Titanium Complexes Stabilized by *N*-(*tert*-Hydrocarbyl)anilide Ligation: A Synthetic Investigation

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The complexes $\mathrm{Ti(NRAr_F)_2(NMe_2)_2}$ (**4**, R = $\mathrm{C(CD_3)_2CH_3}$, $\mathrm{Ar_F}$ = 2,5-$\mathrm{C_6H_3FMe}$), $\mathrm{Ti(NRAr_F)_2(NMe_2)(I)}$ (**5**), $\mathrm{Ti(NRAr_F)_2(NMe_2)(CH_2SiMe_3)}$ (**6**), and $\mathrm{Ti(NRAr_F)_2(I)(CH_2SiMe_3)}$ (**7**) have been synthesized in 77, 71, 70, and 84% yield, respectively, in a four step sequence of alternating salt elimination and dimethylamide deprotection steps. The complex $\mathrm{Ti(NRAr)(I)_2(OAr')}$ (**11**, Ar = 3,5-$\mathrm{C_6H_3Me_2}$, Ar′ = 2,6-$\mathrm{C_6H_3{}^iPr_2}$) was prepared in 65% yield via the complexes $\mathrm{Ti(NRAr)(NMe_2)_3}$ (**9**) and $\mathrm{Ti(NRAr)(NMe_2)_2(OAr')}$ (**10**), which were generated in situ, spectroscopically characterized, and not isolated. The complexes $\mathrm{Ti(NR'Ar)(NMe_2)_3}$ (**12**, R′ = $\mathrm{C(CD_3)_2Ph}$, $\mathrm{Ti(NR'Ar)(NMe_2)_2(OAr'')}$ (**13**, Ar″ = 2,6-$\mathrm{C_6H_3{}^tBu_2}$), and $\mathrm{Ti(NR'Ar)(NMe_2)(OAr'')(I)}$ (**14**) were prepared in 83, 83, and 95% isolated yield, respectively, via a salt-elimination, protonolysis, and dimethylamide deprotection sequence. Treatment of **14** with (i) neopentyllithium, (ii) thermolysis at 65 °C, and (iii) excess methyl iodide at 70 °C led to the isolation in 62% yield of the cyclometallated compound $\overline{\mathrm{Ti}\mathrm{(NR'Ar)(O\text{-}2,6\text{-}C_6H_3[^tBu][CMe_2C}\mathrm{H_2}}\mathrm{])(I)}$ (**17**) via an intermediate neopentyl complex (**15**) which was not isolated. The titanium(III) “ate” complex $\mathrm{(ArR'N)_2Ti(\mu\text{-}Cl)_2Li(TMEDA)_{\mathit{n}}}$ (**18**, TMEDA = $\mathrm{Me_2NCH_2CH_2NMe_2}$, *n* = ca. 3) was isolated in 80% yield as green crystals upon treatment of $\mathrm{TiCl_3(THF)_3}$ (THF = tetrahydrofuran) with 2 equiv of $\mathrm{Li(NR'Ar)(OEt_2)}$ in a THF/TMEDA mixture. Chloroform treatment of the ate complex **18** led to the titanium(IV) dichloride $\mathrm{Ti(NR'Ar)_2Cl_2}$ (**19**). The titanium(III) ate complex $\mathrm{(ArRN)_2Ti(\mu\text{-}Cl)_2Li(TMEDA)}$ (**20**) was isolated in 57% yield in a manner analogous to the preparation of **18**. Alkylation of **20** with $\mathrm{LiCH(SiMe_3)_2}$ led to the mixed amido−alkyl titanium(III) complex $\mathrm{Ti(NRAr)_2(CH[SiMe_3]_2)}$ (**21**) in 72% isolated yield. A single-crystal X-ray diffraction study carried out for **21** revealed an η^3 bonding mode for one of the NRAr ligands and a typical η^1 bonding mode for the other. The diamagnetic dimeric complex $\mathrm{(\mu\text{-}NCPhCPhN)[Ti(NRAr)_2(CH[SiMe_3]_2)]_2}$ (**23**) was obtained in 82% yield via the blue benzonitrile adduct $\mathrm{Ti(NRAr)_2(CH[SiMe_3]_2)(NCPh)}$ (**22**), which was not isolated. A robust green pivalonitrile adduct $\mathrm{Ti(NRAr)_2(CH[SiMe_3]_2)(NCCMe_3)}$ (**24**) was observed upon treatment of **21** with pivalonitrile. Addition of azidotrimethylsilane to **24** delivered the titanium(IV) azido complex $\mathrm{Ti(NRAr)_2(CH[SiMe_3]_2)(N_3)}$ (**25**) in 37% isolated yield. Treatment of **21** with 0.5 equiv of $\mathrm{I_2}$ in benzene provided $\mathrm{Ti(NRAr)_2(CH[SiMe_3]_2)(I)}$ (**26**) in 68% yield.

Introduction

Group 4 organometallic molecules are under heavy investigation as catalysts and as stoichiometric reagents for a wide range of transformations including olefin polymerization,[1] reductive coupling,[2−6] and hydrogenation catalysis.[7−11] While the discovery of well-behaved metallocene-based catalysts for stereospecific polymerization of prochiral olefins has led to a renewed interest in such systems, the search is on for non-cyclopentadienyl ligand systems that may provide catalysts with improved properties. Thus, group 4 organometallic molecules with N- or O-donor ancillary ligands,[12−18] or boron-based ligands,[19−22] are now under inspection in the hopes that these may provide the next generation

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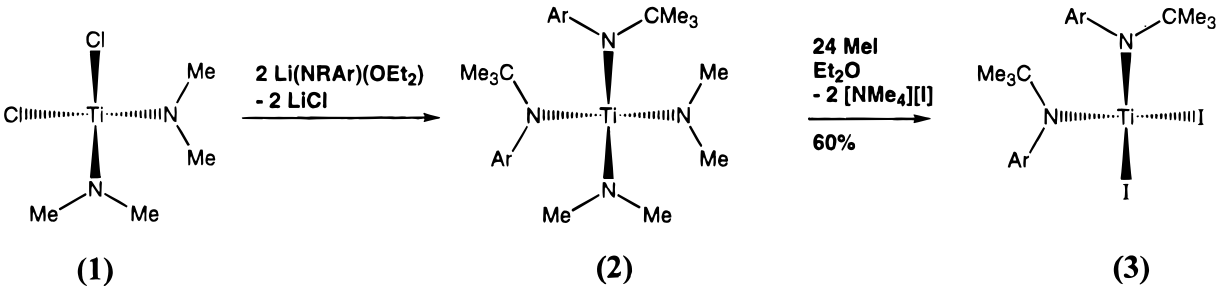
Scheme 1



of reagents or catalysts. While the focus is largely centered on cationic organometallic complexes of group 4 transition metals,[23,24] species that are d^0 and highly electrophilic, alternative ancillary ligand systems are also under investigation for d^1 and d^2 group 4 complexes[25−27] and for group 3[28] and group 5[29−31] metal complexes.

