe_2$ (1.860(2) Å) and Ti−NCMe (2.227(2) Å) distances are within the previously observed ranges for Ti−$NCMe_2$ and Ti−NCMe bonds.[73,74] However, despite the formal positive charge of the complex, the Ti−$NCMe_3$ bond distance of 1.755(2) Å is considerably longer than expected, on the basis of previous structural data,[73,74] and is attributed to the presence of the strongly σ- and π-donating $NCMe_2$ ligand. The orientation of the $NCMe_2$ ligand (methyl groups lying in the {Ti(1),N(2),N(3),N(5),N(6)} best-fit least-squares plane) is consistent with N(2p) → Ti(3d) π donation also occurring in this plane to give a Ti=N=CMe_2 "heteroallene" moiety.[68] The two π components of the formal Ti−N_{imido} triple bond therefore use the $3d_\pi$ orbitals lying perpendicular to the {Ti(1),N(2),N(3),N(5),N(6)} plane.

Solutions of the ketimide $[Ti(N^tBu)(Me_3[9]aneN_3)(NCMe_2)(NCMe)][BAr^F{}_4]$ (**8-BAr^F$_4$**) are stable for several days at room temperature but over extended periods isomerize cleanly to the corresponding β-diketiminate $[Ti(N^tBu)(Me_3[9]aneN_3)\{N(H)CMeCHCMeN(H)\}][BAr^F{}_4]$ (**10-BAr^F$_4$**) in 93% isolated yield (eq 2). This compound has been structurally characterized (see below), and the NMR spectra are consistent with this. In particular, the ^1H spectrum featured the expected resonances for the N(H)CMeCHCMeN(H) ligand with a broad singlet of relative integral 2 H at 6.41 ppm for the N−H protons and a binomial triplet ($^4J = 1.9$ Hz) of integral 1 H at 4.92 ppm for the C(Me)CHCMe methine proton, which couples to the two equivalent N−H protons. These and the ^{13}C data correspond favorably with those for Bercaw's scandocene derivative $Cp^*{}_2Sc\{N(H)CArCHCArN(H)\}$ (Ar = 4-C_6H_4OMe). The IR spectrum of **10-BAr^F$_4$** featured a ν(N−H) band at 3329 cm^{-1}, which can also be favorably compared with the band for the scandium analogue.



(2)

$\mathbf{8}^+$ $\mathbf{10}^+$

While β-diketiminato ("nacnac") ligands are of importance in transition-metal and lanthanide chemistry,[75] the vast majority of these are substituted with alkyl or aryl groups on the nitrogen atoms. Moreover, the rearrangement of a nitrile−ketimide species to the corresponding β-diketiminate has not been previously reported in group 4 chemistry. However, examples of this process have been previously observed in the reactions of neutral scandium[76] and chromium[77] cyclopendadienyl alkyls and likely mechanisms have been discussed.[76]

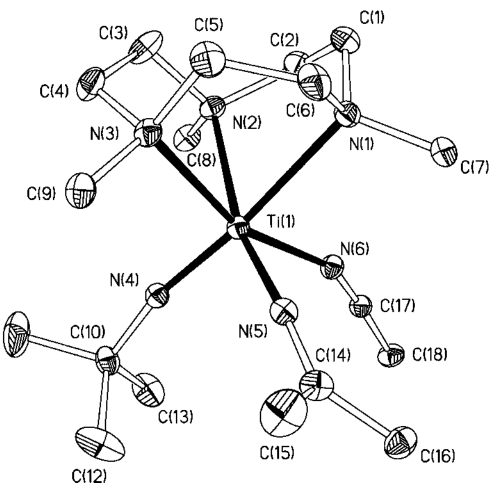


Figure 1. Displacement ellipsoid plot (15% probability) of $[Ti(N^tBu)(Me_3[9]aneN_3)(NCMe_2)(NCMe)]^+$ ($\mathbf{8}^+$). H atoms are omitted for clarity.

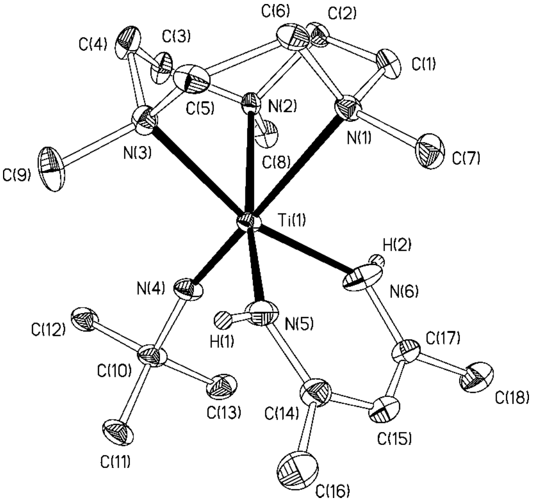


Figure 2. Displacement ellipsoid plot (20% probability) of $[Ti(N^tBu)(Me_3[9]aneN_3)\{N(H)CMeCHCMeN(H)\}]^+$ ($\mathbf{10}^+$). Carbon-bound H atoms and CH_2Cl_2 of crystallization are omitted. H atoms are drawn as spheres of arbitrary radius.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Ti(N^tBu)(Me_3[9]aneN_3)\{N(H)CMeCHCMeN(H)\}]^+$ ($\mathbf{10}^+$)

Ti(1)−N(1)	2.393(2)	Ti(1)−N(2)	2.293(2)
Ti(1)−N(3)	2.283(2)	Ti(1)−N(4)	1.697(5)
Ti(1)−N(5)	2.022(3)	Ti(1)−N(6)	2.011(4)
N(5)−C(14)	1.315(4)	N(6)−C(17)	1.304(4)
C(14)−C(15)	1.392(6)	C(15)−C(17)	1.409(6)
N(5)−H(1)	0.84(6)	N(6)−H(2)	0.74(7)
Ti(1)−N(4)−C(10)	168.7(5)	Ti(1)−N(5)−C(14)	129.0(3)
Ti(1)−N(6)−C(17)	132.0(3)	N(5)−Ti(1)−N(6)	85.95(14)

The cation $[Ti(N^tBu)(Me_3[9]aneN_3)(\{N(H)CMeCHCMeN(H)\})]^+$ ($\mathbf{10}^+$) features an approximately octahedral titanium center, with triazacyclononane, imido, and β-diketiminate ligands (Figure 2 and Table 2).[78] The Ti−N_{imide}−C angle of 168.7(5)° and the Ti=N_{imide} distance of 1.697(5) Å are within the expected ranges for a four-electron-donor *tert*-butylimido ligand.[73,74] It is interesting to compare the rather unexceptional Ti=N_{imide} distance in $\mathbf{10}^+$ with the significantly longer distance

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[78] The *tert*-butyl group is disordered. We refer here to the major orientation.

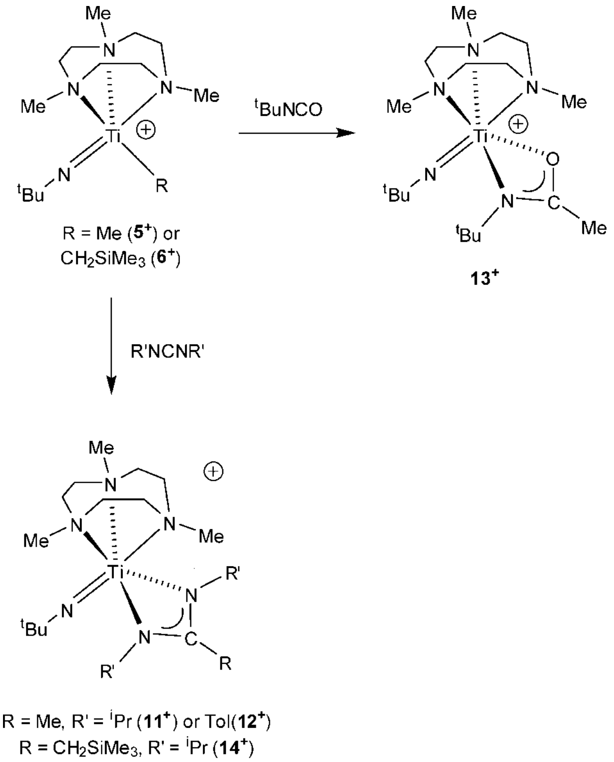
in the ketimide isomer **8**$^+$. The N-bound H atoms were located in a Fourier difference map and positionally and isotropically refined.

There are only two previous examples of crystallographically characterized complexes containing a N(H)CMeCHCMeN(H) ligand: one for platinum(4+)[79] and one for zirconium(4+).[80] Although no other titanium complexes of N(H)CMeCHCMeN(H) are known, numerous crystallographically characterized examples of the more common N-alkyl- and N-aryl-substituted homologues have been described. For 41 reported examples the mean Ti−N distance is 2.046 Å, with values ranging from 1.934 to 2.237 Å.[73,74] The values of 2.022(3) and 2.011(4) Å for **10**$^+$ are within this range and are very close to the mean value. The bond lengths and angles of the β-diketiminato ligand are in agreement with previous observations. A cationic titanium imido "nacnac" complex was reported recently by Mindiola and co-workers.[57]

Reactions with Isocyanates and Carbodiimides. In contrast to the situation for organonitriles, $2\pi + 2\pi$ cycloaddition reactions between titanium imido complexes and isocyanates and carbodiimides (to form ureate and guanidinate complexes, respectively) are very well established.[81−86] However, as shown in Scheme 1, reaction of [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Me]$^+$ (**5**$^+$) with diisopropylcarbodiimide, di-*p*-tolylcarbodiimide, or *tert*-butyl isocyanate gave exclusively in each case the corresponding Ti−Me migratory *insertion* product: namely, the amidinates [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$){MeC(NR)$_2$}]$^+$ (**11**$^+$, R = ^{i}Pr; **12**$^+$, R = Tol) and the amidate [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$){OC(Me)N^{t}Bu}]$^+$ (**13**$^+$). The corresponding reaction between [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)CH$_2$SiMe$_3$]$^+$ (**6**$^+$) and diisopropylcarbodiimide afforded [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$){Me$_3$SiCH$_2$C(N^{i}Pr)$_2$}]$^+$ (**14**$^+$). All four reactions were quantitative on the NMR-tube scale, demonstrating a clear preference for migratory insertion into the Ti−alkyl bonds rather than cycloaddition to Ti═N$_{\text{imide}}$, even in the case of [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)CH$_2$SiMe$_3$]$^+$ (**6**$^+$), in which the steric factors associated with the Ti−CH$_2$SiMe$_3$ and Ti═NCMe$_3$ linkages are very similar.

The spectroscopic and other analytical data for all four insertion products are consistent with the solid-state structures (see below) and those proposed in Scheme 1. In particular, the ^{1}H−^{13}C HMBC spectra show clear correlations between the migrated alkyl groups and the quaternary carbons of the newly formed R*C*(NR′)$_2$ and O*C*(Me)N^{t}Bu ligands. The diisopropylcarbodiimide insertion products **11-BAr$^F_4$** and **14-BAr$^F_4$** have been crystallographically authenticated. The molecular structures of cations **11**$^+$ and **14**$^+$ are shown in Figure 3, and selected distances and angles are given in Table 3. The metric data all lie within previously reported ranges for titanium and the ligands under consideration.[73,74] There are no significant differences between the two structures, other than a somewhat longer Ti(1)−N(4) bond in **14**$^+$ and the different alkyl substituents at C(5) of the amidinate ligands. The Ti−N$_{\text{imido}}$ distances are again significantly shorter in **11**$^+$ and **14**$^+$ than in the ketimido cation **8**$^+$. A number of titanium complexes containing both amidinate and terminal imido ligands have been reported previously.[86−91] Of particular relevance are the neutral half-sandwich acetamidinate complexes Cp*Ti(NR){MeC(N^{i}Pr)$_2$} (R = ^{t}Bu, 2,6-C$_6$H$_3$Me$_2$), the isoelectronic and isolobal analogues of **11**$^+$ and **14**$^+$.[86,89]

Scheme 1. Reactions of [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)R]$^+$ (5$^+$, R = Me; 6$^+$, R = CH$_2$SiMe$_3$) with carbodiimides and ^{t}BuNCO



Reactions of [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Me]$^+$ (5$^+$) with Internal Alkynes RCCPh (R = Ph, SiMe$_3$). Alkynes also present a fundamental problem in site selectivity, being well-known to insert into cationic metal−alkyl bonds (forming σ-vinyl products)[48,92−96] and also to undergo cycloaddition reactions with group 4 M═NR bonds in general, forming azametallacyclobutenes.[13,17,57,97−103] This is a key step in the group 4 hydroami-

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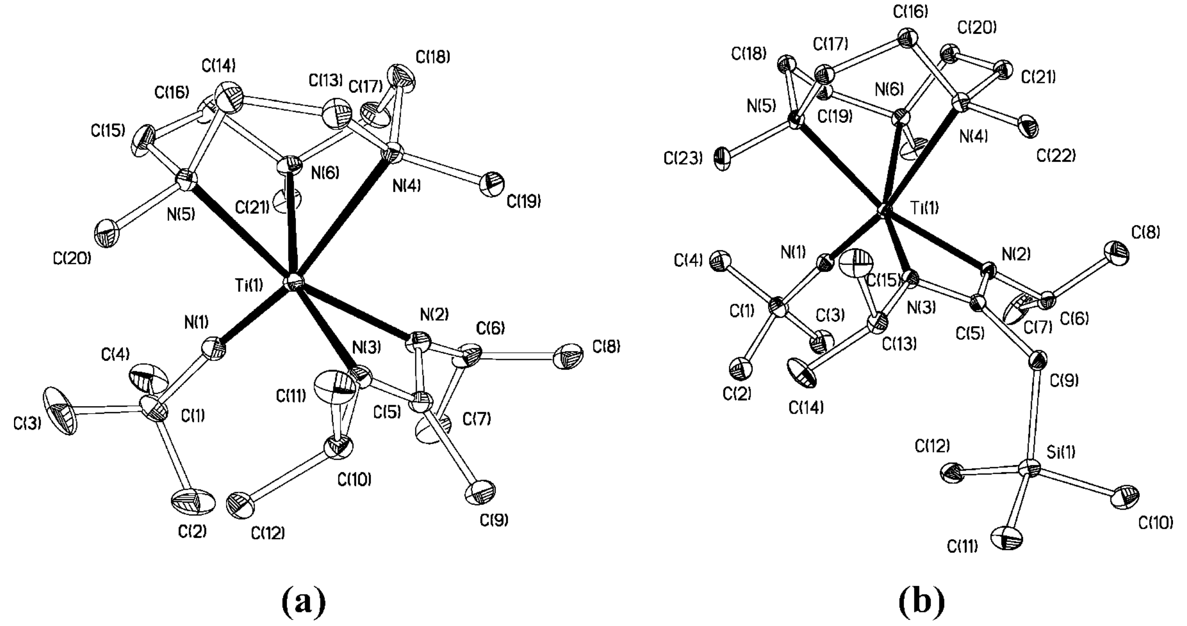


