

Synthesis, Structural Characterization, and Preliminary Reactivity Profile of a Series of Monocyclopentadienyl, Monoacetamidinate Titanium(III) Alkyl Complexes Bearing β -Hydrogens

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Alkylation of Cp*TiCl₂[N(i-Pr)C(Me)N(i-Pr)] (Cp* = η^5 -C₅Me₅) (1) with two equivalents of an alkyllithium reagent provided high yields of the thermally stable, crystalline, paramagnetic titanium(III) alkyl complexes of general structure Cp*Ti(R)[N(i-Pr)C(Me)N(i-Pr)] where R = Et (2), n-Bu (3), i-Bu (4), neopentyl (5), and *n*-hexyl (6). Solid-state structural characterization of compounds 2–5 by single-crystal X-ray analysis revealed the absence of α - or β -hydrogen agostic interactions between the metal center and the alkyl group R. Isocyanides (R'NC) undergo quantitative 1,1-insertion into the titanium–carbon bond of the alkyl group of 2–6 to provide high yields of the corresponding series of crystalline, paramagnetic Ti(III) η^2 -iminoacyl derivatives, Cp*Ti[η^2 -N(R')=CR)][N(i-Pr)C(Me)N(i-Pr)] (7–11, respectively), which were also structurally characterized by X-ray crystallography for compounds 7 and 9–11. Finally, compounds 3–5 were oxidized with PbCl₂ in diethyl ether to cleanly generate the respective Ti(IV) monochloro, monoalkyl complexes Cp*Ti(R)(Cl)[N(i-Pr)C(Me)N(i-Pr)] (12–14, respectively), the solid-state structures of which were also determined by single-crystal X-ray analyses.

Introduction

The organometallic chemistry of group 4 metal {M = Ti, Zr, and Hf} complexes incorporating formal M(III, d¹) centers with open-shell electronic configurations is, at present, still far less developed vis-à-vis the wealth of information now available regarding the structures, stabilities, and chemical reactivity associated with the corresponding M(II, d²) and M(IV, d⁰) formal oxidation states.¹⁻³ As the demand for new metal-catalyzed organic transformations that can be conducted with high efficiency and selectivity remains unabated, it is essential that this gap in knowledge be significantly narrowed. In this regard, the scientific record has remained largely silent on the synthesis, structural characterization, and chemical reactivity of molecularly discrete organometallic Ti(III) complexes

ever since the seminal contributions made by Teuben and coworkers⁴ over 20 years ago first introduced the bis(η^5 -pentamethylcyclopentadienyl), monoalkyl complexes, Cp*₂TiR (Cp* = η^5 -C₅Me₅), where R = Me (Ia), Et (Ib), n-Pr (Ic), CH₂Ph (Id), and Np (Np = CH₂CMe₃) (Ie). Unfortunately, due to the low thermal stabilities displayed in solution for Ib and Ic at ambient temperature as the result of a low activation barrier for rapid and reversible β -hydrogen transfer from the R group to the metal, the only solid-state structural information

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for this series of compounds that has been reported to date is for the derivative Ie, in which no β -hydrogens are present.^{4b} Indeed, to the best of our knowledge, to date, only *two* structurally characterized Ti(III) alkyl complexes bearing β -hydrogens have been reported in the literature, and in each case, the compound represented a single isolated example.⁵ In addition, while the Teuben group briefly explored the chemical reactivity of Ia and Ib, structural identification of the products of these reactions rested on vibrational spectroscopy and elemental analyses and not on solid-state molecular structures and geometric parameters acquired through single-crystal X-ray crystallography.

Over the past decade, we have established and documented the unique ability of the η^5 -cyclopentadienyl/ η^2 -amidinate (CpAm) ligand environment to support the synthesis and structural characterization of neutral and cationic, mid- to high-valent, second- and third-row group 4 {Zr and Hf} and group 5 {Ta} metal complexes bearing alkyl substituents that are (kinetically) stable toward both β -hydrogen and β -alkyl group transfer processes.^{6–8} Regarding first-row group 4 metal congeners, Mountford and co-workers⁹ have established the solid-state structures and solution chemistry of the mononuclear CpAm Ti(IV) imido complexes of general formula Cp*Ti(=NR)[N(R¹)C(R²)N(R³)]. Hagadorn and co-workers¹⁰