Our interest in the chemistry of group 4 complexes has centered on inorganic reactions that utilize a d^1 titanium center as a specific one-electron reductant.[32,33] This aspect of group 4 chemistry has manifested itself previously in the context of a bis(cyclopentadienyl) ancillary ligand set,[34] and also in the context of O-donor ancillary ligands,[35] but the area is essentially in its infancy. We have discovered new implementations of d^1 titanium(III) as a specific 1e reductant for terminal oxo complexes of vanadium(V)[33] and also for terminal oxo and nitrido complexes of molybdenum(VI).[32] Utilization of the latter substrates led to unprecedented examples of radical alkoxide C−O bond cleavage.[32]

The present work concerns synthetic strategies leading to organometallic titanium complexes supported either by bis(amido) ligation or by mixed amido/aryloxide ligation. The class of amido ligands we employ here are sterically-demanding *N-tert*-hydrocarbylanilide ligands, introduced recently for the stabilization of low-coordinate transition metal complexes.[36−42] The synthetic methods described here build on our earlier note describing the cleavage of titanium dimethylamides with methyl iodides,[43] a deprotection protocol. Since several of the complexes described here are halogeno species analogous to the prototypical complexes $Cp_2M(R)(X)$ [M = Ti, Zr; X = halogen, triflate, or noncoordinating anion], they are potential precursors to organometallic cations of titanium(IV) or to neutral organometallic titanium(III) radicals. A highlight of the present work involves the synthesis, characterization, and initial reactivity studies of the monomeric organometallic titanium(III) complex $Ti(NRAr)_2(CH[SiMe_3]_2)$ (**21**).

Results and Discussion

(i) Dimethylamide Cleavage by Methyl Iodide. We described recently the use of methyl iodide in the cleavage of titanium dimethylamides,[43] a reaction that results in replacement of the dimethylamide functionality by iodide[44] and gives tetramethylammonium iodide as a solid byproduct insoluble in common organic solvents. This reaction type (Scheme 1) is a nonprotic alternative to the use of amine hydrohalides,[45] most commonly pyridine or lutidine hydrohalides, that also lead to replacement of dimethylamide by halide, but which give a secondary ammonium salt possessing acidic protons as a byproduct.

The methyl iodide strategy is exemplified by the chemistry in Scheme 1. The mixed dimethylamide chloride complex $Ti(NMe_2)_2Cl_2$ (**1**) is a versatile starting material prepared by the literature method involving conproportionation of equimolar quantities of $TiCl_4$ and $Ti(NMe_2)_4$.[46] Addition of 2 equiv of the lithium amide etherate $Li(NRAr)(OEt_2)$[47] to **1** leads to metathesis, producing the mixed tetraamide $Ti(NRAr)_2(NMe_2)_2$ (**2**) in essentially quantitative yield. Addition of methyl

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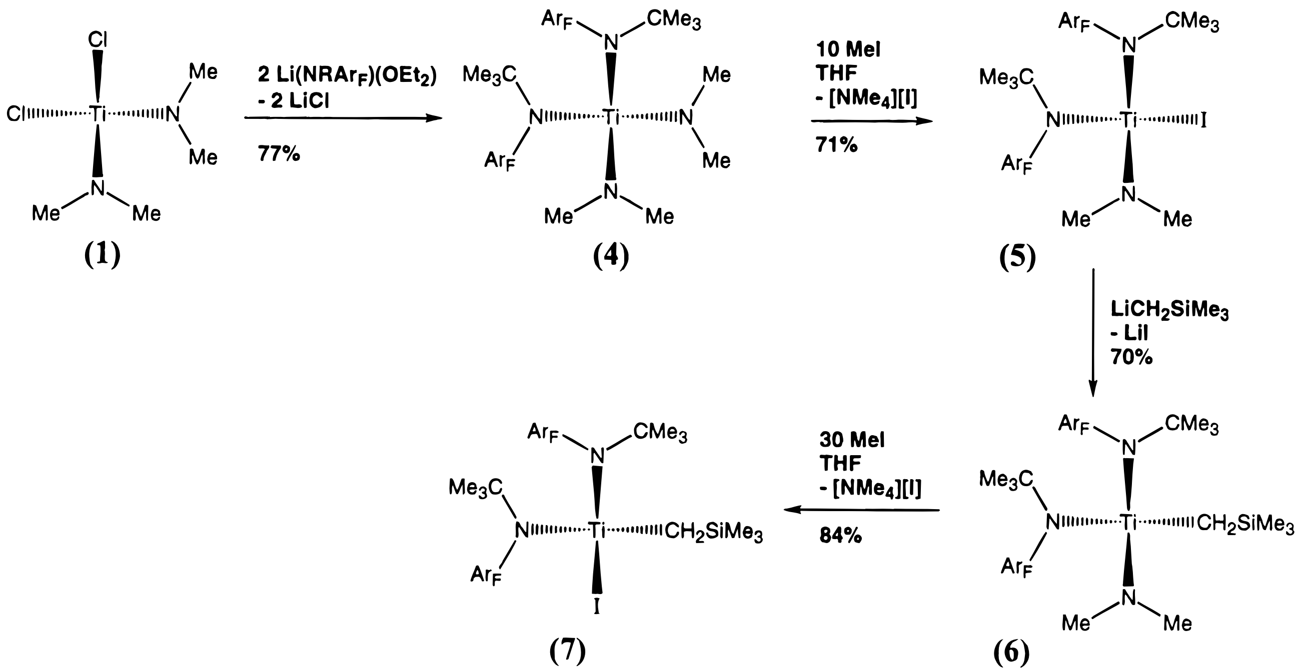
Scheme 2



iodide to **2**, generated in situ, gives smooth conversion to the desired bis(amido) dihalide complex $Ti(NRAr)_2I_2$ (**3**), which was isolated in 60% recrystallized yield.[43]