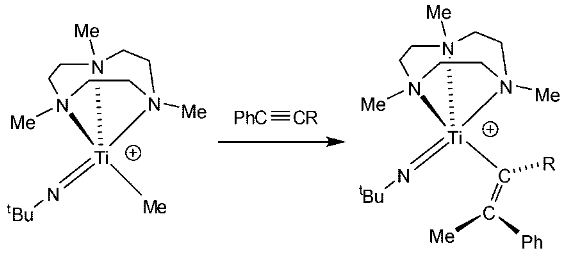
Figure 3. Displacement ellipsoid plots (20% probability) of (a) $[Ti(N^tBu)(Me_3[9]aneN_3)\{MeC(N^iPr)_2\}]^+$ ($\mathbf{11}^+$) and (b) $[Ti(N^tBu)(Me_3[9]aneN_3)\{Me_3SiCH_2C(N^iPr)_2\}]^+$ ($\mathbf{14}^+$). H atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Ti(N^tBu)(Me_3[9]aneN_3)\{MeC(N^iPr)_2\}]^+$ (11^+) and $[Ti(N^tBu)(Me_3[9]aneN_3)\{Me_3SiCH_2C(N^iPr)_2\}]^+$ (14^+)

param	$\mathbf{11}^+$	$\mathbf{14}^+$
Ti(1)−N(1)	1.718(2)	1.7085(18)
Ti(1)−N(2)	2.102(2)	2.1083(17)
Ti(1)−N(3)	2.120(2)	2.1276(16)
Ti(1)−N(4)	2.465(2)	2.5252(18)
Ti(1)−N(5)	2.286(2)	2.2787(17)
Ti(1)−N(6)	2.270(2)	2.2968(17)
N(2)−C(5)	1.337(3)	1.343(3)
N(3)−C(5)	1.344(3)	1.341(3)
Ti(1)−N(1)−C(1)	175.7(2)	177.77(15)
N(2)−C(5)−N(3)	113.0(2)	113.92(17)

nation of alkynes by transition metals.[104,105] Furthermore, in the case of terminal alkynes, there is the possibility of C−H bond activation by attack at either the M=NR[53,100,106] or M−alkyl bonds.[107]

The reactions of $[Ti(N^tBu)(Me_3[9]aneN_3)Me]^+$ ($\mathbf{5}^+$) with selected internal alkynes are summarized in eq 3.[108] With PhCCPh the migratory insertion product $[Ti(N^tBu)(Me_3[9]aneN_3)\{PhCC(Ph)Me\}][BAr^F_4]$ (**15-BAr$^F_4$**) was formed in 69% isolated yield. Although broad at room temperature, at −40 °C the ^{1}H and ^{13}C NMR data of $\mathbf{15}^+$ showed that this complex possesses C_1 symmetry, as indicated for example by three singlets at 3.21, 3.08, and 2.19 ppm for the macrocycle methyl groups in the ^{1}H spectrum. The presence of a C(Ph)=C(Ph)Me group was confirmed by the observation of long-range couplings from the methyl group protons to the two vinylic carbons and also to the ipso carbon of one of the phenyl groups. A number of neutral and cationic group 4 vinyl complexes of the type $L_nMC(R)=CRR'$ have been structurally authenticated,[92,93,109] and the ^{13}C chemical shifts of the vinylic carbons of 192.2 (Ti−*C*=C) and 133.7 (C=*C*(Ph)Me) ppm compare favorably with the corresponding shifts in the analogous group 4 metallocenium cations.[93]



(3)

$\mathbf{5}^+$ R′ = Ph ($\mathbf{15}^+$) or $SiMe_3$ ($\mathbf{16}^+$)

Reaction of $\mathbf{5}^+$ with the unsymmetrical internal alkyne $Me_3SiCCPh$ afforded exclusively $[Ti(N^tBu)(Me_3[9]aneN_3)\{Me_3SiCC(Ph)Me\}][BAr^F_4]$ (**16-BAr$^F_4$**) in 78% isolated yield (quantitative when followed by NMR in CD_2Cl_2). The C_1 symmetrical cation $\mathbf{16}^+$ has ^{1}H and ^{13}C NMR features similar to those of $\mathbf{15}^+$, and the connectivity within the $Me_3SiCC(Ph)Me$ fragment was conclusively established by ^{1}H−^{13}C correlation experiments. A single ^{29}Si NMR resonance was seen at −16.8 ppm. No evidence was found for an alternative isomer in which the titanium methyl group had migrated to the carbon bearing the $SiMe_3$ substituent. Although we have not been able to obtain diffraction-quality crystals of either product, on the basis of the NMR data and DFT calculations described below, $\mathbf{15}^+$ and $\mathbf{16}^+$ are unequivocally assigned approximately trigonal-bipyramidal geometries at titanium.

The titanium centers in the five-coordinate $\mathbf{15}^+$ and $\mathbf{16}^+$ have formal 14-valence-electron counts, thus raising the possibility

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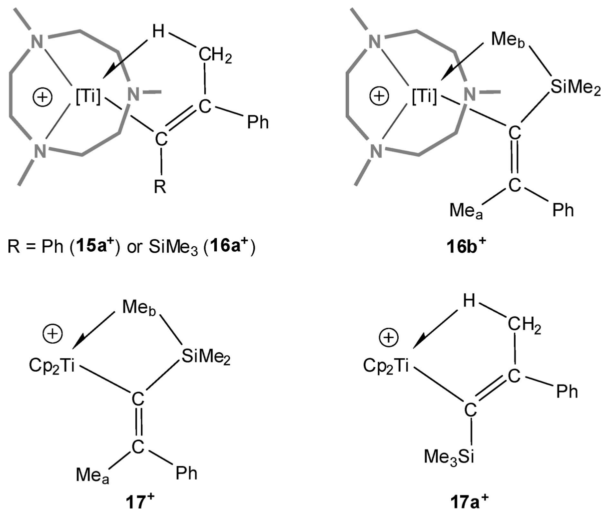
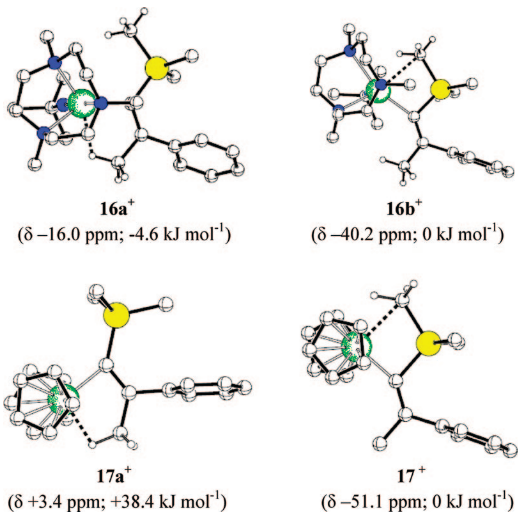


Figure 4. Potential agostic interactions in [Ti(N^{t}Bu)(Me$_3$-[9]aneN$_3$){RCC(Ph)Me}]$^+$ (R = Ph, SiMe$_3$), the β-Si−C agostic structure of [Cp$_2$Ti{Me$_3$SiCC(Ph)Me}]$^+$, and a γ-C−H agostic isomer.[92]


16a$^+$ (δ −16.0 ppm; -4.6 kJ mol^{-1})

16b$^+$ (δ −40.2 ppm; 0 kJ mol^{-1})

17a$^+$ (δ +3.4 ppm; +38.4 kJ mol^{-1})

17$^+$ (δ −51.1 ppm; 0 kJ mol^{-1})

Figure 5. DFT minimized alternative isomers of [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$){Me$_3$SiCC(Ph)Me}]$^+$ (**16a$^+$**, **16b$^+$**) and [Cp$_2$Ti{Me$_3$SiCC(Ph)Me}]$^+$ (**17$^+$**, **17a$^+$**). Computed ^{29}Si shifts and electronic energies relative to the β-Si−C agostic isomer are given in parentheses.

of agostic interactions. These could take the form of a γ-C−H agostic bond from the migrated methyl group (Figure 4, **15a$^+$** or **16a$^+$**), or (for **16$^+$**) a β-Si−C interaction, depicted as **16b$^+$**. Indeed, **16-BAr$^F_4$** is related to Eisch's landmark compound [Cp$_2$Ti{Me$_3$SiCC(Ph)Me}][AlCl$_4$] (**17-AlCl$_4$**; cf. Figure 4), the X-ray structure of which showed a pronounced β-Si−C agostic interaction.[92] Horton has reported analogous reactions of zirconocenium methyl cations with Me$_3$SiCCMe to give β-Si−C agostic insertion products.[93] The high-field-shifted ^{29}Si resonances (δ less than −50 ppm) in these were attributed to the β-Si−C agostic interactions. Since no ^{29}Si data were reported for **17$^+$**, we prepared it on the NMR-tube scale in order to make a comparison with the data for **16$^+$**. The sequential reaction of Cp$_2$TiMe$_2$ with [CPh$_3$][BAr$^F_4$] and Me$_3$SiCCPh afforded **17$^+$** quantitatively and cleanly, and the ^{1}H and ^{13}C NMR data were fully consistent with the previously reported X-ray structure. The ^{29}Si NMR resonance for **17$^+$** appeared at −54.9 ppm, consistent with its solid-state geometry and the data reported by Horton for the zirconocenium systems.[93]

In contrast to the very upfield ^{29}Si resonances for these metallocenium systems, the corresponding shift for **16$^+$** appeared at only −16.8 ppm. This is comparable to that of free Me$_3$SiCCPh itself (δ −18.6 ppm) and organic vinyl-substituted trimethylsilanes R(R′)C=C(R″)SiMe$_3$ (range δ −4.3 to −11.5 ppm).[110,111] On the other hand, the shift for **16$^+$** is comparable to that of [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)(CH$_2$SiMe$_3$)]$^+$ (**6$^+$**; δ −15.9 ppm), which does contain a β-Si−C agostic bond.[66] On the basis of the ^{29}Si NMR data alone, the bonding situation in **16$^+$** is somewhat ambiguous. However, we have recently shown how the combination of DFT (NMR and geometry calculations) and ^{29}Si NMR spectroscopy is a powerful technique to identify β-Si−C agostic interactions.[66] To clarify the bonding situation, models of **16a$^+$**, **16b$^+$**, **17$^+$**, and **17a$^+$** (Figure 4) were optimized at the DFT (B3PW91) level and ^{29}Si chemical shifts computed in the GIAO approximation with IGLO-II type basis sets (see Computational Details). The DFT minimized structures are represented in Figure 5 along with the computed ^{29}Si shifts and the energies relative to the β-Si−C agostic isomers. It is clear that the titanocenium system **17$^+$** has a strong preference for a β-Si−C agostic structure (−38.4 kJ mol^{-1} more stable than the γ-C−H agostic alternative **17a$^+$**) and that the observed ^{29}Si resonance (−54.9 ppm) is consistent with this structure (calculated −51.1 ppm). In contrast, **16$^+$** prefers slightly the γ-C−H agostic structure (−4.6 kJ mol^{-1}), and again the observed ^{29}Si resonance (−16.8 ppm) is consistent with this (calculated −16.0 ppm). The differences in structural preferences are attributed to the higher electronegativity of titanium and greater ease of deformation for the [Cp$_2$TiX]$^+$ fragment (X = σ-donor ligand) compared to the isolobal [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)X]$^+$, as we have described previously.[66]

The magnitude of the experimental average $^1J_{CH}$ value for the Me$_3$SiCC(Ph)*Me* methyl in **17$^+$** (*not* involved in a γ-C−H agostic interaction) is 128 Hz, some ca. 4−5 Hz larger than that in the γ-C−H agostic cations **15$^+$** (124 Hz) and **16$^+$** (123 Hz). Similar differences are also found in the average computed $^1J_{CH}$ values (**15a$^+$**, 113.5 Hz; **16a$^+$** 112.8 Hz; **17$^+$**, 117.2 Hz),[112] although the absolute magnitudes are underestimated relative to experiment by ca. 10%, as found previously.[66,67] At first sight this suggests that the lower average $^1J_{CH}$ values in **15$^+$** and **16$^+$** support the presence of γ-C−H agostic ground-state interactions.[113−115] However, the calculated average $^1J_{CH}$ values for the alternative isomers are not that dissimilar (**16b$^+$**, 114.4 Hz; **17a$^+$**, 117.9 Hz),[116] with the titanocenium system **17a$^+$** still having the higher calculated average $^1J_{CH}$ value even though it is now the one with the γ-C−H interaction. Therefore, the ^{29}Si NMR shifts allow a much better indication of the actual isomer formed (namely γ-C−H vs. β-Si−C agostic) than the *average* $^1J_{CH}$ values.[117]

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(112) Individual C−H bond values: **15a$^+$**, 103.6 (H closest to Ti), 115.8, 121.0 Hz; **16a$^+$**, 95.9 (H closest to Ti), 119.5, 123.0 Hz; **17$^+$**, 115.7, 117.4, 118.5 Hz.