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further developed two novel classes of geometrically constrained bisamidinate ligands and employed these for investigating the syntheses and structures of dinuclear CpAm Ti(IV) and Ti(III) complexes. Finally, we have previously reported the syntheses and structural characterization of several derivatives of CpAm Ti(IV) dimethyl complexes of general formula (η^5 - C_5R_5)Ti(Me)₂[N(R¹)C(Me)N(R²)] (R = H and Me) that are conveniently prepared in high yield via carbodiimide insertion into a Ti–Me bond of preformed $(\eta^5$ -C₅R₅)Ti(Me)₃.¹¹ Herein, we now report the results of investigations that serve to extend the utility of the CpAm ligand set for accessing a new family of structurally characterized Ti(III) alkyl complexes bearing β -hydrogens of general structure Cp*Ti(R)[N(i-Pr)C(Me)N-(i-Pr)] that further includes a preliminary screening of chemical reactivity involving insertions of isocyanides, R'NC, into the titanium-carbon bond to form the corresponding series of Ti(III) η^2 -iminoacyl derivatives, Cp*Ti[η^2 -CR=NR'][N(i-Pr)-C(Me)N(i-Pr)], as well as PbCl₂-mediated chemical oxidation to provide the corresponding Ti(IV) chloro, alkyl complexes, Cp*Ti(R)(Cl)[N(i-Pr)C(Me)N(i-Pr)], in high yield. These findings serve as a complement to those reported by Teuben and co-workers for similar reactions involving Ia-Ie. In addition, since the solution chemistry of the new series of CpAm Ti(III) monoalkyl complexes appears to be completely devoid of β -hydrogen transfer processes, this report should prove useful in the further development of Ti(III)-based organometallic chemistry, including the design of molecularly discrete Ti(III) catalysts for the (stereoselective) coordination polymerization of styrene and α -olefins.^{3,8}

Results and Discussion

A. Synthesis and Structural Characterization of Cp*Ti(R)-[N(i-Pr)C(Me)N(i-Pr). Scheme 1 summarizes synthetic methodology that was employed in the present work.12 Succinctly, reaction of the CpAm Ti(IV) dichloride precursor Cp*Ti(Cl)2-[N(i-Pr)C(Me)N(i-Pr)] (1)¹³ with 2 equiv of an alkyllithium (RLi) reagent in diethyl ether (Et₂O) at ambient temperature provided the paramagnetic, dark purple products 2-6, which, except for the oily material obtained in the case of 6 where R =Hex, could be obtained in analytically pure form in high yield through recrystallization from pentane at -30 °C. Elemental (C, H, and N) analyses obtained for 2-5 proved to be fully consistent with the CpAm Ti(III) monoalkyl formulation that is depicted for these compounds in Scheme 1, and fortunately, in the case of 6, a crystalline product could be subsequently obtained from its reaction with 2,6-dimethylphenylisocyanide, the structural characterization of which also served to unequivocally establish the identity of this CpAm Ti(III) alkyl derivative (vide infra).

Given the paramagnetic nature of 2-6, ¹H NMR spectroscopy could not be used to establish with certainty the molecular structures of this series of compounds. Fortunately, however, this task could be accomplished through single-crystal X-ray analyses of 2-5, which yielded the solid-state molecular structures and selected geometric parameters that are presented in Figure 1 and Table 1, respectively.¹² From

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these data, it can be seen that all four compounds share a similar idealized C_s -symmetric piano-stool molecular geometry for the CpAmTiR ligand environment. Importantly, none of the solidstate structures show any evidence to support the existence of α - or β -hydrogen agostic interactions between the alkyl substituent and the metal center.¹⁴ The data in Table 1 also reveal that while most of the selected geometric parameters remain essentially invariant for the series of compounds, the Ti1-C19-C20 bond angle dramatically increases as the steric bulk of the alkyl substituent increases [cf. 116.73(19)° for 2, 119.2(6)° for 3, 120.15(10)° for 4, and 128.91(10)° for 5]. On the basis of this simple inspection, it can be concluded that the CpAm ligand environment about the metal is uniquely set up to position much of the steric bulk of the alkyl substituent "underneath" the η^2 -amidinate fragment, and an increase in nonbonded steric interactions that occurs between the alkyl substituent and the CpAm fragment is most readily accommodated through a single bond-angle distortion about the alkyl group α -carbon. Similar observations have been previously documented by us for neutral and cationic CpAm Zr(IV) and CpAm Hf(IV) complexes with large β -hydrogenbearing alkyl substituents, including t-Bu groups.^{6a,f} In the case of the isobutyl derivative 4, a small distortion away from an idealized tetrahedral geometry is observed for the β -carbon, as revealed by the sum of the bond angles C19– C20-C21, C19-C20-C22, and C21-C19-C22, which is \sim 333°, and this value can be compared to 327° expected for a tetravalent, tetracoordinate geometry vs 360° for trigonalcoplanar carbon. However, it can be reasonably concluded that the origin of this distortion is most likely the result of steric strain rather than being the manifestation of a secondarv β -hydrogen agostic interaction.^{6f}