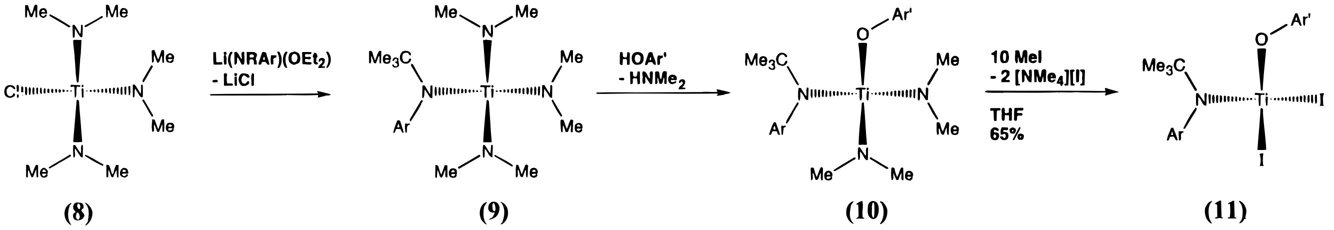
The two-step procedure outlined in Scheme 1 offered advantages over the alternative one-step process in which 2 equiv of $Li(NRAr)(OEt_2)$ would be added to $TiCl_4$ in the hopes of producing $Ti(NRAr)_2Cl_2$ directly. First, the use of exactly two dimethylamide protecting groups as present in **1** delivers control of the stoichiometry, since **1** possesses exactly two metathetically replaceable halogens, in contrast to $TiCl_4$. Second, the strongly π-donating dimethylamide ligands in **1** render the titanium(IV) center much less susceptible to reduction than is the case for $TiCl_4$. This potential side reaction, electron transfer, is important to consider in the context of metathetical salt-elimination reactions involving strongly reducing species such as lithium amides. Finally, the fact that Scheme 1 depicts a two-step procedure is mitigated by the fact that it is carried out without isolation or purification of intermediate **2**.

(ii) Bis(amido) Organometallic Complex of Titanium(IV). In a series of papers treating new low-coordinate transition metal complexes and their reactions with small molecules, we have introduced sterically-demanding *N*-*tert*-butylanilide ligands (e.g. NRAr in Scheme 1) as bulky ancillary N-donor ligands.[36-42] Among the attractive features of such ligands is that they are readily tunable in that a plethora of variously substituted anilines may be employed in their synthesis. Partially fluorinated anilines are especially attractive in this respect. The chemistry displayed in Scheme 2 was carried out in order to assess the effect of a single ortho fluorine substituent on the course of dimethylamide cleavage by methyl iodide, along the lines discussed in the context of Scheme 1 above.

Treatment of bis(dimethylamide) dichloride **1** with 2 equiv of the singly fluorinated lithium amide etherate $Li(NRAr_F)(OEt_2)$ in diethyl ether led to clean expulsion of 2 equiv of LiCl with production of the mixed tetraamide $Ti(NRAr_F)_2(NMe_2)_2$ (**4**). Complex **4** is a crystalline solid isolable in 77% recrystallized yield; this property contrasts starkly with the situation for the nonfluorinated mixed tetraamide **2** which could only be obtained as an oil. Treatment of **4** with an excess of methyl iodide in THF (28 °C) led to replacement of only one of the two dimethylamide functionalities by iodide. Monoiodide monodimethylamide **5** was isolated in 71% recrystallized yield subsequent to such treatment. This observation can be rationalized by assuming that the fluorinated amido ligand renders the titanium center in **4** more electron-deficient than that in **2**, leading to stronger dimethylamido−titanium π interactions in the case of **4**. Replacement of the first dimethylamide by iodide, generating **5**, results in an even stronger metal−nitrogen π interaction for the remaining dimethylamide such that it is not susceptible to further attack by methyl iodide. The unfluorinated complex corresponding to **5** in Scheme 1 (not shown) is attacked readily by methyl iodide, leading directly to two substitutions.

It is occasionally the case that alkyllithium or Grignard alkylations of a dihalogeno species such as Cp_2MCl_2 (M = Ti, Zr) leads to complex mixtures when the mixed halogeno alkyl complex is the desired product. Several strategies have been designed to circumvent this difficulty, including initial preparation of the dialkyl species followed by metal−carbon bond oxidation and including conproportionation of the dialkyl species with the corresponding dihalogeno species. In this context it should be noted that complex **5**, because of the presence of one dimethylamide protecting group, is poised to undergo a selective monoalkylation upon treatment with 1 equiv of a Grignard or alkyllithium reagent. Thus, treatment of **5** with trimethylsilylmethyl lithium led to smooth production of the monoalkylated species $Ti(NRAr_F)_2(NMe_2)(CH_2SiMe_3)$ (**6**), which was isolated as mustard yellow sheets in 70% recrystallized yield. Removal of the dimethylamide protecting group was effected by treatment of **6** with excess methyl iodide in THF, delivering the iodo (trimethylsilyl)methyl complex **7** in 84% crude yield as a yellow oil. The choice of

Scheme 3



solvent is important for the dimethylamide deprotection step, in that the reaction (28 °C) proceeds relatively rapidly in THF, at a moderate or slow pace in diethyl ether, and extremely slowly in hydrocarbon solvents such as hexane.

(iii) Amido−Aryloxide Titanium(IV) Diiodide Complex. An important class of O-donor ligands in organometallic chemistry are the 2,6-disubstituted aryloxides. The most ubiquitous members of this class are 2,6-diisopropylphenoxide, 2,6-di-*tert*-butylphenoxide, and 2,6-diphenylphenoxide. The latter variant has been employed to great advantage by Rothwell and coworkers in the development of reductive coupling chemistry on the $Ti(O\text{-}2,6\text{-}C_6H_3Ph_2)_2$ template. The chemistry in this section constitutes the deliberate construction of a mixed aryloxide/amide ancillary ligand set. The goal of this inquiry is to set the stage for production of (i) a three-coordinate titanium species bearing C, N, and O donors or (ii) to set the stage for the production of a chiral-at-metal electrophilic titanium(IV) species.