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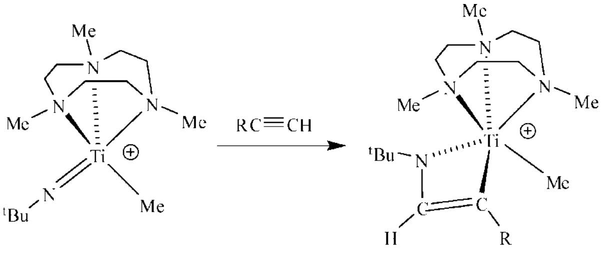
(116) Individual C−H bond values: **16b$^+$**, 109.5, 115.9, 117.7 Hz; **17a$^+$**, 86.9 (H closest to Ti), 133.2, 133.5 Hz.

(117) The individual ^1J values for the γ-agostic Me groups are of course very different from those for their nonagostic counterparts, but these values are not available from the NMR experiments.

Reactions of [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Me]$^+$ (5$^+$) with Terminal Alkynes RCCH (R = Ph, SiMe$_3$). The reactions of [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Me]$^+$ (**5**$^+$) with terminal alkynes RCCH (R = SiMe$_3$, Ph) are shown in eq 4.[108] These differ strikingly from those with the internal alkynes RCCPh and the other substrates discussed so far.



(4)

5$^+$

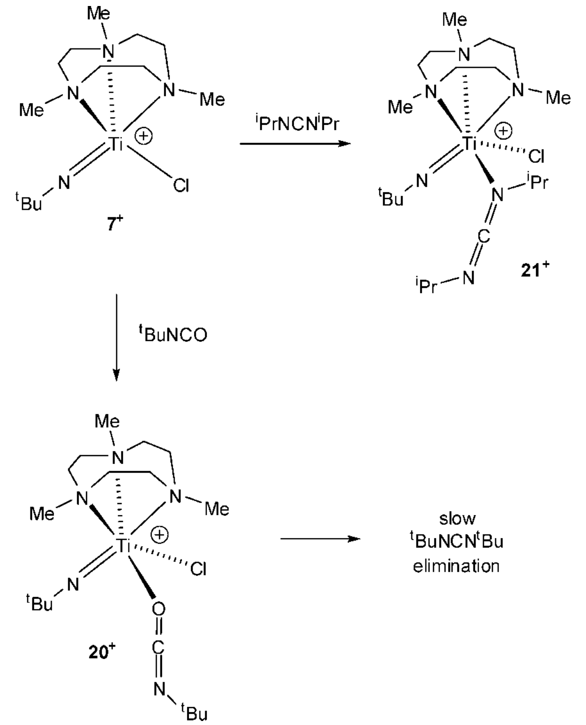
R = SiMe$_3$ (**18**$^+$) or Ph (**19**$^+$)

In each of these cases reaction takes place only at the Ti=N^{t}Bu bond to form exclusively the $2\pi + 2\pi$ cycloaddition products [Ti{^{t}BuNC(H)CR}(Me$_3$[9]aneN$_3$)Me][BAr$^F{}_4$] (R = SiMe$_3$ (**18-BAr$^F{}_4$**), Ph (**19-BAr$^F{}_4$**)) in 55−64% isolated yield. These compounds are most efficiently prepared at low temperature in CH$_2$Cl$_2$ and isolated at −78 °C by addition of hexanes. On standing at room temperature in CD$_2$Cl$_2$ they convert ($t_{1/2}$ = ca. 1 h) to the corresponding chloride cations [Ti{^{t}BuNC(H)CR}(Me$_3$[9]aneN$_3$)Cl]$^+$, which are described in further detail below.

The ^{1}H and ^{13}C NMR data for the two cations are comparable and fully consistent with the C_1-symmetric structures proposed. The formation of the new N(^{t}Bu)−C(H) bonds was unambiguously confirmed by long-range correlations between the azatitanacyclobutene C(*H*)=C hydrogen atoms and the *C*Me$_3$ quaternary atoms of the *tert*-butyl groups. The C(*H*)=C hydrogen atoms in the new compounds appear at δ 11.38 and 11.07 ppm, respectively. These distinctive shifts are comparable to those found previously for compounds containing a TiN(R)C(H)=C(R′) ring.[101,102] The ^{1}H shifts for the Ti−Me groups are −0.51 and −0.29 ppm, consistent with metal-bound methyl ligands, whereas in the insertion products **15**$^+$and **16**$^+$ the migrated methyl groups appear at 2.12 and 1.82 ppm, respectively. The ^{29}Si shift of −9.7 ppm in **18**$^+$ is consistent with the SiMe$_3$ group being bound to a vinylic carbon[110,111] and implies that there is no β-Si−C agostic interaction with the six-coordinate titanium center. Experimentally, the difference in reactivity of **5**$^+$ toward internal (insertion into Ti−Me) and terminal (cycloaddition to Ti=N^{t}Bu) alkynes appears to be governed by steric considerations.

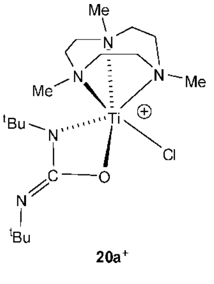
Reactions of [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl]$^+$ (7$^+$) with Unsaturated Substrates. The reactions of the imido alkyl cations **5**$^+$ and **6**$^+$ with the majority of the polar unsaturated substrates investigated (MeCN, carbodiimides, ^{t}BuNCO, PhCCR) have shown migratory insertion as the preferred pathway. However, this leaves open the question of whether five-coordinate cations of the type [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)X]$^+$ could in fact undergo cycloaddition reactions with these substrates at the Ti=N^{t}Bu bond in the *absence* of a competing Ti−alkyl group. To address this question, we turned to the in situ generated monochloride cation [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl]$^+$ (**7**$^+$), which is formed quantitatively by methide abstraction from Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)(Me)Cl.[66] Furthermore, the steric requirements of a chloride ligand are similar to those of a methyl group, and so, **7**$^+$ is an ideal system for modeling the potential reactivity of the Ti=N^{t}Bu bond in [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)R]$^+$ in the absence of a competing insertion pathway.

Scheme 2. Reactions of [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl]$^+$ (7$^+$) with ^{t}BuNCO and ^{i}PrNCN^{i}Pr

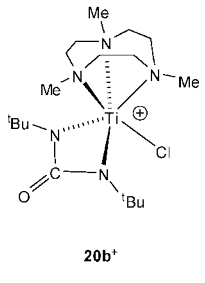


Reactions of [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl]$^+$ with ^{t}BuNCO and ^{i}PrNCN^{i}Pr. Addition of ^{t}BuNCO or ^{i}PrNCN^{i}Pr (1 equiv) to in situ generated [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl][BAr$^F{}_4$] (**7-BAr$^F{}_4$**) in CH$_2$Cl$_2$ formed [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl(OCN^{t}Bu)][BAr$^F{}_4$] (**20-BAr$^F{}_4$**) or [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)(^{i}PrNCN^{i}Pr)Cl][BAr$^F{}_4$] (**21-BAr$^F{}_4$**) in ca. 70% isolated yield (Scheme 2). The NMR spectra for the two compounds were sharp and consistent with C_1 symmetry. Both are unstable in solution, forming mixtures of products after several hours. In contrast, both the chloride cation **7**$^+$ itself and its pyridine adduct [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl(py)]$^+$ are stable for days in CD$_2$Cl$_2$. For **20**$^+$ the major organic product was identified as di-*tert*-butylcarbodiimide. For **21**$^+$ an organic product could not be identified.

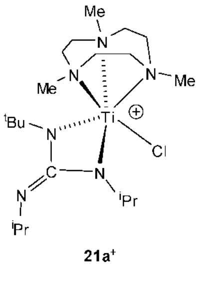
The formation of ^{t}BuNCN^{t}Bu is the expected outcome of a Ti=N^{t}Bu + ^{t}BuNCO $2\pi + 2\pi$ cycloaddition reaction followed by extrusion, forming a “Ti=O” species and the carbodiimide via the N,O-bound ureato intermediate [Ti{^{t}BuNC(N^{t}Bu)O}(Me$_3$[9]aneN$_3$)Cl]$^+$ (**20a**$^+$).[17] The decomposition of **21**$^+$ could also proceed through the guanidato intermediate [Ti{^{t}BuNC(N^{i}Pr)N^{i}Pr}(Me$_3$[9]aneN$_3$)Cl]$^+$ (**21a**$^+$).



20a$^+$



20b$^+$



21a$^+$

Owing to their instability in solution, we have been unable to obtain diffraction-quality crystals of **20-BAr$^F{}_4$** or **21-BAr$^F{}_4$**.

At first sight the ^{1}H data and elemental analyses could be equally consistent with the cycloaddition products **20a**$^+$ and **21a**$^+$ discussed above (especially since ^{t}BuNCN^{t}Bu is one of the ultimate products from the reaction with ^{t}BuNCO). A further potential isomer of **20**$^+$, namely the symmetrically bound *N*,*N*-ureate complex [Ti{^{t}BuNC(O)N^{t}Bu}(Me$_3$[9]aneN$_3$)Cl]$^+$ (**20b**$^+$), is inconsistent with the observation of two sets of *tert*-butyl group resonances in the NMR spectra. Furthermore, **20b**$^+$ is not a viable intermediate for the formation of ^{t}BuNCN^{t}Bu.

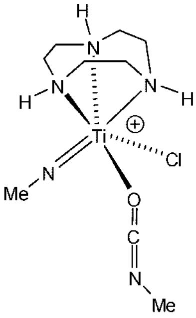
The solution ^{13}C{^{1}H} NMR and solid-state IR data for **20-BAr^F$_4$** and **21-BAr^F$_4$** support their formulation as the unusual σ adducts illustrated in Scheme 2. First the ^{13}C NMR shifts of the imido *tert*-butyl quaternary carbons (70.9 and 72.0, respectively) are strongly indicative of terminal Ti=N^{t}Bu groups, which typically appear at ca. 70 ppm for the types of compound described herein and at 72.2 ppm for [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl(py)]$^+$.[66] It is well-established that heterocumulene cycloaddition to Ti=N^{t}Bu results in a ca. 10−15 ppm upfield shift of the quaternary resonance relative to that of the starting imide.[81,86] The corresponding resonance for the coordinated ^{t}BuN*C*O in **20**$^+$ is observed at 59.2 ppm.

Second, the IR spectra of **20-BAr^F$_4$** and **21-BAr^F$_4$** show strong bands at 2357 and 2133 cm^{-1}, respectively, assigned to the coordinated heterocumulenes which are shifted to higher wavenumbers compared to the asymmetric stretches of the free ligands (2258 and 2114 cm^{-1}, respectively). In contrast, cycloaddition products of the type **20a**$^+$ and **21a**$^+$ exhibit C=NR stretches in the 1620−1750 cm^{-1} region.[81,86] In both **20-BAr^F$_4$** and **21-BAr^F$_4$** there is a band around 1643 cm^{-1} assigned to a mode of the [BAr^F$_4$]$^-$ anion invariably present (1641−1643 cm^{-1}) in all of the species described herein and also, for example, in [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl(py)]$^+$.[66] The asymmetric stretch of coordinated carbodiimides has been reported at 2126−2143 cm^{-1} in certain palladium σ adducts.[118] In the case of **20**$^+$ there is the additional possibility of linkage isomerism associated with the σ-^{t}BuNCO ligand which may be N or O coordinated. It has previously been reported that N coordination of isocyanates results in a lowering of the asymmetric stretching frequency compared to the free ligand,[119] suggesting that **20**$^+$ is an O-bound adduct, as illustrated in Scheme 2. Consistent with this hypothesis, no NOE interaction was observed between the isocyanate methyl protons and those of the rest of the cation **20**$^+$.

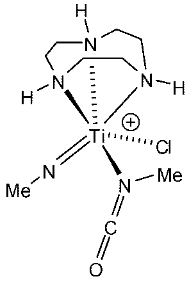
There are few literature examples of σ adducts of carbodiimides and isocyanates, particularly for early transition metals. Cotton et al. reported the neutral carbodiimide complexes (RNCN^{t}Bu)$_2$PdX$_2$ (R = Me, ^{t}Bu; X = Cl, Br),[118] and the X-ray structure of (^{t}BuNCN^{t}Bu)$_2$PdCl$_2$ revealed two σ-bonded carbodiimide ligands.[120] Isocyanate π adducts of Co,[121] Mo,[122] and Ni[123,124] are known, but σ adducts are less common. Villa and Powell have reported isocyanate N-bound σ adducts of Ni(II) and Cu(II) on the basis of infrared spectroscopic data.[119] Several isocyanate adducts of Zr, Mn, Fe, Co, Ni, Cu, and Zn have been described in the patent literature,[125] but no structural data were presented, and the complexes were assigned on the basis of combustion analysis alone. Jain and Rivest reported a titanium EtNCO σ adduct which featured a band at 1845 cm^{-1}, probably indicative of an N-bound adduct.[126] The increased σ-donor properties of nitrogen versus oxygen account for the general observation of N-bound isocyanate adducts in the literature. Therefore, **20-BAr^F$_4$** appears to be the first documented example of an O-bound isocyanate adduct.