B. Thermal Stability of of Cp*Ti(R)[N(i-Pr)C(Me)N(i-Pr)]. In the solid-state and hydrocarbon (pentane, benzene, and toluene) solutions, compounds 2-6 proved to be indefinitely stable at room temperature under an inert atmosphere of dinitrogen. These solutions were also shown to be thermally robust at elevated temperature for extended periods of time (e.g., 50 °C, 72 h), with no evidence for decomposition involving release of 1-alkenes being obtained by ¹H NMR spectroscopy. This high degree of thermal stability is in keeping with that reported by Stephen and co-workers^{5b} for the half-sandwich, β -diketiminato Ti(III) n-butyl derivative (η^5 -C₅H₅)Ti(n-Bu)[HC-(CMeNC₆H₃(i-Pr)₂)₂], as well as our own prior observations of significantly high barriers for β -hydrogen transfer (abstraction) processes within analogous neutral second- and thirdrow group 4 and 5 CpAm metal alkyl complexes.^{6,7} Finally, of potential interest with respect to possible mechanisms for 1-hexene production via early transition-metal-catalyzed selective ethene trimerization,¹⁵ no qualitative difference could be discerned between the thermal stability displayed by the n-butyl derivative **3** vs that of the n-hexyl analogue **6**, thereby suggesting the absence of any unique intra- or intermolecular pathways involving abstraction of more remote γ -, δ -, or ε hydrogen atoms within the longer *n*-alkyl chain of the latter.

C. Chemical Reactivity of Cp*Ti(R)[N(i-Pr)C(Me)N(i-Pr)]. i. 1,1-Migratory Insertion of R'NC. We have previously shown that cationic CpAm group 4 Zr(IV) and Hf(IV) alkyl complexes are highly active initiators for the living coordination polymerization of ethene, α -olefins, and α, ω -nonconjugated dienes.⁸ In contrast, compounds 2-6 were all found to be completely inert in solution toward 1,2- (or 2,1-) migratory insertion of alkenes and dienes into the titanium-carbon bond, including ethene, propene, 1,3-butadiene, 1,5-hexadiene, cyclopentene, norbornene, and styrene. On the other hand, with isocyanides R'NC (R' = t-Bu or 2,6-Me₂C₆H₃), 1,1-migratory insertion proceeded quantitatively overnight in pentane solution at room temperature to provide the corresponding paramagnetic, dark blue or dark purple crystalline CpAm Ti(III) η^2 iminoacyl derivatives 7-11 in excellent yields according to Scheme 1.16 Similar 1,1-insertion of an isocyanide into the titanium-carbon bond of Ib was previously established by the Teuben group; however, no validating solid-state molecular structure for the product of this reaction was ever reported.⁴ In the present study, single-crystal X-ray analyses were performed for compounds 7 and 9-11, and the data presented in Figure 2 and Table 2 for the solid-state molecular structures and selected geometric parameters, respectively, for these compounds confirm a bidentate η^2 -iminoacyl coordination mode, as depicted in Scheme 1.^{12,16} As Table 2 reveals, the geometrical parameters about the Ti(III) metal center and the η^2 -iminoacyl C=N bond length remain fairly constant for this series of complexes in spite of variations in the nature of the migrating R group and of the R' group of the isocyanide involved in the 1,1-insertion process. However, the influence of varying magnitudes of nonbonded