Scheme 3 begins with titanium monochloride tris(dimethylamide) (**8**), a species which, like compound **1**, is available via conproportionation of $TiCl_4$ with $Ti(NMe_2)_4$ employing the proper stoichiometric ratio.[46] We introduced the bulky amido ligand quantitatively upon treatment of **8** with 1 equiv of $Li(NRAr)(OEt_2)$, giving mixed tetraamide **9**, which did not require purification. Protonolysis of one dimethylamido substituent occurred smoothly and selectively upon treatment of **9** with 1 equiv of 2,6-diisopropylphenol. Dimethylamine, which was thereby liberated, was removed in vacuo. Compound **10** exhibited NMR spectroscopic properties consistent with its formulation as the desired bis(dimethylamido) *N*-*tert*-butylanilido aryloxide species, and it reacted smoothly with an excess of methyl iodide in THF to give the corresponding diiodide complex $Ti(NRAr)(I)_2(OAr')$ (**11**) in 65% overall yield from **8**. Solutions of **11** are blood-red in color, and crystals of the complex are purple. All characterization data are consistent with the identity of compound **11** as formulated.

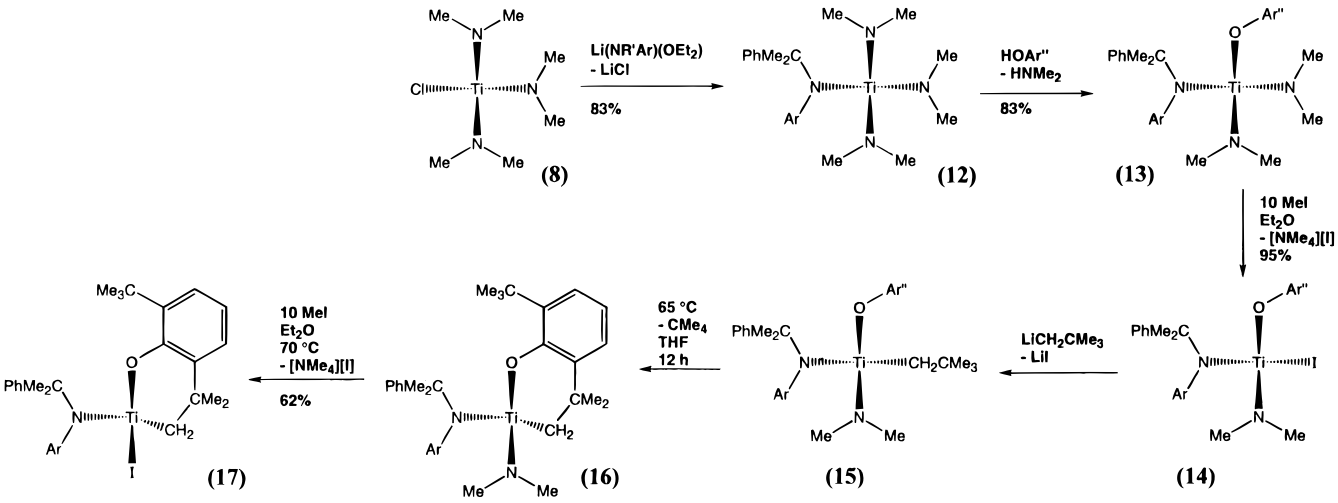
Compound **11** is poised for alkylation by treatment with a Grignard reagent or an alkyllithium reagent. Preliminary results indicate that the compound does in fact react smoothly with $LiCH_2SiMe_3$ to generate $Ti(NRAr)(OAr')(CH_2SiMe_3)I$ and with $LiCH_2CMe_2Ph$ to generate $Ti(NRAr)(OAr')(CH_2CMe_2Ph)I$. NMR characterization revealed the presence of diastereotopic $TiCH_2$ protons and $CHMe_2$ methyls for these chiral-at-metal four coordinate complexes.

Thus far we have described the reactions of the three bis(dimethylamido) complexes **2**, **4**, and **10** with methyl iodide. It is of interest to note that only the partially fluorinated ancillary ligand set present in **4** resulted in a titanium center sufficiently electrophilic to protect the second dimethylamide from alkylation. One would expect the diisopropylphenoxide ligand to be a weaker donor than NRAr, allowing us to forward the following electronic ordering: $Ti(NRAr)_2 < Ti(NRAr)(OAr') < Ti(NRAr_F)_2$ for the electrophilicity at titanium. However, we cannot discount the possibility that the unique behavior of **4** is a consequence of the fact that this ligand, unlike the others, has the potential to behave as a bidentate N,F donor.

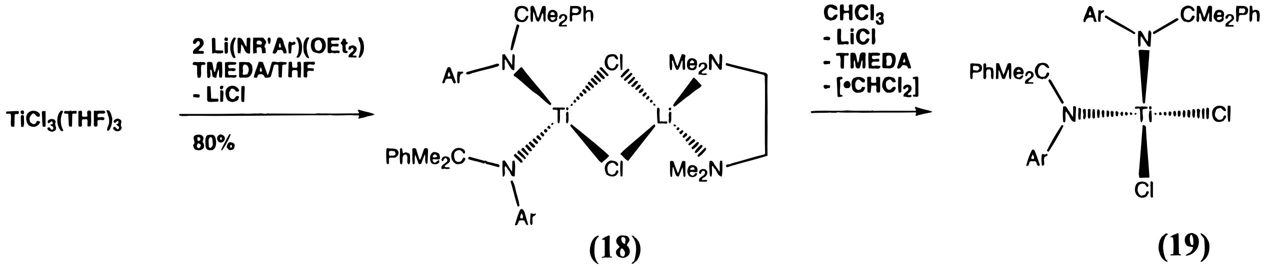
(iv) Cyclometalation Involving a Titanium(IV) Amido−Aryloxide Complex. In the above sections we utilized two variants of the *N*-*tert*-butylanilide ligand type, the difference being the substitution pattern on the aromatic ring. This general class of ligands is also variable at the N-connected tertiary hydrocarbyl position. Here we describe a variant possessing CMe_2Ph as the tertiary hydrocarbyl in conjunction with a synthetic sequence aiming, as in the previous section, at a titanium target bearing C, N, and O donors.