Table 4. Key DFT Calculated and Experimentally Observed Stretching Frequencies (ν) of Various Species[127]

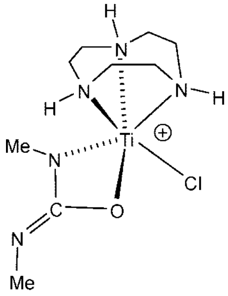
species	ν_{calcd} (cm^{-1})	ν_{obsd} (cm^{-1})
^{t}BuNCO	2258	2258
[Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl(OCN^{t}Bu)]$^+$ (**20**$^+$)		2357
MeNCO	2287	
[Ti(NMe)(H$_3$[9]aneN$_3$)Cl(OCMe)]$^+$ (**20-Oq**$^+$)	2409	
[Ti(NMe)(H$_3$[9]aneN$_3$)Cl{N(Me)CO}]$^+$ (**20-Nq**$^+$)	2182	
[Ti{MeNC(NMe)O}(H$_3$[9]aneN$_3$)Cl]$^+$ (**20a-q**$^+$)	1682	
[Ti{MeNC(O)NMe}(H$_3$[9]aneN$_3$)Cl]$^+$ (**20b-q**$^+$)	1710	



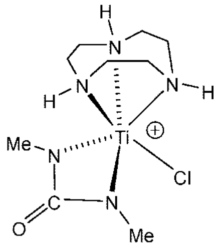
20-Oq$^+$



20-Nq$^+$



20a-q$^+$



20b-q$^+$

To further test our interpretation of **20**$^+$, we carried out DFT calculations on selected compounds (Table 4) to obtain computed stretching frequencies for various models of the potential isomers. These are the O- and N-bound σ-adducts **20-Oq**$^+$and **20-Nq**$^+$ and the N,O- and N,N-bound ureates **20a-q**$^+$ and **20b-q**$^+$. To improve computational efficiency for the model σ adducts, we substituted Me$_3$[9]aneN$_3$ by the H-substituted homologue and the *tert*-butyl groups were replaced by methyl groups. The computed asymmetric stretch in **20-Oq**$^+$ lies to higher frequency of free MeNCO, whereas that of the N-bound isomer **20-Nq**$^+$ appears at a lower frequency. In contrast, both ureate complexes have ν(C=N) or ν(C=O) values in the ca. 1680−1710 cm^{-1} range, consistent with previous experimentally observed values. The DFT results therefore support the structure proposed in Scheme 2 for [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl(OCN^{t}Bu)]$^+$ (**20**$^+$).

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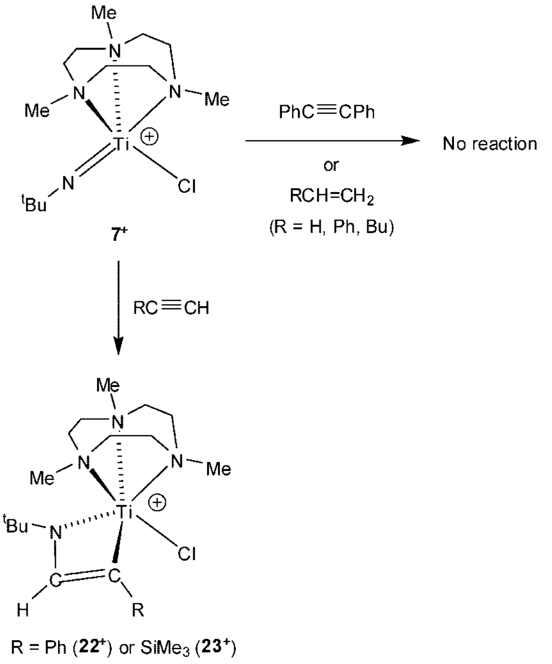
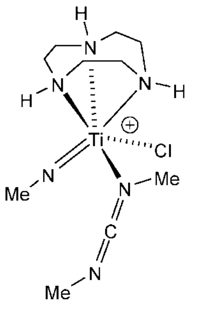
(127) Values in parentheses are corrected to ν(obsd)/ν(calcd) = 0.9427 in accordance with the calculated and observed values for ^{t}BuNCO.

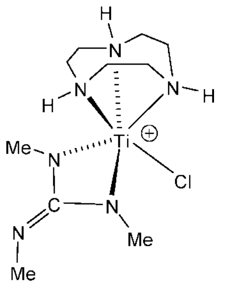
Scheme 3. Reactions of [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl]$^+$ (7$^+$) with Alkynes



As a final comparison, we carried out analogous calculations on the model carbodiimide-derived products [Ti(NMe)(H$_3$[9]aneN$_3$)Cl(MeNCNMe)]$^+$ (**21-q**$^+$, a model for **21**$^+$) and the corresponding guanidinate cycloaddition product [Ti{MeNC(NMe)NMe}(H$_3$[9]aneN$_3$)Cl]$^+$ (**21a-q**$^+$). The strong asymmetric stretch of the coordinated MeNCNMe (2191 cm^{-1}) in **21-q**$^+$ appears at a frequency higher than that calculated for the free carbodiimide (2157 cm^{-1}), whereas **21a-q**$^+$ shows no significant absorption in this region and instead has a strong ν(C=N) band at 1650 cm^{-1}. These data again support the assignment of **21**$^+$ as a σ-bound adduct (ν 2133 cm^{-1}; cf. 2114 cm^{-1} for free ^{i}PrNCN^{i}Pr).



21-q$^+$



21a-q$^+$

Reactions of [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl]$^+$with Alkynes. Scheme 3 summarizes the reactions of **7**$^+$ with PhCCPh, PhCCH, and Me$_3$SiCCH.

As for the reactions with **5**$^+$, PhCCH reacted smoothly with **7-BAr$^F_4$** to form a cycloaddition product, namely [Ti{^{t}BuNC(H)CPh}(Me$_3$[9]aneN$_3$)Cl][BAr$^F_4$] (**22-BAr$^F_4$**), in 67% yield. The NMR data for **22**$^+$ are analogous to those of the methyl analogue **18**$^+$ formed from **5**$^+$. The presence of the ^{t}BuNC(H)CPh unit was confirmed by a correlation between the C(*H*)=C hydrogen atom (11.68 ppm) and the *C*Me$_3$ carbon atom (66.6 ppm) and an NOE interaction between this hydrogen atom and those of the *tert*-butyl substituent.

The analogous reaction between Me$_3$SiCCH and **7-MeBAr$^F_3$** also gave a cycloaddition product, [Ti{^{t}BuNC(H)CSiMe$_3$}(Me$_3$[9]aneN$_3$)Cl][MeBAr$^F_3$] (**23-MeBAr$^F_3$**), with NMR and other data analogous to those of **22**$^+$ and the methyl cation **19**$^+$. In contrast, no reaction occurred between **7**$^+$ and PhCCPh, suggesting that this substrate is too sterically demanding to couple with the Ti=N^{t}Bu linkage. The corresponding reaction with the less sterically encumbered MeCCMe gave a mixture of unknown products when the reaction was followed by ^{1}H NMR spectroscopy.

Several examples of the reversible cycloaddition of alkynes to M=NR linkages have been reported in the literature,[53,57] and we were interested to probe for this in the cycloaddition products [Ti{^{t}BuNC(H)CR}(Me$_3$[9]aneN$_3$)Cl]$^+$. Addition of pyridine (1 equiv) to an NMR-tube sample of **22**$^+$ in CD$_2$Cl$_2$ afforded no reaction for at least 16 h. In contrast, [Ti{^{t}BuNC(H)CSiMe$_3$}(Me$_3$[9]aneN$_3$)Cl]$^+$ (**23**$^+$) reacted immediately with pyridine, giving free Me$_3$SiCCH and the known adduct [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl(py)]$^+$.[66] The difference in behavior of **22**$^+$ and **23**$^+$ is attributed to the greater steric repulsion associated with the SiMe$_3$ substituent in the latter.

Reactions of [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl]$^+$ with Alkenes. Activation of Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl$_2$ with MAO[43,44] or of Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Me$_2$ with [CPh$_3$][BAr$^F_4$][45] provides highly productive ethylene polymerization catalysts. The catalytically active species in these systems are proposed to be monoalkyl cations of the type [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)R]$^+$, with the imido group acting as spectator ligand. However, as mentioned, Jensen and Børve have suggested[63,64] that the isolobal, catalytically active bis(imido)chromium cations [Cr(NR′)$_2$R]$^+$ undergo ethylene addition at one of the Cr=NR bonds to provide a modified catalyst system during the polymerization process. In light of these results and the cycloaddition reactions observed between RCCH and **5**$^+$and **7**$^+$, it was clearly of relevance to probe the reactivity of the Ti=N^{t}Bu bond in complexes of the type [Ti(^{t}BuN)(Me$_3$[9]aneN$_3$)X]$^+$ toward alkenes.

Unfortunately, the high reactivity of the compounds [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)R]$^+$ (R = Me, CH$_2$SiMe$_3$) for ethylene polymerization prohibited controlled probing of the reactivity of the Ti=N^{t}Bu bond. Stoichiometric reactions with styrene or hexene also yielded mixtures containing alkene oligomers. However, as established above, the chloride cation [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl]$^+$ (**7**$^+$) provides an alternative basis for assessing the reactivity of the Ti=N^{t}Bu linkage itself. Reactions of **7**$^+$ with ethylene, 1-hexene, and styrene were carried out on the NMR-tube scale in CD$_2$Cl$_2$. In each case no reaction was observed after 16 h, the resonances observed in the ^{1}H NMR spectra corresponding to **7**$^+$ and the unreacted alkene. It is therefore very likely that cationic catalyst systems derived from Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl$_2$ or Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Me$_2$ do not undergo modification of the Ti=NR bond during the course of the polymerization process.

Conclusions

Our experimental study of the reactions of the three different cations [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)R]$^+$ (**5**$^+$, R = Me; **6**$^+$, R = CH$_2$SiMe$_3$) and [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl]$^+$ (**7**$^+$) with a series of polar and nonpolar unsaturated substrates has provided a comprehensive evaluation of reaction site selectivity in catalytically active and well-defined imido alkyl cations. Experimentally, migratory insertion into the Ti−Me bond is almost exclusively observed, except in the case of certain terminal alkynes. The reactions of alkyl cations were supplemented by parallel studies of the otherwise analogous chloride cation **7**$^+$, allowing experimental evaluation of the intrinsic Ti=N^{t}Bu bond reactivity in the absence of a competing Ti−alkyl group. A unique O-bound isocyanate complex was also formed during these studies, as well as further insights into the characteristics of β-Si−C agostic interactions. In the following paper we report extensive DFT studies which compliment the experimental work and offer an interpretation of the kinetic and thermodynamic factors underpinning these titanium imido alkyl and chloride cations.

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or of dinitrogen. Protio and deuterio solvents were predried over activated 4 Å molecular sieves and were refluxed over the appropriate drying agent, distilled, and stored under dinitrogen in Teflon valve ampules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H, ^{13}C{^{1}H}, ^{19}F, ^{29}Si, and ^{2}H NMR spectra were recorded on Varian Mercury-VX 300, Varian Unity Plus 500, and Bruker AV500 spectrometers. ^{1}H and ^{13}C assignments were confirmed when necessary with the use of DEPT-135, DEPT-90, and two-dimensional ^{1}H−^{1}H and ^{13}C−^{1}H NMR experiments. ^{1}H and ^{13}C spectra were referenced internally to residual protio solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ 0 ppm). ^{19}F spectra were referenced externally to $CFCl_3$. ^{29}Si spectra were referenced externally to tetramethylsilane. Chemical shifts are quoted in δ (ppm) and coupling constants in hertz. Infrared spectra were prepared as Nujol mulls between NaCl plates and were recorded on Perkin-Elmer 1600 and 1710 series FTIR spectrometers. Infrared data are quoted in wavenumbers (cm^{-1}). Mass spectra were recorded by the mass spectrometry service of Oxford University's Department of Chemistry and elemental analyses by the analytical services of the University of Oxford Inorganic Chemistry Laboratory or by the Elemental Analysis Service at the London Metropolitan University.

Literature Preparations and Other Starting Materials. The compounds Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)R$_2$ (**3**, R = Me (**3**); **4**, R = CH$_2$SiMe$_3$) and Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl(Me) were prepared according to published methods.[43,45] The compounds BAr^F$_3$ and [Ph$_3$C][BAr^F$_4$] (Ar^F = C$_6$F$_5$) were provided by DSM Research. All other compounds and reagents were purchased and used without further purification.

[Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)(NCMe$_2$)(NCMe)][BAr^F$_4$] (8-BAr^F$_4$). To a solution of Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Me$_2$ (**3**; 50 mg, 0.156 mmol) in C$_6$H$_5$Cl (2 mL) was added [Ph$_3$C][BAr^F$_4$] (144 mg, 0.156 mmol) in C$_6$H$_5$Cl (2 mL) to give a bright orange solution. After 5 min MeCN (15.9 μL, 0.312 mmol) was added to give a yellow solution. The solution was concentrated to approximately 1 mL, after which pentane (4 mL) was added with stirring to give a yellow precipitate. The precipitate was filtered off, washed with pentane (3 × 2 mL), and dried in vacuo. Yield: 128 mg (77%). Diffraction-quality single crystals were obtained by careful layering of a CH$_2$Cl$_2$ solution with Me$_3$SiOSiMe$_3$. ^{1}H NMR (CD$_2$Cl$_2$, 499.9 MHz, 293 K): 3.57 (1H, m, CH$_2$), 3.41 (1H, m, CH$_2$), 3.12 (3H, s, NMe), 3.10 (3H, s, NMe), 2.92−2.85 (3H, overlapping m, CH$_2$), 2.75−2.71 (2H, overlapping m, CH$_2$), 2.67 (1H, m, CH$_2$), 2.60−2.40 (4H, overlapping m, CH$_2$), 2.38 (3H, s, NCMe), 2.17 (3H, s, NMe), 1.91 (6H, s, NCMe$_2$), 1.01 (9H, s, NCMe$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 125.7 MHz, 293 K): 164.7 (N*C*Me$_2$), 148.5 (br d, $^1J_{C-F}$ = 243 Hz, 2-C$_6$F$_5$), 138.6 (br d, $^1J_{C-F}$ = 245 Hz, 4-C$_6$F$_5$), 136.6 (br d, $^1J_{C-F}$ = 248 Hz, 3-C$_6$F$_5$), 125.7 (N*C*Me), 66.7 (N*C*Me$_3$), 57.1 (CH$_2$), 56.8 (CH$_2$), 55.8 (CH$_2$), 55.1 (CH$_2$), 55.0 (CH$_2$), 54.3 (CH$_2$), 53.7 (NMe), 52.0 (NMe), 47.6 (NMe), 32.0 (NC*Me*$_3$), 27.9 (NC*Me*$_2$), 2.8 (NC*Me*). ^{19}F NMR (CD$_2$Cl$_2$, 282.4 MHz, 293 K): −133.1 (d, ^3J = 19.8 Hz, 2-C$_6$F$_5$), −165.1 (t, ^3J = 19.8 Hz, 4-C$_6$F$_5$), −167.7 (app t, app ^3J = 19.8 Hz, 3-C$_6$F$_5$). IR (NaCl plates, Nujol mull, cm^{-1}): 2311 (w), 2281 (w), 1697 (s), 1643 (s), 1514 (s), 1349 (m), 1276 (m), 1247 (s), 1209 (w), 1188 (w), 1154 (w), 1085 (s, br), 1061 (m), 1005 (s), 981 (s), 776 (s), 757 (m), 746 (w), 684 (m), 662 (m). Anal. Found (calcd for C$_{42}$H$_{39}$BF$_{20}$N$_6$Ti): C, 47.6 (47.3); H, 3.8 (3.7); N, 7.5 (7.9).

[Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$){NCMe(CH$_2$SiMe$_3$)}(NCMe)][BAr^F$_4$] (9-BAr^F$_4$). To a solution of Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)(CH$_2$SiMe$_3$)$_2$ (**4**; 50 mg, 0.108 mmol) in CH$_2$Cl$_2$ (2 mL) was added [Ph$_3$C][BAr^F$_4$] (99 mg, 0.108 mmol) in CH$_2$Cl$_2$ (2 mL). After 5 min MeCN (12.1 μL, 0.237 mmol) was added. The solution was heated to 40 °C for 15 min, during which time the solution changed from orange to yellow. The solution was concentrated to approximately 1 mL, after which pentane (2 mL) was added, resulting in a yellow oil. The mother liquor was decanted away and the oil washed with pentane (3 × 2 mL). When reduced pressure was applied to the oil, a yellow powder was obtained. Yield: 74 mg (60%). ^{1}H NMR (CD$_2$Cl$_2$, 499.9 MHz, 293 K): 3.56 (1H, m, NCH$_2$), 3.41 (1H, m, NCH$_2$), 3.11 (3H, s, NMe), 3.09 (3H, s, NMe), 2.92−2.85 (3H, overlapping m, NCH$_2$), 2.75−2.71 (2H, overlapping m, NCH$_2$), 2.67 (1H, m, NCH$_2$), 2.60−2.45 (4H, overlapping m, NCH$_2$), 2.36 (3H, s, NCMe), 2.18 (3H, s, NMe), 1.88 (3H, s, NC*Me*(CH$_2$SiMe$_3$)), 1.80 (2H, br. s, C*H$_2$*SiMe$_3$), 1.03 (9H, s, NCMe$_3$), 0.16 (9H, s, SiMe$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 125.7 MHz, 293 K): 166.3 (N*C*Me(CH$_2$SiMe$_3$)), 149.2 (N*C*Me), 148.2 (br d, $^1J_{C-F}$ = 243 Hz, 2-C$_6$F$_5$), 138.3 (br d, $^1J_{C-F}$ = 245 Hz, 4-C$_6$F$_5$), 136.3 (br d, $^1J_{C-F}$ = 245 Hz, 3-C$_6$F$_5$), 66.5 (N*C*Me$_3$), 56.8 (NCH$_2$), 56.4 (NCH$_2$), 55.6 (NCH$_2$), 54.8 (NCH$_2$), 54.7 (NCH$_2$), 53.9 (NCH$_2$), 53.3 (NMe), 51.7 (NMe), 47.4 (NMe), 34.5 (*C*H$_2$SiMe$_3$), 31.8 (NC*Me*$_3$), 28.5 (NC*Me*(CH$_2$SiMe$_3$)), 2.5 (NC*Me*), −0.7 (SiMe$_3$). ^{19}F NMR (CD$_2$Cl$_2$, 282.4 MHz, 293 K): −133.5 (d, ^3J = 10.6, 2-C$_6$F$_5$), −164.0 (t, ^3J = 19.6 Hz, 4-C$_6$F$_5$), −167.9 (app t, app ^3J = 18.1 Hz, 3-C$_6$F$_5$). ^{29}Si NMR (HMQC ^{1}H-observed, 299.9 MHz, 293 K): 0.1 (CH$_2$SiMe$_3$). IR (NaCl plates, Nujol mull, cm^{-1}): 2313 (w), 2285 (w), 1667 (s), 1643 (m), 1514 (s), 1351 (w), 1275 (m), 1241 (s), 1206 (w), 1087 (s), 1005 (m), 980 (s), 841 (m), 775 (s), 757 (m), 726 (w), 684 (m), 662 (m). Anal. Found (calcd for C$_{45}$H$_{47}$BF$_{20}$N$_6$SiTi): C, 47.4 (47.5); H, 4.2 (4.2); N, 6.8 (7.4).

[Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$){N(H)CMeCHCMeN(H)}][BAr^F$_4$] (10-BAr^F$_4$). [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)(NCMe$_2$)(NCMe)][BAr^F$_4$] (**8-BAr^F$_4$**; 20.0 mg, 0.019 mmol) was dissolved in CD$_2$Cl$_2$ (0.75 mL). The reaction was monitored by ^{1}H NMR spectroscopy. After 7 weeks the ^{1}H NMR spectrum corresponded to pure **10$^+$**. The volatiles were evaporated under reduced pressure to give **10-BAr^F$_4$** as an orange powder. Yield: 18.5 mg (93%). ^{1}H NMR (CD$_2$Cl$_2$, 499.9 MHz, 293 K): 6.41 (2H, br s, NH), 4.92 (1H, t, ^4J = 1.9 Hz, {N(H)C(Me)}$_2$C*H*), 3.78 (2H, m, CH$_2$), 3.18 (6H, s, NMe *cis*), 3.11 (2H, m, CH$_2$), 2.82 (2H, m, CH$_2$), 2.75 (2H, m, CH$_2$), 2.48 (2H, m, CH$_2$), 2.35 (2H, m, CH$_2$), 2.17 (6H, s, N(H)C*Me*), 1.81 (3H, s, NMe *trans*), 0.88 (9H, s, NCMe$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 293 K): 170.1 (N(H)*C*Me), 148.5 (br d, $^1J_{C-F}$ = 240 Hz, 2-C$_6$F$_5$), 138.6 (br d, $^1J_{C-F}$ = 246 Hz, 4-C$_6$F$_5$), 136.6 (br d, $^1J_{C-F}$ = 246 Hz, 3-C$_6$F$_5$), 96.4 ({N(H)C(Me)}$_2$*C*H), 69.2 (N*C*Me$_3$), 56.3 (CH$_2$), 56.1 (CH$_2$), 53.0 (CH$_2$), 52.4 (NMe *cis*), 47.5 (NMe *trans*), 30.9 (NC*Me*$_3$), 28.2 (N(H)C*Me*). ^{19}F NMR (CD$_2$Cl$_2$, 282.4 MHz, 293 K): −133.5 (d, ^3J = 10.6, 2-C$_6$F$_5$), −164.0 (t, ^3J = 19.6 Hz, 4-C$_6$F$_5$), −167.9 (app t, app ^3J = 18.1 Hz, 3-C$_6$F$_5$). IR (NaCl plates, Nujol mull, cm^{-1}): 3329 (w), 1643 (m), 1552 (m), 1514 (s), 1299 (m), 1276 (m), 1243 (m), 1087 (s), 980 (s), 847 (w), 775 (m), 757 (m), 684 (m), 662 (m). Anal. Found (calcd for C$_{42}$H$_{39}$BF$_{20}$N$_6$Ti): C, 47.2 (47.3); H, 3.6 (3.7); N, 7.7 (7.9).

[Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$){MeC(N^{i}Pr)$_2$}][BAr^F$_4$] (11-BAr^F$_4$). To a stirred solution of Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Me$_2$ (**3**; 100 mg, 0.312 mmol) in C$_6$H$_5$Cl (5 mL) was added [Ph$_3$C][B(C$_6$F$_5$)$_4$] (288 mg, 0.312 mmol) in C$_6$H$_5$Cl (5 mL) to give a bright orange solution. After 5 min ^{i}PrNCN^{i}Pr (48.9 μL, 0.312 mmol) was added to give a pink solution. After 1 h the dark orange solution was concentrated to approximately 5 mL and then pentane (10 mL) was added slowly. The supernatant was decanted away from the resulting purple oil, which was dried in vacuo. The resulting pink powder was filtered off, washed with pentane (2 × 5 mL), and dried in vacuo. Yield: 199 mg (57%). Diffraction-quality single crystals were obtained by careful layering of a CH_2Cl_2 solution with hexane. ^{1}H NMR (CD_2Cl_2, 299.9 MHz, 293 K): 4.02 (2H, app sept, app ^3J = 6.8 Hz, C*H*Me$_2$), 3.83 (2H, m, CH_2), 3.22 (6H, s, NMe *cis*), 3.19 (2H, m, CH_2), 2.86 (4H, overlapping m, CH_2), 2.59 (2H, m, CH_2), 2.46 (2H, m, CH_2), 2.26 (3H, s, C*Me*), 2.10 (3H, s, NMe *trans*), 1.42 (6H, d, ^3J = 6.8 Hz, CH*Me*$_2$), 1.29 (6H, d, ^3J = 6.8 Hz, CH*Me*$_2$), 1.01 (9H, s, $NCMe_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz, 293 K): 167.2 (*C*Me), 148.5 (br d, $^1J_{C-F}$ = 238 Hz, 2-C_6F_5), 138.6 (br d, $^1J_{C-F}$ = 247 Hz, 4-C_6F_5), 136.7 (br d, $^1J_{C-F}$ = 250 Hz, 3-C_6F_5), 70.1 (N*C*Me$_3$), 57.2 (CH_2), 56.2 (CH_2), 54.4 (CH_2), 52.2 (NMe *cis*), 49.8 (*C*HMe$_2$), 47.1 (NMe *trans*), 32.4 (NC*Me*$_3$), 25.5 (CH*Me*$_2$), 25.4 (CH*Me*$_2$), 14.3 (C*Me*). ^{19}F NMR (CD_2Cl_2, 282.1 MHz, 293 K): −133.5 (d, ^3J = 10.6 Hz, 2-C_6F_5), −164.0 (t, ^3J = 20.4 Hz, 4-C_6F_5), −167.9 (app t, app ^3J = 18.1 Hz, 3-C_6F_5). IR (NaCl plates, Nujol mull, cm^{-1}): 1643 (m), 1514 (s), 1277 (m), 1229 (w), 1208 (w), 1005 (m), 982 (s), 776 (m), 757 (m), 684 (m), 662 (m). ES$^+$MS (MeCN): *m/z* 431.5 (2%) [M]$^+$, 143.1 (100%) [^{i}PrNHCMeNH^{i}Pr]$^+$. Anal. Found (calcd for $C_{45}H_{47}BF_{20}N_6Ti$): C, 48.5 (48.7); H, 4.3 (4.3); N, 7.4 (7.6).

[Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$){MeC(NTol)$_2$}][BAr^F$_4$] (12-BAr^F$_4$). To a solution of Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Me$_2$ (**3**; 50 mg, 0.156 mmol) in C_6H_5Cl (2 mL) was added [Ph$_3$C][BAr^F$_4$] (144 mg, 0.156 mmol) in C_6H_5Cl (2 mL) to give a bright orange solution. After 5 min *p*-tolylcarbodiimide (35 mg, 0.156 mmol) was added to give a pink solution. The solution was concentrated to approximately 1 mL, and then pentane (4 mL) was added with stirring to give a pink oil. The supernatant was decanted and the oil washed with pentane (3 × 2 mL). When reduced pressure was applied to the oil, a pink powder was obtained. Yield: 108 mg (57%). ^{1}H NMR (CD_2Cl_2, 299.9 MHz, 293 K): 7.22 (4H, d, ^3J = 8.1 Hz, 3-C_6H_4Me), 7.04 (4H, d, ^3J = 8.1 Hz, 2-C_6H_4Me), 3.92 (2H, m, CH_2), 3.23 (2H, m, CH_2), 3.07 (6H, s, NMe *cis*), 2.80 (2H, m, CH_2), 2.65−2.53 (4H, overlapping m, CH_2), 2.35 (6H, s, Ph*Me*), 2.33 (2H, m, CH_2), 2.32 (3H, s, NMe *trans*), 2.05 (3H, s, N$_2$CMe), 1.17 (9H, s, $NCMe_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz, 293 K): 166.2 (N$_2$*C*Me), 148.5 (br d, $^1J_{C-F}$ = 238 Hz, 2-C_6F_5), 144.4 (1-C_6H_4Me), 138.6 (br d, $^1J_{C-F}$ = 247 Hz, 4-C_6F_5), 136.6 (br d, $^1J_{C-F}$ = 250 Hz, 3-C_6F_5), 134.4 (4-C_6H_4Me), 130.5 (3-C_6H_4Me), 124.4 (2-C_6H_4Me), 70.6 (N*C*Me$_3$), 56.4 (CH_2), 56.3 (CH_2), 53.9 (CH_2), 51.6 (NMe *cis*), 47.3 (NMe *trans*), 32.5 (NC*Me*$_3$), 20.9 (Ph*Me*), 14.6 (N$_2$C*Me*). ^{19}F NMR (CD_2Cl_2, 282.1 MHz, 293 K): −133.5 (d, ^3J = 10.6 Hz, 2-C_6F_5), −164.0 (t, ^3J = 20.4 Hz, 4-C_6F_5), −167.9 (app t, app ^3J = 18.1 Hz, 3-C_6F_5). IR (NaCl plates, Nujol mull, cm^{-1}): 1643 (m), 1513 (s), 1413 (s), 1275 (m), 1231 (m), 1087 (s), 1002 (m), 980 (s), 853 (w), 804 (w), 775 (m), 756 (m), 745 (w), 684 (m), 662 (m). Anal. Found (calcd for $C_{53}H_{47}BF_{20}N_6Ti$): C, 53.1 (52.8); H, 4.0 (3.9); N, 6.5 (7.0).

[Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$){OC(Me)N^{t}Bu}][BAr^F$_4$] (13-BAr^F$_4$). To a solution of Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Me$_2$ (**3**; 50 mg, 0.156 mmol) in C_6H_5Cl (2 mL) was added [Ph$_3$C][BAr^F$_4$] (144 mg, 0.156 mmol) in C_6H_5Cl (2 mL) to give a bright orange solution. After 5 min ^{t}BuNCO (17.8 μL, 0.156 mmol) was added to give a red solution. The solution was concentrated to approximately 1 mL, and then pentane (4 mL) was added with stirring to give a red oil. The supernatant was decanted and the oil washed with pentane (3 × 2 mL). When reduced pressure was applied to the oil, a pink powder was obtained. Yield: 81 mg (48%). ^{1}H NMR (CD_2Cl_2, 299.9 MHz, 293 K): 4.21 (1H, m, CH_2), 3.68 (1H, m, CH_2), 3.37−2.95 (4H, overlapping m, CH_2), 3.30 (3H, s, NMe), 3.08 (3H, s, NMe), 2.83−2.27 (6H, overlapping m, CH_2), 2.30 (3H, s, CMe), 2.04 (3H, s, NMe), 1.51 (9H, s, CNCMe$_3$), 1.01 (9H, s, Ti═NCMe$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz, 293 K): 175.5 (*C*Me), 148.5 (br d, $^1J_{C-F}$ = 238 Hz, 2-C_6F_5), 138.6 (br d, $^1J_{C-F}$ = 247 Hz, 4-C_6F_5), 136.7 (br d, $^1J_{C-F}$ = 250 Hz, 3-C_6F_5), 70.0 (Ti═N*C*Me$_3$), 57.4 (CH_2), 56.6 (CH_2), 55.4 (CH_2), 55.3 (CH_2), 55.1 (CH_2), 53.6 (CN*C*Me$_3$), 53.3 (CH_2), 52.7 (NMe), 51.3 (NMe), 47.5 (NMe), 31.7 (Ti═NC*Me*$_3$), 31.6 (CNC*Me*$_3$), 21.6 (C*Me*). ^{19}F NMR (CD_2Cl_2, 282.1 MHz, 293 K): −133.5 (d, ^3J = 10.6 Hz, 2-C_6F_5), −164.0 (t, ^3J = 20.4 Hz, 4-C_6F_5), −167.9 (app t, app ^3J = 18.1 Hz, 3-C_6F_5). IR (NaCl plates, Nujol mull, cm^{-1}): 1643 (m), 1621 (m), 1514 (s), 1298 (w), 1275 (m), 1237 (w), 1209 (w), 1087 (s), 1004 (m), 979 (s), 909 (w), 775 (m), 756 (m), 724 (w), 684 (m), 662 (m). Anal. Found (calcd for $C_{43}H_{42}BF_{20}N_5OTi$): C, 47.2 (47.7); H, 3.9 (3.9); N, 6.0 (6.5).

[Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$){Me$_3$SiCH$_2$C(N^{i}Pr)$_2$}][BAr^F$_4$] (14-BAr^F$_4$). To a stirred solution of Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)(CH$_2$SiMe$_3$)$_2$ (**4**; 100 mg, 0.215 mmol) in CH_2Cl_2 (10 mL) was added ^{i}PrNCN^{i}Pr (34 μL, 0.215 mmol) followed by a solution of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (198 mg, 0.215 mmol) in CH_2Cl_2 (20 mL). After 1 h the dark orange solution was concentrated to approximately 3 mL, and then pentane (10 mL) was added dropwise. The supernatant was decanted away from the resulting purple oil, which was redissolved in Et$_2$O (10 mL); then the solution was concentrated. A microcrystalline pink solid formed on standing. This was filtered off and dried in vacuo. Yield: 78 mg (31%). Diffraction-quality single crystals were obtained by slow diffusion of pentane into a CH_2Cl_2 solution. ^{1}H NMR (CD_2Cl_2, 499.9 MHz, 293 K): 3.96 (2H, app sept, app ^3J = 6.6 Hz, C*H*Me$_2$), 3.86 (2H, m, NCH$_2$), 3.26 (6H, s, NMe *cis*), 3.18 (2H, m, NCH$_2$), 2.98 (2H, m, NCH$_2$), 2.86 (2H, m, NCH$_2$), 2.65−2.50 (4H, overlapping m, NCH$_2$), 2.25 (2H, s, C*H*$_2$SiMe$_3$), 2.12 (3H, s, NMe *trans*), 1.41 (6H, d, ^3J = 6.6 Hz, CH*Me*$_2$), 1.21 (6H, d, ^3J = 6.6 Hz, CH*Me*$_2$), 1.01 (9H, s, $NCMe_3$), 0.16 (9H, s, SiMe$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz, 293 K): 168.5 (*C*CH$_2$SiMe$_3$), 148.5 (br d, $^1J_{C-F}$ = 238 Hz, 2-C_6F_5), 138.6 (br d, $^1J_{C-F}$ = 247 Hz, 4-C_6F_5), 136.7 (br d, $^1J_{C-F}$ = 250 Hz, 3-C_6F_5), 70.8 (N*C*Me$_3$), 57.5 (NCH$_2$), 56.6 (NCH$_2$), 54.2 (NCH$_2$), 52.4 (NMe *cis*), 50.4 (*C*HMe$_2$), 47.2 (NMe *trans*), 32.7 (NC*Me*$_3$), 26.4 (CH*Me*$_2$), 25.1 (CH*Me*$_2$), 17.1 (C*H*$_2$SiMe$_3$), −0.1 (Si*Me*$_3$). ^{19}F NMR (CD_2Cl_2, 282.1 MHz, 293 K): −133.5 (d, ^3J = 10.6 Hz, 2-C_6F_5), −164.0 (t, ^3J = 20.4 Hz, 4-C_6F_5), −167.9 (app t, app ^3J = 18.1 Hz, 3-C_6F_5). ^{29}Si NMR (HMQC ^{1}H-observed, CD_2Cl_2, 299.9 MHz, 293 K): 2.1 (CH$_2$SiMe$_3$). IR (NaCl plates, Nujol mull, cm^{-1}): 1642 (m), 1513 (s), 1204 (w), 979 (s), 775 (w), 757 (w), 683 (w), 663 (m). ES$^+$MS (MeCN): *m/z* 503.6 (12%) [M]$^+$, 215.2 (100%) [^{i}PrNHC(CH$_2$SiMe$_3$)NH^{i}Pr]$^+$, 172.2 (13%) [Me$_3$[9]aneN$_3$H]$^+$. Anal. Found (calcd for $C_{48}H_{55}BF_{20}N_6SiTi$): C, 48.9 (48.8); H, 4.8 (4.7); N, 7.2 (7.1).

[Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$){PhCC(Ph)Me}][BAr^F$_4$] (15-BAr^F$_4$). To a solution of Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Me$_2$ (**3**; 50 mg, 0.156 mmol) in C_6H_5Cl (2 mL) was added [Ph$_3$C][BAr^F$_4$] (144 mg, 0.156 mmol) in C_6H_5Cl (2 mL) to give a bright orange solution. After 5 min PhCCPh (28 mg, 0.156 mmol) was added. The reaction mixture was stirred for 1 h, during which time it darkened in color. The deep red solution was concentrated to approximately 1 mL, and then pentane (4 mL) was added with stirring to give an orange-brown oil. The supernatant was decanted and the oil washed with pentane (3 × 2 mL). When reduced pressure was applied to the oil, a dark orange powder was obtained. Yield: 125 mg (69%). ^{1}H NMR (CD_2Cl_2, 499.9 MHz, 233 K): 7.40−7.00 (10H, overlapping m, C_6H_5), 4.05 (1H, m, CH_2), 3.99 (1H, m, CH_2), 3.35−2.95 (3H, overlapping m, CH_2), 3.21 (3H, s, NMe), 3.08 (3H, s, NMe), 2.90−2.70 (4H, overlapping m, CH_2), 2.55−2.45 (3H, overlapping m, CH_2), 2.19 (3H, s, NMe), 2.12 (3H, s, C*Me*(Ph)), 1.20 (9H, s, $NCMe_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz, 233 K): 192.2 (TiC), 148.2 (br d, $^1J_{C-F}$ = 243 Hz, 2-C_6F_5), 143.5 (1-C_6H_5), 142.4 (1-C_6H_5), 138.3 (br d, $^1J_{C-F}$ = 245 Hz, 4-C_6F_5), 136.3 (br d, $^1J_{C-F}$ = 245 Hz, 3-C_6F_5), 133.7 (*C*Me(Ph)), 130.0 (2 or 3-C_6H_5), 128.1 (2 or 3-C_6H_5), 127.8 (2 or 3-C_6H_5), 126.6 (2 or 3-C_6H_5), 125.9 (4-C_6H_5), 125.4 (4-C_6H_5), 70.6 (N*C*Me$_3$), 55.3 (CH_2), 55.2 (CH_2), 54.5 (2 × CH_2), 54.3 (CH_2), 54.0 (CH_2), 52.9 (NMe), 52.4 (NMe), 48.6 (NMe), 31.1 (NC*Me*$_3$), 24.0 (C*Me*(Ph)). ^{19}F NMR (CD_2Cl_2, 282.1

MHz, 233 K): −133.5 (d, ^3J = 10.6 Hz, 2-C$_6$F$_5$), −164.0 (t, ^3J = 20.4 Hz, 4-C$_6$F$_5$), −167.9 (app t, ^3J = 18.1 Hz, 3-C$_6$F$_5$). IR (NaCl plates, Nujol mull, cm^{-1}): 1643 (s), 1593 (w), 1563 (w), 1514 (s), 1297 (m), 1275 (s), 1233 (s), 1210 (m), 1156 (w), 1086 (s), 1023 (m), 979 (s), 909 (w), 775 (s), 756 (s), 743 (s), 702 (s), 685 (s), 662 (s). Anal. Found (calcd for C$_{52}$H$_{43}$BF$_{20}$N$_4$Ti): C, 53.7 (53.7); H, 4.0 (3.7); N, 4.5 (4.8).

[Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)(Me$_3$SiCCPhMe)][BAr$^F{}_4$] (16-BAr$^F{}_4$). To a solution of Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Me$_2$ (**3**; 50 mg, 0.156 mmol) and Me$_3$SiCCPh (30.7 μL, 0.156 mmol) in CH$_2$Cl$_2$ (1 mL) at −35 °C was added a solution of [Ph$_3$C][BAr$^F{}_4$] (144 mg, 0.156 mmol) in CH$_2$Cl$_2$ (1 mL). The resulting deep red solution was immediately cooled to −78 °C, and then hexane (4 mL) was added with stirring to give an orange oil. The supernatant was decanted and the oil washed with hexane (3 × 2 mL). When reduced pressure was applied to the oil, an orange powder was obtained which contained 0.5 equiv of hexane per titanium by ^{1}H NMR. Yield: 147 mg (78%). ^{1}H NMR (CD$_2$Cl$_2$, 299.9 MHz, 233 K): 7.31 (2H, app t, app ^3J = 8.2 Hz, 3-C$_6$H$_5$), 7.24 (1H, t, ^3J = 7.3 Hz, 4-C$_6$H$_5$), 7.15 (2H, d, ^3J = 8.2 Hz, 2-C$_6$H$_5$), 4.10 (1H, m, CH$_2$), 3.84 (1H, m, CH$_2$), 3.40−2.74 (8H, overlapping m, CH$_2$), 3.15 (3H, s, NMe), 3.03 (3H, s, NMe), 2.68−2.44 (2H, overlapping m, CH$_2$), 2.44 (3H, s, NMe), 1.82 (3H, s, C*Me*(Ph)), 1.13 (9H, s, NCMe$_3$), −0.14 (9H, s, SiMe$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75.5 MHz, 233 K): 205.9 (TiC), 148.5 (br d, $^1J_{C-F}$ = 241 Hz, 2-C$_6$F$_5$), 147.4 (1-C$_6$H$_5$), 143.9 (*C*Me(Ph)), 138.6 (br d, $^1J_{C-F}$ = 247 Hz, 4-C$_6$F$_5$), 136.7 (br d, $^1J_{C-F}$ = 250 Hz, 3-C$_6$F$_5$), 128.0 (3-C$_6$H$_5$), 127.1 (2-C$_6$H$_5$), 126.5 (4-C$_6$H$_5$), 70.3 (N*C*Me$_3$), 55.9 (CH$_2$), 55.3 (CH$_2$), 54.7 (CH$_2$), 54.2 (CH$_2$), 54.1 (2 × CH$_2$), 52.5 (NMe), 52.2 (NMe), 50.1 (NMe), 31.0 (NC*Me*$_3$), 21.3 (C*Me*(Ph)), 2.4 (SiMe$_3$). ^{19}F NMR (CD$_2$Cl$_2$, 282.1 MHz, 233 K): −133.5 (d, ^3J = 10.6 Hz, 2-C$_6$F$_5$), −164.0 (t, ^3J = 20.4 Hz, 4-C$_6$F$_5$), −167.9 (app t, ^3J = 18.1 Hz, 3-C$_6$F$_5$). ^{29}Si NMR (HMQC ^{1}H-observed, CD$_2$Cl$_2$, 299.9 MHz, 233 K): −16.8 (SiMe$_3$). IR (NaCl plates, Nujol mull, cm^{-1}): 1643 (s), 1597 (w), 1514 (s), 1297 (w), 1275 (s), 1235 (m), 1087 (s), 980 (s), 853 (m), 775 (s), 757 (s), 726 (w), 703 (w), 684 (m), 662 (m). Anal. Found (calcd for C$_{49}$H$_{47}$BF$_{20}$N$_4$SiTi·0.5C$_6$H$_{14}$): C, 51.8 (52.0); H, 4.6 (4.5); N, 4.6 (4.7).