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Figure 1. Molecular structures (30% thermal ellipsoids) of compounds 2, 3, 4, and 5. Hydrogen atoms have been removed for the sake of clarity except for those located on the Et, n-Bu, i-Bu, and Np groups, respectively, which are represented by small spheres of arbitrary size.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) forCompounds 2, 3, 4, and 5

2	3	4	5
2.149(3)	2.119(12)	2.1587(14)	2.1708(14)
2.078(2)	2.0739(12)	2.0794(10)	2.0857(11)
2.084(2)	2.0872(12)	2.0867(10)	2.0898(11)
1.537(4)	1.565(13)	1.5373(19)	1.5354(19)
64.55(8)	64.22(5)	64.34(4)	64.13(4)
116.73(19)	119.2(6)	120.15(10)	128.91(10)
	117.3(5)	112.60(12)	110.22(15)
		110.36(13)	109.94(14)
			111.51(12)
		109.92(13)	109.82(19)
	2 2.149(3) 2.078(2) 2.084(2) 1.537(4) 64.55(8) 116.73(19)	2 3 2.149(3) 2.119(12) 2.078(2) 2.0739(12) 2.084(2) 2.0872(12) 1.537(4) 1.565(13) 64.55(8) 64.22(5) 116.73(19) 119.2(6) 117.3(5)	2 3 4 2.149(3) 2.119(12) 2.1587(14) 2.078(2) 2.0739(12) 2.0794(10) 2.084(2) 2.0872(12) 2.0867(10) 1.537(4) 1.565(13) 1.5373(19) 64.55(8) 64.22(5) 64.34(4) 116.73(19) 119.2(6) 120.15(10) 117.3(5) 112.60(12) 110.36(13) 109.92(13)

steric interactions that arise with different combinations of R and R' do emerge for at least two key structural parameters that are listed in Table 2. More specifically, the increased steric bulk when R' = t-Bu vs the case for R' = 2,6-Me₂C₆H₃ appears to manifest in an increase in the parameter Φ , which is defined as the angle between the mean planes determined by N1–Ti1–N2 and N3–Ti1–C19 [cf. 103.5° in 7 vs 74.2–76.3° for 9–11]. In addition, for R' = 2,6-Me₂C₆H₃, as the steric bulk of the migrating R group increases, the Ti–C_α–C_β angle of the iminoacyl carbon atom responds by becoming

increasingly more obtuse [cf. 164.54(13)° for **9** vs 168.02(19)° for **10** (see Table 2)].

ii. Chemical Oxidation. It was serendipitously discovered that upon introduction of a small quantity of dichloromethane (CH_2Cl_2) to a hydrocarbon solution of 3, instantaneous and quantitative oxidation of the metal center occurred with concomitant chloride atom abstraction to cleanly provide the diamagnetic, orange-red CpAm Ti(IV) n-butyl, chloride derivative Cp*Ti(n-Bu)(Cl)[N(i-Pr)C(Me)N(i-Pr)] (12).^{3c} A somewhat less convenient route to 12 involves chemical oxidation of 3 using PbCl₂ in Et₂O in the manner previously reported by Teuben and co-workers,⁴ and in this way, chemical oxidations of 4 and 5 were also carried out to provide the corresponding derivatives Cp*Ti(R)(Cl)[N(i-Pr)C(Me)N(i-Pr)], where R = i-Bu (13) and Np (14), which were also isolated as diamagnetic orange-red crystalline materials according to Scheme 1. Here, it is interesting to note that all attempts to prepare compounds 12-14 through direct reaction of the CpAm Ti(IV) dichloride precursor 1 with one equivalent of the respective organometallic reagents, RLi or RMgCl, were unsuccessful since metal-centered, one-electron reduction to Ti(III) was always the preferred reaction pathway. Thus, it would now appear that the best synthetic route to these and



Figure 2. Molecular structures (30% thermal ellipsoids) of compounds 7, 9, 10, and 11. Hydrogen atoms have been removed for the sake of clarity.