This sequence (Scheme 4) begins once again with $ClTi(NMe_2)_3$ (**8**). Treatment of **8** with 1 equiv of $Li(NR'Ar)(OEt_2)$ led in 83% recrystallized yield to mixed tetraamide **12**, isolated as a green-brown powder. Characterization data are consistent with the identity of **12** as formulated. Compound **13**, an orange powder, was also isolated in 83% recrystallized yield, subsequent to protonolysis of a single dimethylamido substituent in **12** with 2,6-di-*tert*-butylphenol. Compound **13** represents the fourth bis(dimethylamido) complex newly synthesized in this study, the others being **2**, **4**, and **10**. It was of obvious interest to examine the reaction of **13** with methyl iodide under conditions similar to those utilized for the other bis(dimethylamido) complexes. The product resulting from treatment of **13** with an excess of methyl iodide was in fact mono(dimethylamide) monoiodide **14**, which was obtained as orange microcrystals in ca. 95% recrystallized yield. Evidently the effect of aryl-for-methyl substitution at the N-connected tertiary hydrocarbyl position leads to increased electrophilicity at the titanium center. Neopentyllithium alkylation of monoiodide **14** led to smooth production of $Ti(NR'Ar)(OAr'')(CH_2CMe_3)(NMe_2)$ (**15**) according to NMR monitoring, but the oily yellow compound resisted repeated attempts at crystallization. Thermolysis at 65 °C of **15** generated in situ led to expulsion of neopentane (not quantified), giving a complex whose NMR spectra are indicative of a cyclometalated aryloxide ligand as depicted in Scheme 4 for **16**. Compound **16** was an oily species, difficult to purify for full characterization. Treatment of **16** with methyl iodide at 70 °C provided **17** in 63% recrystallized yield. Compound **17** retains the cyclometalated 2,6-di-*tert*-butylphenoxide substituent proposed for precursor **16**. Bearing four different groups bound to titanium, compound **17** is chiral-at-metal, consistent with the diastereotopic nature of its titanium-bound methylene unit. Rothwell and co-work-

Scheme 4



Scheme 5



ers have observed C−H activation previously in conjunction with cyclometalation of the 2,6-di-*tert*-butylphenoxide ligand.[48−50] Such intramolecular cyclometalation reactions provide a favorable six-membered ring.

Although the aryloxide ligand in **17** is cyclometalated, the compound does nevertheless contain the desired C, N, and O donors along with an iodide for further elaboration. Preliminary reactivity studies indicate that **17** is readily reduced by sodium amalgam in THF to give a persistent green color; ^{2}H NMR spectroscopy indicates that a single NR′Ar-containing species (δ = ca. 4 ppm) is formed. Future efforts involving **17** will focus on characterization of the green species which is possibly an unique three-coordinate Ti(III) complex supported by a C, N, and O-donor ligand set.

(v) Bis(Amido) Titanium(III) Complexes. In the section above associated with Scheme 1, we described a two-step, one-pot sequence terminating at the desired bis(*N*-*tert*-butylanilido) diiodide complex (**3**), which can be thought of as an alternative to Cp$_2$MX$_2$ (M = Ti, Zr; X = halogen) group 4 starting materials. In this section we show that such a compound can be accessed via an alternative two-step sequence which begins with titanium(III) rather than titanium(IV). The sequence is analogous to that commonly utilized for the preparation of Cp*$_2$TiCl$_2$ (Cp* = η^5-C$_5$Me$_5$).

Gambarotta and co-workers have shown that the ate complex (Cy$_2$N)$_2$Ti(μ-Cl)$_2$Li(TMEDA) [Cy = cyclohexyl] is produced upon treatment of TiCl$_3$(THF)$_3$ with lithium dicyclohexylamide in the presence of TMEDA.[51] This procedure is also successful for the NR′Ar ligand, such that treatment of TiCl$_3$(THF)$_3$ with 2 equiv of Li(NR′Ar)(OEt$_2$) in THF/TMEDA led to the expulsion of 1 equiv of lithium chloride and to production of ate complex (ArR′N)$_2$Ti(μ-Cl)$_2$Li(TMEDA) (**18**) which was obtained in 80% yield as light green crystals (Scheme 5); ca. 3 equiv of TMEDA of crystallization is present in the crystals according to NMR integration of an oxidized sample (see Experimental Section). The green ate complex reacts rapidly and smoothly with excess chloroform giving titanium(IV) dichloride **19** via formal atom transfer. Production of dichloride **19** is necessarily accompanied by elimination of one molecule of lithium chloride; analytical and spectroscopic data are consistent with the formulation of **19** as depicted in Scheme 5.

Ate complex **20** was generated similarly (Scheme 6) via treatment of TiCl$_3$(THF)$_3$ with 2 equiv of Li(NRAr)(OEt$_2$) in THF/TMEDA and was isolated in 57% yield. Bright green crystalline **20** is well-behaved in the sense that it does not retain excess TMEDA of crystallization. Our interest in **20** was to examine the possibility of forming a three-coordinate titanium(III) complex bearing one alkyl and two bulky amido ligands. Treatment of **20** with [(trimethylsilyl)methyl]lithium led to expulsion of lithium chloride and to production of green solutions that turned orange-brown upon warming to 28 °C. NMR examination of the product mixture from such a reaction indicated production of the titanium(IV) dialkyl species Ti(NRAr)$_2$(CH$_2$SiMe$_3$)$_2$, an oily species generated independently from Ti(NRAr)$_2$I$_2$ (**3**) and

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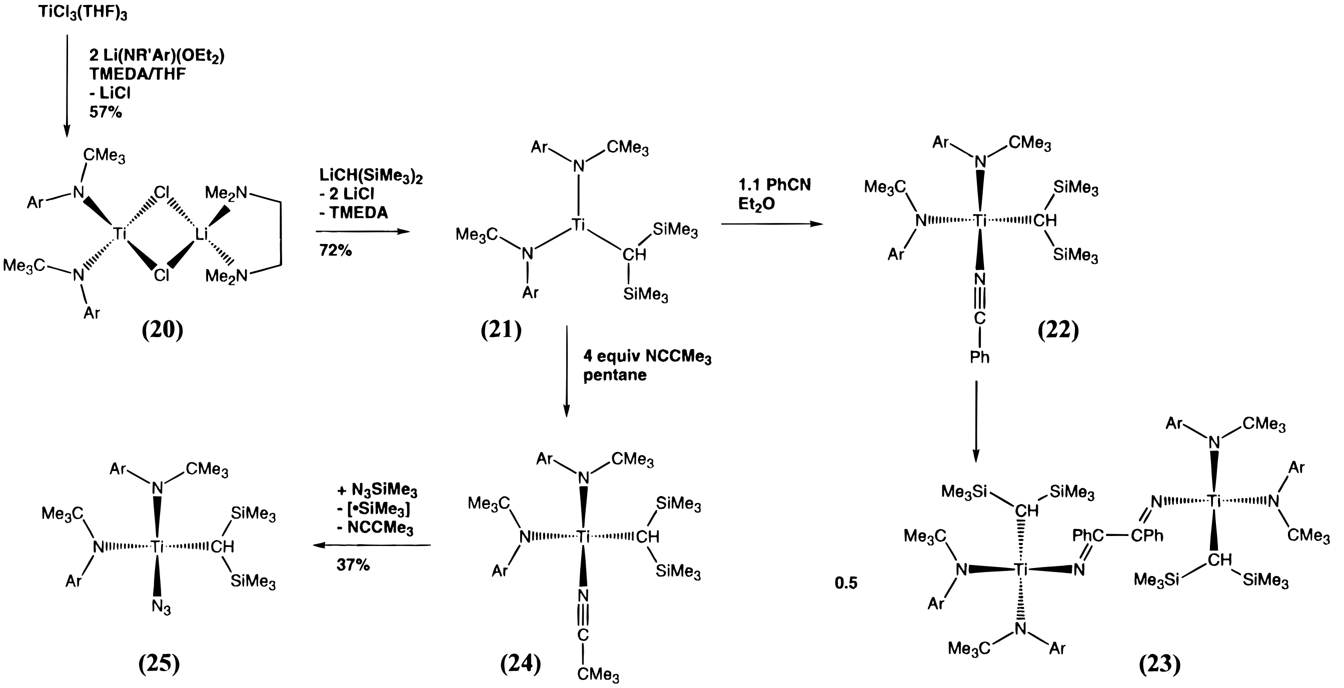
Scheme 6