NMR-Tube-Scale Synthesis of [Cp$_2$Ti(Me$_3$SiCCPhMe)][BAr$^F{}_4$] (17-BAr$^F{}_4$). To a solution of [Cp$_2$TiMe][BAr$^F{}_4$] {generated in situ from Cp$_2$TiMe$_2$ (7.8 mg, 0.038 mmol) and [Ph$_3$C][BAr$^F{}_4$] (35.0 mg, 0.038 mmol)} in C$_6$D$_5$Br (0.75 mL) was added Me$_3$SiCCPh (7.4 μL, 0.038 mmol). After 10 min the ^{1}H NMR spectrum showed quantitative conversion to **17-BAr$^F{}_4$**. ^{1}H NMR (C$_6$D$_5$Br, 299.9 MHz, 293 K): 7.15−6.90 (3- and 4-C$_6$H$_5$, obscured by side-product resonances), 6.73 (2H, d, ^3J = 6.5 Hz, 2-C$_6$H$_5$), 5.74 (10H, s, Cp), 1.26 (3H, s, $^1J_{C-H}$ = 128 Hz, TiCC*Me*), −0.94 (9H, s, SiMe$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_5$Br, 75.4 MHz, 293 K): 251.0 (TiC), 157.5 (TiC*C*), 148.8 (br d, $^1J_{C-F}$ = 239 Hz, 2-C$_6$F$_5$), 142.3 (1-C$_6$H$_5$), 138.6 (br d, $^1J_{C-F}$ = 251 Hz, 4-C$_6$F$_5$), 136.7 (br d, $^1J_{C-F}$ = 246 Hz, 3-C$_6$F$_5$), 129.0 (3-C$_6$H$_5$), 128.1 (4-C$_6$H$_5$), 126.7 (2-C$_6$H$_5$), 115.3 (Cp), 29.9 (TiCC*Me*), 3.3 (SiMe$_3$). ^{19}F NMR (C$_6$D$_5$Br, 282.1 MHz, 293 K): −131.8 (d, ^3J = 10.6 Hz, 2-C$_6$F$_5$), −161.8 (t, ^3J = 21.2 Hz, 4-C$_6$F$_5$), −165.8 (app t, app ^3J = 18.1 Hz, 3-C$_6$F$_5$). ^{29}Si NMR (HMQC ^{1}H-observed, C$_6$D$_5$Br, 299.9 MHz, 293 K): −54.9 (SiMe$_3$).

[Ti{^{t}BuNC(H)CSiMe$_3$}(Me$_3$[9]aneN$_3$)Me][BAr$^F{}_4$] (18-BAr$^F{}_4$). To a solution of Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Me$_2$ (**3**; 50 mg, 0.156 mmol) and Me$_3$SiCCH (22 μL, 0.156 mmol) in CH$_2$Cl$_2$ (1 mL) at −35 °C was added a solution of [Ph$_3$C][BAr$^F{}_4$] (144 mg, 0.156 mmol) in CH$_2$Cl$_2$ (1 mL). The resulting deep orange solution was immediately cooled to −78 °C, then hexane (4 mL) was added with stirring to give an orange oil. The supernatant was decanted and the oil washed with hexane (3 × 2 mL). When reduced pressure was applied to the oil, an orange powder was obtained which contained 1 equiv of hexane per titanium by ^{1}H NMR. Yield: 100 mg (55%). ^{1}H NMR (CD$_2$Cl$_2$, 299.9 MHz, 213 K): 11.38 (1H, s, C*H*(N^{t}Bu)), 3.45−3.30 (2H, overlapping m, CH$_2$), 3.38 (3H, s, NMe), 3.24−2.87 (5H, overlapping m, CH$_2$), 2.87 (3H, s, NMe), 2.70−2.54 (3H, overlapping m, CH$_2$), 2.51−2.38 (2H, overlapping m, CH$_2$), 1.84 (3H, s, NMe), 1.57 (9H, s, NCMe$_3$), 0.19 (9H, s, SiMe$_3$), −0.51 (3H, s, TiMe). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75.5 MHz, 213 K): 240.6 (Ti*C*(SiMe$_3$)), 160.5 (*C*H(N^{t}Bu)), 148.5 (br d, $^1J_{C-F}$ = 241 Hz, 2-C$_6$F$_5$), 138.6 (br d, $^1J_{C-F}$ = 247 Hz, 4-C$_6$F$_5$), 136.7 (br d, $^1J_{C-F}$ = 250 Hz, 3-C$_6$F$_5$), 64.0 (N*C*Me$_3$), 56.1 (CH$_2$), 55.3 (CH$_2$), 55.2 (CH$_2$), 57.7 (CH$_2$), 56.8 (CH$_2$), 56.2 (CH$_2$), 52.4 (NMe), 50.7 (NMe), 50.1 (NMe), 38.6 (TiMe), 30.8 (NC*Me*$_3$), 0.0 (SiMe$_3$). ^{19}F NMR (CD$_2$Cl$_2$, 282.1 MHz, 213 K): −133.5 (d, ^3J = 10.6 Hz, 2-C$_6$F$_5$), −164.0 (t, ^3J = 20.4 Hz, 4-C$_6$F$_5$), −167.9 (app t, ^3J = 18.1 Hz, 3-C$_6$F$_5$). ^{29}Si NMR (HMQC ^{1}H-observed, CD$_2$Cl$_2$, 299.9 MHz, 213 K): −9.7 (SiMe$_3$). IR (NaCl plates, Nujol mull, cm^{-1}): 1643 (s), 1513 (s), 1412 (m), 1296 (m), 1275 (s), 1253 (m), 1201 (s), 1156 (w), 1085 (s), 978 (s), 893 (w), 851 (s), 837 (s), 775 (s), 756 (s), 684 (s), 662 (s). Anal. Found (calcd for C$_{43}$H$_{43}$BF$_{20}$N$_4$SiTi·C$_6$H$_{14}$): C, 50.5 (50.4); H, 5.0 (4.9); N, 4.7 (4.8).

[Ti{^{t}BuNC(H)CPh}(Me$_3$[9]aneN$_3$)Me][BAr$^F{}_4$] (19-BAr$^F{}_4$). To a solution of Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Me$_2$ (**3**; 50 mg, 0.156 mmol) and PhCCH (17.1 μL, 0.156 mmol) in CH$_2$Cl$_2$ (1 mL) at −35 °C was added a solution of [Ph$_3$C][BAr$^F{}_4$] (144 mg, 0.156 mmol) in CH$_2$Cl$_2$ (1 mL). The resulting deep red solution was immediately cooled to −78 °C, and then hexane (4 mL) was added with stirring to give an orange oil. The supernatant was decanted and the oil washed with hexane (3 × 2 mL). When reduced pressure was applied to the oil, an orange powder was obtained which contained 1 equiv of hexane per titanium by ^{1}H NMR. Yield: 117 mg (64%). ^{1}H NMR (CD$_2$Cl$_2$, 299.9 MHz, 213 K): 11.07 (1H, s, C*H*(N^{t}Bu)), 7.33 (2H, app t, app ^3J = 7.6 Hz, 3-C$_6$H$_5$), 7.22 (1H, t, ^3J = 7.4 Hz, 4-C$_6$H$_5$), 7.02 (2H, d, ^3J = 7.1 Hz, 2-C$_6$H$_5$), 3.70−2.20 (12H, overlapping m, CH$_2$), 3.19 (3H, s, NMe), 3.04 (3H, s, NMe), 2.01 (3H, s, NMe), 1.57 (9H, s, NCMe$_3$), −0.29 (3H, s, TiMe). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75.5 MHz, 213 K): 224.3 (Ti*C*(Ph)), 158.4 (*C*H(N^{t}Bu)), 148.5 (br d, $^1J_{C-F}$ = 241 Hz, 2-C$_6$F$_5$), 145.0 (1-C$_6$H$_5$), 138.6 (br d, $^1J_{C-F}$ = 247 Hz, 4-C$_6$F$_5$), 136.7 (br d, $^1J_{C-F}$ = 250 Hz, 3-C$_6$F$_5$), 128.1 (3-C$_6$H$_5$), 127.6 (4-C$_6$H$_5$), 125.5 (2-C$_6$H$_5$), 63.7 (N*C*Me$_3$), 57.6 (CH$_2$), 57.0 (CH$_2$), 56.8 (CH$_2$), 56.7 (CH$_2$), 56.3(CH$_2$), 54.9 (CH$_2$), 51.6 (NMe), 50.8 (NMe), 50.3 (NMe), 39.9 (TiMe), 30.7 (NC*Me*$_3$). ^{19}F NMR (CD$_2$Cl$_2$, 282.1 MHz, 213 K): −133.5 (d, ^3J = 10.6 Hz, 2-C$_6$F$_5$), −164.0 (t, ^3J = 20.4 Hz, 4-C$_6$F$_5$), −167.9 (app t, ^3J = 18.1 Hz, 3-C$_6$F$_5$). IR (NaCl plates, Nujol mull, cm^{-1}): 1643 (s), 1593 (m), 1514 (s), 1275 (s), 1199 (s), 1087 (s), 979 (s), 893 (w), 757 (s), 726 (w), 700 (m), 684 (s), 662 (s). Anal. Found (calcd for C$_{46}$H$_{39}$BF$_{20}$N$_4$Ti·C$_6$H$_{14}$): C, 53.1 (53.3); H, 4.7 (4.6); N, 4.8 (4.8).

[Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)(^{t}BuNCO)Cl][BAr$^F{}_4$] (20-BAr$^F{}_4$). To a solution of Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Cl(Me) (50 mg, 0.147 mmol) in CH$_2$Cl$_2$ (1 mL) was added a solution of [Ph$_3$C][BAr$^F{}_4$] (135 mg, 0.147 mmol) in CH$_2$Cl$_2$ (1 mL). To the resulting orange solution was added ^{t}BuNCO (16.8 μL, 0.147 mmol). Me$_3$SiOSiMe$_3$ (4 mL) was added with stirring to give a yellow solid, which was filtered off, washed with Me$_3$SiOSiMe$_3$ (3 × 2 mL), and dried in vacuo. The solid contained 0.5 equiv of Me$_3$SiOSiMe$_3$ by ^{1}H NMR. Yield: 132 mg (76%). ^{1}H NMR (CD$_2$Cl$_2$, 499.9 MHz, 233 K): 3.76 (1H, m, CH$_2$), 3.61 (1H, m, CH$_2$), 3.30−2.90 (5H, overlapping m, CH$_2$), 3.18 (3H, s, NMe), 3.13 (3H, s, NMe), 2.86−2.56 (3H, overlapping m, CH$_2$), 2.45−2.35 (2H, overlapping m, CH$_2$), 2.22 (3H, s, NMe), 1.51 (9H, s, C=NCMe$_3$), 1.01 (9H, s, Ti=NCMe$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75.5 MHz, 233 K): 148.5 (br d, $^1J_{C-F}$ = 241 Hz, 2-C$_6$F$_5$), 138.6 (br d, $^1J_{C-F}$ = 247 Hz, 4-C$_6$F$_5$), 136.7 (br d, $^1J_{C-F}$ = 250 Hz, 3-C$_6$F$_5$), 70.9 (Ti=N*C*Me$_3$), 59.2 (C=N*C*Me$_3$), 56.4 (CH$_2$), 56.1 (CH$_2$), 55.6 (2 × CH$_2$), 53.3 (2 × CH$_2$), 53.1 (NMe), 52.3 (NMe), 46.7 (NMe), 30.1 (NC*Me*$_3$), 30.0 (NC*Me*$_3$). ^{19}F NMR (CD$_2$Cl$_2$, 282.1 MHz, 293 K): −133.5 (d, ^3J = 10.6 Hz, 2-C$_6$F$_5$), −164.0 (t, ^3J = 20.4 Hz, 4-C$_6$F$_5$), −167.9 (app t, ^3J = 18.1 Hz, 3-C$_6$F$_5$). IR (NaCl plates, Nujol mull, cm^{-1}): 2357 (s), 2258 (w), 1643 (m), 1514 (s), 1297 (w), 1276 (m), 1255 (w), 1238 (m), 1087 (s), 1063 (m), 1000 (m), 980 (s), 846 (m), 827 (w), 775 (m), 756 (m), 684 (m), 662 (m). Anal. Found (calcd for $C_{42}H_{39}BClF_{20}N_5OTi \cdot 0.5C_6H_{18}OSi_2$): C, 45.5 (45.6); H, 4.1 (4.1); N, 5.8 (5.9).

$[Ti(N^tBu)(Me_3[9]aneN_3)(^iPrNCN^iPr)Cl][BAr^F_4]$ (21-BAr^F_4). To a solution of $Ti(N^tBu)(Me_3[9]aneN_3)Cl(Me)$ (50 mg, 0.147 mmol) in CH_2Cl_2 (1 mL) was added a solution of $[Ph_3C][BAr^F_4]$ (135 mg, 0.147 mmol) in CH_2Cl_2 (1 mL). To the resulting orange solution was added $^iPrNCN^iPr$ (23.0 μL, 0.147 mmol). $Me_3SiOSiMe_3$ (4 mL) was added with stirring to give a yellow solid, which was filtered off, washed with $Me_3SiOSiMe_3$ (3 × 2 mL), and dried in vacuo. The solid contained 0.5 equiv of $Me_3SiOSiMe_3$ by ^1H NMR. Yield: 130 mg (73%). ^1H NMR (CD_2Cl_2, 499.9 MHz, 293 K): 4.33 (1H, sept., ^3J = 6.6 Hz, CHMe$_2$), 4.17 (1H, sept, ^3J = 6.6 Hz, CHMe$_2$), 3.82−3.72 (2H, overlapping m, CH_2), 3.29 (3H, s, NMe), 3.28 (3H, s, NMe), 3.25−3.14 (2H, overlapping m, CH_2), 3.10 (1H, m, CH_2), 3.03−2.92 (2H, overlapping m, CH_2), 2.90−2.80 (2H, overlapping m, CH_2), 2.75 (1H, m, CH_2), 2.56−2.48 (2H, overlapping m, CH_2), 2.85 (3H, s, NMe), 1.58 (3H, d, ^3J = 6.6 Hz, CHMe_2), 1.55 (3H, d, ^3J = 6.6 Hz, CHMe_2), 1.47 (3H, d, ^3J = 6.6 Hz, CHMe_2), 1.45 (3H, d, ^3J = 6.6 Hz, CHMe_2), 1.15 (9H, s, $NCMe_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.8 MHz, 293 K): 148.2 (br d, $^1J_{C-F}$ = 243 Hz, 2-C_6F_5), 138.3 (br d, $^1J_{C-F}$ = 245 Hz, 4-C_6F_5), 136.3 (br d, $^1J_{C-F}$ = 245 Hz, 3-C_6F_5), 72.0 (NCMe$_3$), 57.9 (CH_2), 57.8 (CHMe$_2$), 57.3 (CH_2), 56.7 (CH_2), 56.4 (CH_2), 55.2 (CH_2), 54.7 (CH_2), 54.5 (NMe), 53.0 (NMe), 52.1 (CHMe$_2$), 48.4 (NMe), 31.3 (NCMe_3), 24.3 (CHMe_2), 24.1 (CHMe_2), 23.7 (CHMe_2), 23.5 (CHMe_2). ^{19}F NMR (CD_2Cl_2, 282.1 MHz, 293 K): −133.5 (d, ^3J = 10.6 Hz, 2-C_6F_5), −164.0 (t, ^3J = 20.4 Hz, 4-C_6F_5), −167.9 (app t, ^3J = 18.1 Hz, 3-C_6F_5). IR (NaCl plates, Nujol mull, cm^{-1}): 2133 (s), 1643 (m), 1611 (w), 1514 (s), 1298 (w), 1276 (m), 1256 (m), 1233 (m), 1087 (s), 1001 (s), 980 (s), 892 (w), 847 (m), 775 (m), 756 (m), 726 (w), 684 (m), 662 (m). Anal. Found (calcd for $C_{44}H_{44}BClF_{20}N_6Ti \cdot 0.5C_6H_{18}OSi_2$): C, 46.5 (46.6); H, 4.3 (4.4); N, 6.9 (6.9).