Table 2. Selected Bond L	Lengths (A) and Bond Angles	s (deg) for Compounds 7, 9, 10, and 11

parameter	7	9	10	11
Ti1-C19	2.093(2)	2.0976(17)	2.1191(15)	2.0912(15)
Ti1-N1	2.162(19)	2.1857(14)	2.2053(12)	2.1971(12)
Ti1-N2	2.109(2)	2.1086(14)	2.1076(13)	2.1138(13)
Ti1-N3	2.0706(19)	2.0623(14)	2.0554(12)	2.0617(11)
C19-N3	1.287(3)	1.289(2)	1.2919(19)	1.2886(19)
C19-Ti1-N3	36.01(8)	36.10(6)	36.02(5)	36.14(5)
Ti1-C19-N3	71.04(13)	70.46(9)	69.30(8)	70.68(8)
Ti1-N3-C19	72.95(13)	73.44(10)	74.68(9)	73.17(8)
Ti1-C19-C20	161.8(2)	164.54(13)	168.02(19)	167.47(12)
$Ti1-N3-C_{\alpha(N3)}$	153.08(16)	156.43(11)	155.88(10)	158.13(10)
$\Theta_{(N1-Ti1-N2, N3-Ti1-C19)}$	103.5	75.7	74.3	76.3

other Cp*Ti(R)(Cl)[N(R¹)C(R²)N(R³)] derivatives is via the overall two-step reduction/oxidation pathway that is detailed in Scheme 1 (e.g., $1 \rightarrow 3 \rightarrow 12$).

Since compounds 12-14 also now represent a new series of CpAm Ti(IV) alkyl, chloride complexes, single-crystal X-ray analyses were conducted, and Figure 3 presents the solid-state molecular structures that were obtained from

these studies.¹² Once again, these structures are distinguished by the notable lack of any evidence for the existence of either α - or β -hydrogen agostic interactions between the metal center and the R group. This structural feature is in keeping with the high degree of thermal stability that is displayed by these compounds in the solid-state and toluene solutions up to temperatures of at least 90 °C, as supported by ¹H NMR



Figure 3. Molecular structures (30% thermal ellipsoids) of compounds 12, 13, and 14. Hydrogen atoms have been removed for the sake of clarity.



spectroscopy. A notable apparent departure from stability, however, was discovered for compound 14. More specifically, whereas combustion-based elemental analyses (C, H, and N) for compounds 12 and 13 were fully consistent with the Cp*Ti(n-R)(Cl)[N(i-Pr)C(Me)N(i-Pr)] molecular composition where R = n-Bu and i-Bu, respectively, elemental analyses of crystalline 14, which was determined to be analytically pure on the basis of ¹H NMR spectroscopy,¹² consistently yielded, for five separate analyses, C, H, and N percentages that matched an empirical composition for 14 less a CMe₄ fragment. As Scheme 2 reveals, this observation most likely originates with facile hydrogen-atom abstraction from the Cp* ligand by the α -carbon of the Np group to form the "tuck-in" complex 15. There is now considerable precedent in the literature for this type of hydrogen abstraction process, and with respect to Cp* group 4 metal derivatives in particular, the previously introduced Ti(III) alkyl derivatives of Cp*2Ti-R (I) are known to eliminate RH with formation of the tuck-in complex Cp*Ti{ $\eta^5: \eta^1$ - $C_5Me_4(CH_2)$ ^{4a,c,17} and the Ti(IV) dimethyl complex, Cp*₂-Ti(Me)₂, thermally eliminates CH₄ to provide Cp*Ti(Me)-{ η^5 : η^1 -C₅Me₄(CH₂)} in high yield.^{17,18} Finally, Teuben and co-workers¹⁹ have reported that Cp*₂Zr(Cl)(Np) undergoes clean thermal decomposition to provide the tuck-in complex, Cp*Zr(Cl){ $\eta^5:\eta^1-C_5Me_4(CH_2)$ }, in a synthetically useful process.

Conclusion

In summary, the present report serves to establish the CpAm ligand environment as a versatile new experimental platform for expanding our knowledge of the fundamental organometallic chemistry of Ti(III) and, in particular, for molecularly discrete metal complexes that incorporate alkyl substituents bearing β -hydrogens. On the basis of our prior experience with the CpAm ligand set that has successfully supported a wide variety of studies concerning the organometallic chemistry of mid- to high-valent early transition metals, ^{6–8,11,13,20} it is possible that through strategic engineering of nonbonded steric interactions, the newly established class of CpAm Ti(III) alkyl complexes, (η^5 -C₅R'₅)Ti(R)[N(R¹)C(R²)N(R³)], could provide access to a wide variety of desirable reaction paths leading to novel Ti(III)-mediated organic transformations. Efforts toward achieving this goal are currently in progress.

Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of dinitrogen using standard glovebox techniques. Solvents were dried (Na/benzophenone for Et₂O and pentane; Na for toluene) and distilled under argon prior to use. C_6D_6 for NMR spectroscopy was purchased from Cambridge Isotope Laboratories, dried over Na/K, degassed, and vacuum transferred prior to use. Celite was oven-dried (150 °C for several days) prior to use. NpLi and 1 were prepared according to the literature methods. All other alkyllithium reagents were obtained from commercial sources and titrated prior to use. Elemental analyses were performed by Midwest Microlab, LLC. ¹H NMR spectra were recorded at 400 MHz at 25 °C.

Cp*Ti(Et)[N(i-Pr)C(Me)N(i-Pr)] (2). To a solution of 1 (0.545 g, 1.38 mmol) in Et₂O (70 mL) was added EtLi (0.50 M in benzene/cyclohexane, 90:10, 1.4 mL, 2.8 mmol) at ambient temperature. The reaction was stirred for 16 h, during which time the solution changed in color from burgundy to brown. The volatiles were removed *in vacuo*. The resulting crude product was taken up in a minimal amount of pentane, the mixture was filtered through a small pad of Celite in a glass frit, and the filtrate was

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concentrated *in vacuo*. Upon cooling to -35 °C, compound **2** was isolated as a purple crystalline material, which was then recrystallized from pentane at -35 °C to provide analytically pure material. Yield of **2**: 0.331 g (0.938 mmol, 68%). Anal. Calcd for TiC₂₀H₃₇N₂: C, 67.98; H, 10.55; N, 7.93. Found: C, 68.18; H, 10.27; N, 8.08.

Cp*Ti(n-Bu)[**N(i-Pr)C(Me)N(i-Pr)**] (3). To a solution of 1 (0.511 g, 1.29 mmol) in Et₂O (75 mL) was added n-BuLi (1.6 M in hexanes, 1.6 mL, 2.6 mmol) at ambient temperature, and the mixture was stirred for 16 h, during which time the solution changed in color from burgundy to purple. The desired product was isolated according to the general workup procedure. Yield of 3: 0.367 g (0.962 mmol, 75%). Anal. Calcd for TiC₂₂H₄₁N₂: C, 69.27; H, 10.83; N, 7.35. Found: C, 68.94; H, 10.58; N, 7.30.

Cp*Ti(i-Bu)[**N(i-Pr)C(Me)N(i-Pr)**] (4). To a solution of 1 (0.489 g, 1.27 mmol) in Et₂O (75 mL) was added i-BuLi (1.7 M in heptane, 1.5 mL, 2.6 mmol) at ambient temperature. The reaction was stirred for 16 h, during which time the solution changed in color from burgundy to purple. The desired product was isolated according to the general workup procedure. Yield of 4: 0.400 g (1.05 mmol, 83%). Anal. Calcd for TiC₂₂H₄₁N₂: C, 69.27; H, 10.83; N, 7.35. Found: C, 69.36; H, 10.80; N, 7.34.

Cp*Ti(Np)[**N(i-Pr)C(Me)N(i-Pr)**] (5). To a solution of 1 (0.128 g, 0.324 mmol) in Et₂O (75 mL) was added NpLi (0.25 M in hexanes, 2.6 mL, 0.65 mmol) at ambient temperature. The reaction was stirred for 16 h, during which time the solution changed in color from burgundy to purple. The desired product was isolated according to the general workup procedure. Yield of 5: 0.126 g (0.319 mmol, 98%). Anal. Calcd for TiC₂₃H₄₃N₂: C, 69.85; H, 10.96; N, 7.08. Found: C, 69.57; H, 10.52; N, 7.04.

Cp*Ti(n-Hex)[N(i-Pr)C(Me)N(i-Pr)] (6). To a solution of 1 (0.161 g, 0.407 mmol) in Et₂O (75 mL) was added *n*-hexyllithium (2.5 M in *n*-hexane, 0.33 mL, 0.81 mmol) at ambient temperature. The reaction was stirred for 16 h, during which time the solution changed in color from burgundy to bright purple. The desired product was isolated as a purple oil according to the general workup procedure. Yield of **6**: 0.199 g. While the purity of this crude product was not sufficient for obtaining a satisfactory elemental analysis, it is of sufficient purity to be used in subsequent chemical reactions (*vide infra*).