2 equiv of $LiCH_2SiMe_3$ and characterized spectroscopically. These results are in line with the findings of Gambarotta and co-workers who suggested that $(Cy_2N)_2$-Ti(alkyl) species disproportionate to 0.5 equiv $(Cy_2N)_2$-Ti(alkyl)$_2$ and 0.5 equiv "$(Cy_2N)_2Ti$".[25] The fate of the latter titanium(II) fragment is unknown.

(vi) Monomeric Titanium(III) Alkyl Complex. Some time ago the preparation and structural characterization of the three-coordinate titanium(III) homoleptic alkyl complex $Ti(CH[SiMe_3]_2)_3$ was described by Lappert and co-workers.[52,53] The existence of this compound indicates that, at least with the special carbon donor $CH[SiMe_3]_2$, low-coordinate organometallic complexes of titanium(III) can be stabilized kinetically.[52,53] Since we have already shown that structurally characterized $Ti(NRAr)_3$ is a thermally robust entity, it seemed reasonable to expect that $Ti(NRAr)_2$-$(CH[SiMe_3]_2)$ (**21**) would be accessible. In accord with this expectation (Scheme 6) we found that treatment of ate complex **20** with 1 equiv $Li(CH[SiMe_3]_2)$ led to **21**, which was isolated as green blocks in 72% yield. Solution magnetic susceptibility measurements on **21** obtained in benzene solution by the method of Evans[54,55] gave $\mu_{eff} = 2.21\ \mu_B$, significantly higher than 1.73 μ_B, the spin-only value for one unpaired electron. The calculation of μ_{eff} employed Pascal's constants to correct for diamagnetic contributions to the susceptibility[56] but did not include any correction for temperature-independent paramagnetism (TIP). Magnetic susceptibility measurements on solid **21** were also performed from 5 to 300 K using a SQUID magnetometer.[56] The data (Figure 1) are indicative of a paramagnet, giving an excellent fit to the Curie–Weiss law over the temperature range measured. From the least-squares fit displayed in Figure 1 we obtain $\mu_{eff} = 1.66\ \mu_B$; this value was obtained upon inclusion of a parameter corresponding to the sum of all temperature-independent contributions to the susceptibility (see Experimental Section for details) and is, therefore, probably more useful than the value obtained by Evans' method (vide supra).

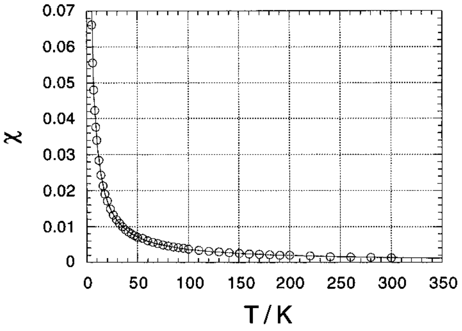


Figure 1. SQUID magnetic susceptibility data for solid $Ti(NRAr)_2(CH[SiMe_3]_2)$ (**21**) from 5 to 300 K fit to the Curie–Weiss law ($\mu = 1.66\ \mu_B$; see Experimental Section for details).

Compound **21** was characterized structurally by single-crystal X-ray diffraction; see Tables 1 and 2 and Figure 2 for selected metrical parameters and an ORTEP diagram. Overall, the most striking aspect of the structure is that one of the NRAr ligands adopts an η^3 bonding mode involving the nitrogen atom, the aryl ipso carbon, and one of the aryl ortho carbons. We have observed this bonding mode previously in the case of $Ti(NRAr)_3$. For $Ti(NRAr)_3$, however, *two* of the three NRAr ligands engage in η^3 bonding, a situation reminiscent of the η^3 bonding mode known for certain benzyl complexes. Given the arrangement of ligands in **21**, the complex can be regarded as an 11e complex, or as a 13e complex if an α-agostic interaction is invoked for the relatively planarized $CH[SiMe_3]_2$ ligand. We have no data indicating the presence of an α-agostic interaction for this complex. The η^1-NRAr ligand can be regarded as an anionic 4e donor ($1\sigma + 1\pi$), while the η^3-NRAr

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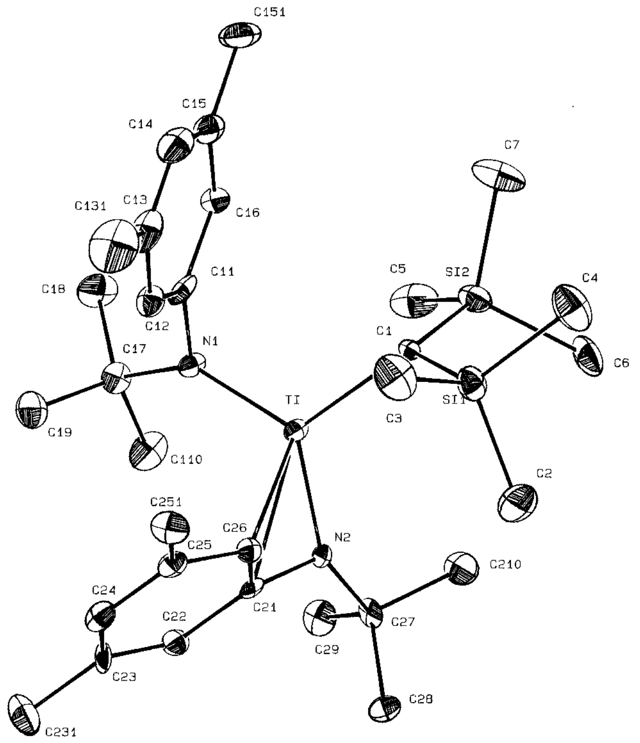

Figure 2. ORTEP drawing of $Ti(NRAr)_2(CH[SiMe_3]_2)$ (**21**) with ellipsoids at the 35% probability level.