$[Ti\{^tBuNC(H)CPh\}(Me_3[9]aneN_3)Cl][BAr^F_4]$ (22-BAr^F_4). To a solution of $Ti(N^tBu)(Me_3[9]aneN_3)Cl(Me)$ (50 mg, 0.147 mmol) in CH_2Cl_2 (1 mL) was added a solution of $[Ph_3C][BAr^F_4]$ (135 mg, 0.147 mmol) in CH_2Cl_2 (1 mL). To the resulting orange solution was added PhCCH (16.1 μL, 0.147 mmol) to give a deep red solution. Hexane (4 mL) was added with stirring to give a red-brown oil. The supernatant was decanted and the oil washed with hexane (3 × 2 mL). When reduced pressure was applied to the oil, an orange powder was obtained. Yield: 109 mg (67%). ^1H NMR (CD_2Cl_2, 499.9 MHz, 293 K): 11.68 (1H, s, CH(N^{t}Bu)), 7.41 (2H, app t, app ^3J = 7.8 Hz, 3-C_6H_5), 7.31 (1H, t, ^3J = 7.5 Hz, 4-C_6H_5), 7.06 (2H, d, ^3J = 8.2 Hz, 2-C_6H_5), 3.70 (1H, m, CH_2), 3.48 (1H, m, CH_2), 3.20−3.10 (3H, overlapping m, CH_2), 3.13 (3H, s, NMe), 3.09 (3H, s, NMe), 2.99−2.86 (4H, overlapping m, CH_2), 2.83−2.71 (3H, overlapping m, CH_2), 2.38 (3H, s, NMe), 1.62 (9H, s, $NCMe_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz, 293 K): 238.1 (TiC), 161.8 (CH(N^{t}Bu)), 148.5 (br d, $^1J_{C-F}$ = 241 Hz, 2-C_6F_5), 145.4 (1-C_6H_5), 138.6 (br d, $^1J_{C-F}$ = 247 Hz, 4-C_6F_5), 136.7 (br d, $^1J_{C-F}$ = 250 Hz, 3-C_6F_5), 129.0 (3-C_6H_5), 127.9 (4-C_6H_5), 126.2 (2-C_6H_5), 66.6 (NCMe$_3$), 58.4 (CH_2), 58.2 (CH_2), 57.7 (CH_2), 57.6 (CH_2), 57.5 (CH_2), 55.9 (CH_2), 53.8 (NMe), 52.7 (NMe), 51.4 (NMe), 31.3 (NCMe_3). ^{19}F NMR (CD_2Cl_2, 282.1 MHz, 293 K): −133.5 (d, ^3J = 10.6 Hz, 2-C_6F_5), −164.0 (t, ^3J = 20.4 Hz, 4-C_6F_5), −167.9 (app t, ^3J = 18.1 Hz, 3-C_6F_5). IR (NaCl plates, Nujol mull, cm^{-1}): 1643 (m), 1514 (s), 1275 (m), 1195 (w), 1156 (w), 1087 (s), 997 (m), 979 (s), 787 (m), 775 (m), 725 (w), 700 (w), 684 (m), 662 (m). Anal. Found (calcd for $C_{45}H_{36}BClF_{20}N_4Ti$): C, 48.8 (48.8); H, 3.3 (3.3); N, 4.9 (5.1).

$[Ti\{^tBuNC(H)CSiMe_3\}(Me_3[9]aneN_3)Cl][MeBAr^F_3]$ (23-$MeBAr^F_3$). To a solution of $Ti(N^tBu)(Me_3[9]aneN_3)Cl(Me)$ (30 mg, 0.088 mmol) in CH_2Cl_2 (0.5 mL) was added a solution of BAr^F_3 (45 mg, 0.088 mmol) in CH_2Cl_2 (0.5 mL). To the resulting light orange solution was added Me_3SiCCH (12.4 μL, 0.088 mmol) to give a deep red solution. The volatiles were removed under reduced pressure to initially yield an orange oil, but on prolonged pumping **23-$MeBAr^F_3$** was obtained as an orange powder. Yield: 50 mg (60%). ^1H NMR (CD_2Cl_2, 499.9 MHz, 293 K): 12.04 (1H, s, CH(N^{t}Bu)), 3.62−3.50 (2H, overlapping m, CH_2), 3.41 (1H, m, CH_2), 3.38 (3H, s, NMe), 3.21−2.65 (9H overlapping m, CH_2), 2.94 (3H, s, NMe), 2.18 (3H, s, NMe), 1.62 (9H, s, $NCMe_3$), 0.44 (3H, br. s, BMe), 0.26 (9H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz, 293 K): 261.1 (TiC), 162.8 (CH(N^{t}Bu)), 148.6 (br d, $^1J_{C-F}$ = 236 Hz, 2-C_6F_5), 137.7 (br d, $^1J_{C-F}$ = 249 Hz, 4-C_6F_5), 136.6 (br d, $^1J_{C-F}$ = 246 Hz, 3-C_6F_5), 67.1 (NCMe$_3$), 58.3 (CH_2), 58.2 (CH_2), 57.9 (CH_2), 57.8 (CH_2), 57.4 (CH_2), 55.5 (CH_2), 53.8 (NMe), 53.6 (NMe), 51.3 (NMe), 31.3 (NCMe_3), 0.6 ($SiMe_3$). ^{19}F NMR (CD_2Cl_2, 282.1 MHz, 293 K): −133.6 (d, ^3J = 21.2 Hz, 2-C_6F_5), −165.4 (t, ^3J = 19.6 Hz, 4-C_6F_5), −168.1 (app t, ^3J = 18.1 Hz, 3-C_6F_5). ^{29}Si NMR (HMQC ^1H-observed, CD_2Cl_2, 299.9 MHz, 293 K): −6.4 ($SiMe_3$). IR (NaCl plates, Nujol mull, cm^{-1}): 1641 (m), 1511 (s), 1297 (w), 1193 (m), 1157 (w), 1085 (s), 999 (m), 934 (m), 893 (w), 838 (m), 803 (m), 786 (m), 660 (w). Anal. Found (calcd for $C_{37}H_{43}BClF_{15}N_4SiTi$): C, 45.0 (46.7); H, 5.8 (4.6); N, 5.7 (5.9).

NMR-Tube-Scale Reaction of $[Ti(N^tBu)(Me_3[9]aneN_3)Cl]^+$ (7^+) with Ethylene. A solution of $[Ti(N^tBu)(Me_3[9]aneN_3)Cl]^+$ (7^+) (generated in situ from $Ti(N^tBu)(Me_3[9]aneN_3)Cl(Me)$ (7.0 mg, 0.021 mmol) and BAr^F_3 (10.5 mg, 0.021 mmol)) in CD_2Cl_2 (0.75 mL) was degassed by three freeze−pump−thaw cycles, and the headspace of the NMR tube was evacuated. The sample was then exposed to ethylene at 1.2 bar. A ^1H NMR spectrum recorded after 10 min showed resonances for **7-$MeBAr^F_3$** and a singlet at 5.40 ppm corresponding to ethylene. This was essentially unchanged after 16 h.

NMR-Tube-Scale Reaction of $[Ti(N^tBu)(Me_3[9]aneN_3)Cl]^+$ (7^+) with 1-Hexene and Styrene. To a solution of $[Ti(N^tBu)(Me_3[9]aneN_3)Cl]^+$ (7^+) (generated in situ from $Ti(N^tBu)(Me_3[9]aneN_3)Cl(Me)$ (7.0 mg, 0.021 mmol) and BAr^F_3 (10.5 mg, 0.021 mmol)) in CD_2Cl_2 (0.75 mL) was added 1-hexene (2.5 μL, 0.021 mmol). A ^1H NMR spectrum recorded after 10 min showed resonances for **7-$MeBAr^F_3$** and 1-hexene. This was unchanged after 16 h. An analogous result was obtained with styrene.

Crystal Structure Determination of $[Ti(N^tBu)(Me_3[9]aneN_3)(NCMe_2)(NCMe)][BAr^F_4]$ (8-BAr^F_4), $[Ti(N^tBu)(Me_3[9]aneN_3)\{N(H)CMeCHCMeN(H)\}][BAr^F_4] \cdot CH_2Cl_2$ (10-$BAr^F_4 \cdot CH_2Cl_2$), $[Ti(N^tBu)(Me_3[9]aneN_3)\{MeC(N^iPr)_2\}][BAr^F_4]$ (11-BAr^F_4), and $[Ti(N^tBu)(Me_3[9]aneN_3)\{Me_3SiCH_2C(N^iPr)_2\}][BAr^F_4]$ (14-BAr^F_4). Crystal data collection and processing parameters are given in Table 5. Crystals were mounted on a glass fiber using perfluoropolyether oil and cooled rapidly to 150 K under a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer. Intensity data were processed using the DENZO-SMN package.[128] The structures were solved using the direct-methods program SIR92,[129] which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[130] Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically. Further details are given in the CIF data (Supporting Information). Full listings of atomic coordinates, bond lengths and angles, and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre.

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Table 5. X-ray Data Collection and Processing Parameters for [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)(NCMe$_2$)(NCMe)][BAr$^F{}_4$] (8-BAr$^F{}_4$), [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$){N(H)CMeCHCMeN(H)}][BAr$^F{}_4$]·CH$_2$Cl$_2$ (10-BAr$^F{}_4$·CH$_2$Cl$_2$), [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$){MeC(N^{i}Pr)$_2$}][BAr$^F{}_4$] (11-BAr$^F{}_4$), and [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$){Me$_3$SiCH$_2$C(N^{i}Pr)$_2$}][BAr$^F{}_4$] (14-BAr$^F{}_4$)

	8-BAr$^F{}_4$	**10-BAr$^F{}_4$·CH$_2$Cl$_2$**	**11-BAr$^F{}_4$**	**14-BAr$^F{}_4$**
empirical formula	$C_{42}H_{39}BF_{20}N_6Ti$	$C_{43}H_{41}BCl_2F_{20}N_6Ti$	$C_{45}H_{47}BF_{20}N_6Ti$	$C_{48}H_{55}BF_{20}N_6SiTi$
fw	1066.48	1151.42	1110.58	1182.76
temp/K	150	150	150	150
wavelength/Å	0.710 73	0.710 73	0.710 73	0.710 73
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	11.6237(2)	12.3574(2)	19.1070(2)	11.9619(2)
b/Å	12.7345(3)	14.2186(2)	13.2045(2)	12.7619(2)
c/Å	17.5683(4)	14.5834(2)	20.4267(3)	17.9840(2)
α/deg	110.7643(8)	86.5110(6)	90	75.5723(5)
β/deg	100.4617(9)	85.6190(6)	113.4938(7)	80.1952(5)
γ/deg	102.2640(10)	74.5440(7)	90	86.9238(5)
V/Å^3	2280.25(9)	2460.30(6)	4726.40(11)	2619.78(7)
Z	2	2	4	2
d(calcd)/Mg m^{-3}	1.553	1.554	1.561	1.499
abs coeff/mm^{-1}	0.309	0.398	0.301	0.299
R indices ($I > 3\sigma(I)$)^a				
R1	0.0513	0.0506	0.0414	0.0402
wR2	0.0660	0.0632	0.0485	0.0476

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Computational Details. All the calculations have been performed with the Gaussian03 package[131] at the B3PW91 level.[132,133] The titanium atom was represented by the relativistic effective core potential (RECP) from the Stuttgart group (12 valence electrons) and its associated basis set,[134] augmented by an f polarization function ($\alpha = 0.869$).[135] The silicon atom was represented by RECP from the Stuttgart group and the associated basis set,[136] augmented by a d polarization function.[137] The remaining atoms (C, H, N, O) were represented by a 6-31G(d,p) basis set.[138] Full optimizations of geometry without any constraint were performed, followed by analytical computation of the Hessian matrix to confirm the nature of the located extrema as minima on the potential energy surface. NMR chemical shift and J_{CH} coupling constants were computed using the GIAO method[139,140] at the B3PW91 level. For the NMR parameters, all-electron calculations were considered where the basis set for Ti was the TZP basis set of Ahlrichs[141] and all the other atoms were described with the IGLO-II basis set.[142]

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Supporting Information Available: CIF files giving X-ray crystallographic data for the structure determinations of [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)(NCMe$_2$)(NCMe)][BAr$^F{}_4$](**8-BAr$^F{}_4$**)[Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$){N(H)CMeCHCMeN(H)})][BAr$^F{}_4$]·CH$_2$Cl$_2$ (**10-BAr$^F{}_4$·CH$_2$Cl$_2$**), [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$){MeC(N^{i}Pr)$_2$}][BAr$^F{}_4$] (**11-BAr$^F{}_4$**), and [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$){Me$_3$SiCH$_2$C(N^{i}Pr)$_2$}]-[BAr$^F{}_4$] (**14-BAr$^F{}_4$**) and text and tables giving the complete reference for Gaussian 03 and DFT computed Cartesian coordinates for the optimized molecules and their electronic energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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