Cp^{*}**Ti**[η^2 -C(Et)=N(t-Bu)][N(i-Pr)C(Me)N(i-Pr)] (7). To a solution of 2 (0.107 g, 0.303 mmol) in pentane (4 mL) was added t-BuNC (0.040 g, 0.481 mmol). The reaction mixture was then stirred for 18 h and then cooled to -30 °C, whereupon the desired product was obtained as a paramagnetic dark blue crystalline material. Yield of 7: 0.127 g (0.291 mmol, 96%). Anal. Calcd for TiC₂₅H₄₆N₃: C, 68.79; H, 10.62; N, 9.63. Found: C, 69.01; H, 10.59; N, 9.87.

Cp*Ti[η^2 -**C**(**n-Bu**)=**N**(2,6-**Me**₂**C**₆**H**₃)][**N**(**i**-**Pr**)**C**(**Me**)**N**(**i**-**Pr**)] (8). To a solution of 3 (0.084 g, 0.220 mmol) in pentane (2 mL) was added 2,6-dimethylphenylisocyanide (0.035 g, 0.264 mmol) in pentane (2 mL) at ambient temperature. The reaction was stirred for 18 h and then cooled to -30 °C, whereupon the desired product was obtained as a paramagnetic dark purple crystalline material. Yield of 8: 0.062 g (0.121 mmol, 55%). Anal. Calcd for TiC₃₁H₅₀N₃: C, 72.63; H, 9.83; N, 8.20. Found: C, 72.64; H, 9.74; N, 8.26.

Cp*Ti[η^2 -**C**(**i**-**Bu**)=**N**(**2,6**-**Me**_2**C**₆**H**₃)][**N**(**i**-**Pr**)**C**(**Me**)**N**(**i**-**Pr**)] (9). To a solution of **4** (0.122 g, 0.320 mmol) in pentane (2 mL) was added 2,6-dimethylphenylisocyanide (0.050 g, 0.384 mmol) in pentane (3 mL) at ambient temperature, and the solution immediately darkened. The reaction mixture was then stirred for 18 h and then cooled to -30 °C, whereupon the desired product was obtained as a paramagnetic dark purple crystalline material. Yield of **9**: 0.100 g (0.195 mmol, 61%). Anal. Calcd for TiC₃₁H₅₀N₃: C, 72.63; H, 9.83; N, 8.20. Found: C, 72.76; H, 9.93; N, 8.08.

 $Cp*Ti[\eta^2-C(Np)=N(2,6-Me_2C_6H_3)][N(i-Pr)C(Me)N(i-Pr)]$ (10). To a solution of 5 (0.060 g, 0.152 mmol) in pentane (2 mL) was added 2,6-dimethylphenylisocyanide (0.024 g, 0.182 mmol) in pentane (3 mL). The reaction mixture was then stirred for 18 h and then cooled to -30 °C, whereupon the desired product was obtained as a paramagnetic dark purple crystalline material. Yield of **10**: 0.049 g (0.093 mmol, 61%). Anal. Calcd for TiC₃₂H₅₂N₃: C, 72.98; H, 9.95; N, 7.98. Found: C, 72.72; H, 9.92; N, 8.03.

Cp*Ti[η^2 -C(**n-Hex**)=N(2,6-Me₂C₆H₃)][N(i-Pr)C(Me)N(i-Pr)] (11). The crude product obtained for 6 was taken up in pentane (4 mL), and to the solution was added 2,6-dimethylphenylisocyanide (0.064 g, 0.488 mmol) in pentane (3 mL) at ambient temperature. The reaction mixture was then stirred for 18 h and then cooled to -30 °C, whereupon the desired product was obtained as a paramagnetic dark purple crystalline material. Yield of 11: 0.104 g (0.192 mmol, 47%). Anal. Calcd for TiC₃₃H₅₄N₃: C, 73.31; H, 10.07; N, 7.77. Found: C, 73.42; H, 9.97; N, 7.75.