Table 1. Selected Bond Lengths (Å) for $Ti(NRAr)_2(CH[SiMe_3]_2)$ (21)

Ti−N1	1.917(5)	Ti−N2	1.962(5)
Ti−C1	2.137(7)	Ti−C21	2.407(7)
Ti−C26	2.440(8)	Si1−C1	1.862(8)
N1−C17	1.493(8)	N2−C21	1.363(9)
N2−C27	1.506(8)	C24−C25	1.376(9)
C21−C22	1.427(9)	C21−C26	1.440(9)
C22−C23	1.35(1)	C25−C26	1.39(1)
C23−C24	1.41(1)		

Table 2. Selected Bond Angles (deg) for $Ti(NRAr)_2(CH[SiMe_3]_2)$ (21)

N1−Ti−N2	121.7(2)	Ti−N2−C27	143.8(5)
N1−Ti−C1	116.3(2)	C21−N2−C27	123.5(6)
N1−Ti−C21	107.3(2)	Ti−C1−Si1	118.8(4)
N1−Ti−C26	110.8(3)	Ti−C1−Si2	114.7(4)
N2−Ti−C1	117.0(3)	Ti−N1−C11	103.4(4)
N2−Ti−C21	34.5(2)	N2−Ti−C26	63.6(2)
C1−Ti−C21	135.5(2)	Ti−N1−C17	138.9(4)
C1−Ti−C26	115.4(3)	Ti−N2−C21	90.9(4)
C21−Ti−C26	34.5(2)	Ti−C21−N2	54.6(3)
Ti−C21−C22	136.4(5)	Ti−C21−C26	74.0(4)
Ti−C26−C21	71.5(4)	Ti−C26−C25	134.4(5)
Si1−C1−Si2	117.9(4)	C11−N1−C17	116.7(5)
N2−C21−C26	114.4(6)	N2−C21−C22	129.0(7)
C21−C26−C25	120.1(7)	C22−C21−C26	116.0(7)

ligand is also probably best regarded as an anionic 4e donor because its N atom is somewhat pyramidalized and thus it probably cannot donate strongly to titanium in the π sense. The η^3-NRAr ligand can, however, donate 2e from the C═C π system that interacts with the Ti center, an interaction expected to disrupt the aromaticity of the aryl substituent. C−C bond length alternation is accordingly observed (Table 1) for the interacting aryl ring, as was the case for the η^3-NRAr ligands in $Ti(NRAr)_3$. The Ti−C bond length in **21** is in a range typical of titanium(III) alkyl complexes.[57−59]

We decided initially to probe the reactivity of **21**, with organoazides. These, as we have shown recently, may sometimes serve as nitrogen atom donors. Initial experiments were disappointing in that, according to NMR spectroscopy of crude reaction mixtures, multiple products resulted. Seeking to temper the reactivity of **21** we examined its behavior in the presence of nitriles. This led to the discovery (Scheme 6) that benzonitrile reacts rapidly with **21** (ether, −35 °C), giving a color change to deep blue, presumably corresponding to formation of adduct **22**. Upon warming and stirring for 17 h at 28 °C, an orange crystalline material formulated as $(\mu\text{-NCPhCPhN})[Ti(NRAr)_2(CH[SiMe_3]_2)]_2$ (**23**) precipitated in 82% yield. Formulation of **23** as a nitrile-coupled product is in line with previous examples of such coupling modes mediated by titanium(III) and is consistent with NMR spectroscopic data for the complex.

Addition of excess pivalonitrile to dark green **21** (pentane, 28 °C) induced a color change to light green, presumably corresponding to adduct **24**. Subsequent addition of trimethylsilyl azide gave an orange-yellow solution from which an orange powder consisting of azide **25** was obtained in 37% yield. NMR spectroscopy of the crude reaction mixture suggested that azide **25** had formed in good yield; the low isolated yield we attribute to inefficient isolation. Azide **25** exhibits a characteristic $\nu(N_3)$ at 2107 cm^{-1} in its infrared spectrum.[60] In its ^{1}H NMR spectrum, diamagnetic **25** exhibits a single $SiMe_3$ resonance, which we attribute to the bis(trimethylsilyl)methyl ligand on the basis of its relative integral. Azide **25** arises formally from N_3 radical abstraction from trimethylsilyl azide by **21**. Abstraction of the N_3 radical from hindered organoazides by decamethylvanadocene has been noted previously.[61]

Concluding Remarks

In this paper we have reported on the synthesis of a variety of titanium(III) and -(IV) complexes bearing novel *N*-(*tert*-hydrocarbyl)anilide ligands, a class of ligands which we are developing for a myriad of applications. Herein we have shown that the reactivity of complexes supported by *N*-(*tert*-hydrocarbyl)anilide ligation can be altered profoundly via ortho-fluorine substitution or via variation of the hydrocarbyl substituent; consider the contrasting reactions of **2**, **6**, **10**, **13**, and **16** with methyl iodide. The work presented herein lays the groundwork for the preparation of new organometallic complexes of titanium(III) and -(IV) as exemplified by the preparation of complexes **21**, **6**, **7**, and **15**−**17**. Synthetic strategies involving titanium(IV) can be controlled by the use of dimethylamido ligands as protecting groups, as we have reported previously[43] and expanded upon herein. Synthetic strategies starting with titanium(III) utilize ate complexes, such as **18** and **20**, as pivotal precursors.