Cp*Ti(n-Bu)(Cl)[N(i-Pr)C(Me)N(i-Pr)] (12). To a solution of **3**(0.133 g, 0.349 mmol) in Et₂O (10 mL) was added PbCl₂ (0.048 g, 0.173 mmol) all at once. The reaction was stirred for 2 h at ambient temperature, during which time the solution changed in color from purple to orange. After the general workup procedure, the desired product was isolated and recrystallized from pentane to provide a diamagnetic orange-red crystalline material. Yield of **12**: 0.094 g (0.225 mmol, 61%). ¹H NMR (C₆D₆): δ 3.65 (m, 1H, CH(CH₃)₂), 3.28 (m, 1H, CH(CH₃)₂), 2.25 (m, 1H, TiCH₂), 1.98 (s, 15H, C₅Me₅), 1.74 (s, 3H, CH₃), 1.37 (d, 3H, CH(CH₃)₂, 1.33 (d, 3H, CH(CH₃)₂, 1.32–1.19 (m, 4H, CH₂CH₂CH₂CH₃), 1.09 (d, 3H, CH(CH₃)₂, 1.05 (d, 3H, CH(CH₃)₂, 0.97 (t, 3H, CH₃), 0.69 (t, 1H, TiCH₂). Anal. Calcd for TiC₂₂H₄₁N₂Cl: C, 63.38; H, 9.91; N, 6.72. Found: C, 63.49; H, 9.71; N, 6.60.

Cp*Ti(i-Bu)(Cl)[N(i-Pr)C(Me)N(i-Pr)] (13). To a solution of **4** (0.181 g, 0.474 mmol) in Et₂O (10 mL) was added PbCl₂ (0.066 g, 0.237 mmol) at ambient temperature. The reaction was stirred for 2 h at ambient temperature, during which time the solution changed in color from purple to orange. After the general workup procedure, the desired product was isolated and recrystallized from pentane to provide a diamagnetic orange-red crystalline material. Yield of **13**: 0.083 g (0.199 mmol, 42%). ¹H NMR (C₆D₆): δ 3.70 (m, 1H, CH(CH₃)₂), 3.34 (m, 1H, CH(CH₃)₂), 2.28 (m, 1H, CH₂CH(CH₃)₂), 1.97 (s, 15H, C₅Me₅), 1.72 (s, 3H, CH₃), 1.37 (d, 3H, CH(CH₃)₂), 1.23 (d, 3H, CH(CH₃)₂), 1.22 (d, 6H, CH₂CH(CH₃)₂), 1.15 (t, 1H, TiCH₂), 1.13 (d, 3H, CH(CH₃)₂), 1.07 (d, 3H, CH(CH₃)₂), 0.88 (m, 1H, TiCH₂). Anal. Calcd for TiC₂₂H₄₁N₂Cl: C, 63.38; H, 9.91; N, 6.72. Found: C, 63.03; H, 10.06; N, 6.75.

Cp*Ti(Np)(Cl)[**N(i-Pr)C(Me)N(i-Pr)**] (14). To a solution of **5** (0.196 g, 0.496 mmol) in Et₂O (10 mL) was added PbCl₂ (0.069 g, 0.248 mmol). The reaction was stirred for 2 h at ambient temperature, during which time the solution changed in color from purple to orange. After the general workup procedure, the desired product was isolated and recrystallized from pentane to provide a diamagnetic orange-red crystalline material. Yield of 14: 0.085 g (0.197 mmol, 40%). ¹H NMR (C₆D₆): δ 3.72 (m, 1H, CH(CH₃)₂), 3.45 (m, 1H, CH(CH₃)₂), 1.96 (s, 15H, C₅Me₅), 1.70 (s, 3H, CH₃), 1.37 (d, 3H, CH(CH₃)₂), 1.36 (s, 9H, CH₂C(CH₃)₃), 1.23 (d, 3H, CH(CH₃)₂), 1.16 (d, 3H, CH(CH₃)₂), 1.11 (d, 3H, CH(CH₃)₂), 0.89 (s, 1H, TiCH₂), 0.10 (d, 1H, TiCH₂). Anal. Calcd for TiC₂₃H₄₃N₂Cl: C, 64.09; H, 10.06; N, 6.50. Found: C, 60.78; H, 8.75; N, 7.14.

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Supporting Information Available: Details of single-crystal X-ray analyses, including tables of bond lengths, angles, and anisotropic displacement parameters for the solid-state structures and complete X-ray crystallographic data (CIF) for compounds 2-5, 7, and 9-12. This material is available free of charge via the Internet at http://pubs.acs.org.