Experimental Section

Anhydrous diethyl ether, tetrahydrofuran, and toluene were purchased from Mallinckrodt; 1,2-dimethoxyethane was ob-

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tained from Fisher Scientific; benzene was purchased from J. T. Baker; *n*-pentane and *n*-hexane were purchased from EM Science. The ethereal solvents (diethyl ether, tetrahydrofuran, 1,2-dimethoxyethane) were distilled, under nitrogen, from purple sodium benzophenone ketyl. The aliphatic hydrocarbons and benzene were distilled, under nitrogen, from very dark blue to purple sodium benzophenone ketyl solubilized with a small quantity of tetraglyme. Toluene was refluxed over molten sodium for at least 2 days and then distilled under nitrogen. Chloroform was refluxed over potassium carbonate for at least 2 days before being distilled under nitrogen. Distilled solvents were transferred under vacuum into bombs before being pumped into a Vacuum Atmospheres drybox. Benzene-d_6 was degassed and dried over blue sodium benzophenone ketyl and transferred under vacuum into a storage vessel. Chloroform-*d* was degassed and dried over 4 Å sieves. Tetramethylethylenediamine (TMEDA), methyl iodide, and trimethylacetonitrile were degassed and distilled from calcium hydride. 2,6-Diisopropylphenol was degassed and distilled. 2,6-Di-*tert*-butylphenol was crystallized from diethyl ether. Sieves of 4 Å and alumina were dried in vacuo overnight at a temperature above 150 °C. $\mathrm{TiCl_3(THF)_3}$,[62,63] $\mathrm{TiCl(NMe_2)_3}$ (**8**),[46] $\mathrm{TiCl_2(NMe_2)_2}$ (**1**),[46] $\mathrm{LiCH(SiMe_3)_2}$,[64] $\mathrm{(CD_3)_2C{=}NAr}$,[47] HNRAr,[47] $\mathrm{HNRAr_F}$,[65] $\mathrm{Li(NRAr)(OEt_2)}$,[47] and $\mathrm{Li(NRAr_F)(OEt_2)}$[65] were prepared by standard procedures. Other chemicals were used as received. Magnetic susceptibilities were measured by the method of Evans.[54,55] ^{1}H and ^{13}C NMR spectra were recorded on Varian XL-300, Varian Unity-300, or Brucker AC-250 spectrometers. Chemical shifts are reported with respect to internal solvent (7.15 and 128.0 ppm for ^{1}H and ^{13}C NMR spectra, respectively, taken in benzene-d_6). ^{2}H NMR chemical shifts are reported with respect to external $\mathrm{C_6D_6}$ (taken as 7.15 ppm). EPR spectra were recorded on a Brucker ESP 300 spectrometer in sealed quartz tubes in toluene at either ambient temperature or low temperature by using a liquid nitrogen cooled nitrogen stream. Spectra were simulated using the program EPR-SIM. CHN analyses were performed by Oneida Research Services, Whitesboro, NY. Melting points were obtained in sealed glass capillaries and are uncorrected.

HNR′Ar. $\mathrm{(CD_3)_2C{=}NAr}$ (15.4 g, 92.2 mmol) was dissolved in $\mathrm{Et_2O}$ (20 mL) and chilled to −35 °C. Phenyllithium (145 mL of a 1.8 M solution in cyclohexane/ether, 261 mmol) was frozen solid and then was placed at 28 °C to thaw. Just as it became possible to stir, the imine solution was added to the partially-thawed LiPh solution. The reaction mixture was stirred for 23 h, at which time it was removed from the glovebox and slowly poured over ~300 mL ice contained in a 1 L Erlenmeyer flask. The organic layer was separated, and the aqueous layer was extracted with petroleum ether (~200 mL). The organic layer was filtered through a column of alumina (2 × 25 cm), and the solvent was removed in vacuo leaving a thick brown oil (16.75 g, 68.3 mmol, 74%). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 7.50 (d, 2H), 7.32 (t, 2H), 7.20 (m, 1H), 6.25 (s, 1H, para), 5.98 (s, 2H, ortho), 3.92 (s, 1H, NH), 2.10 (s, 6H, Ar*Me*).

Li(NR′Ar)(OEt₂). HNR′Ar (16.75 g, 68.25 mmol) was dissolved in pentane (60 mL), and the solution was chilled to −35 °C. *n*-Butyllithium (47 mL of a 1.6 M solution in hexanes, 75.7 mmol) was added via pipet as the solution was stirred. A thick brown oil precipitated 20 min after the addition. Addition of $\mathrm{Et_2O}$ (5.50 g, 74.3 mmol) elicited the formation of a white precipitate which was collected on a frit and dried in vacuo (9.24 g, 28.45 mmol, 42%). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 7.6 (br s, 2H), 7.15 (br s, 2H), 7.05 (s, 1H), 6.38 (br s, 2H), 5.95 (br s, 1H), 3.10 (q, 4H, $\mathrm{O(C}\mathit{H}_2\mathrm{CH_3)_2}$), 2.05 (br s, 6H, Ar*Me*), 0.94 (t, 6H, $\mathrm{O(CH_2C}\mathit{H}_3)_2$).

Compound 4: Ti(NRAr_F)₂(NMe₂)₂. A solution of $\mathrm{Li(NRAr_F)(OEt_2)}$ (3.00 g, 11.24 mmol) in ether (20 mL) at −30 °C was added to a stirring slurry of $\mathrm{Ti(NMe_2)_2Cl_2}$ (1.16 g, 5.61 mmol) in ether (40 mL) at −30 °C. The solution rapidly changed from brown-red to yellow with a large amount of white precipitate. The reaction was stirred for 14 h at 30 °C. Lithium chloride was removed by filtration through glass fibers to give a dark yellow filtrate, which was evaporated in vacuo and reconstituted in pentane (15 mL). Very large yellow-orange crystals of **4** were collected in two crops (2.20 g, 4.33 mmol, 77.2%; mp 127−129 °C). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 6.98 (d, 1H, Ar), 6.90 (dd, 1H, Ar), 6.65 (m, 1H, Ar), 3.075 (br s, 6H, N*Me*₂), 2.220 (s, 3H, Ar*Me*), 1.068 (s, 3H, $\mathrm{NC(CD_3)_2C}\mathit{H}_3$). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): δ 158.252 (d, J_{CF} = 239 Hz, C1), 138.297 (d, $^2J_{\mathrm{CF}}$ = 12.9 Hz, C2), 134.16 (d, J_{CH} = 159 Hz, C6 or C4), 131.640 (s, C5), 125.343 (d, J_{CH} = 158.9, C4 or C6), 114.902 (dd, J_{CF} = 23.4 Hz, J_{CH} = 160.1 Hz, C3), 60.796 (s, $\mathrm{N}\mathit{C}\mathrm{(CD_3)_2CH_3}$), 45.146 (q, J = 131 Hz, $\mathrm{NMe_2}$), 29.797 (q, J = 125.1 Hz, $\mathrm{NC(CD_3)_2}\mathit{C}\mathrm{H_3}$), 29.3 (m, $\mathrm{CD_3}$), 20.855 (q, J = 126.3, ArMe). Anal. Calcd for $\mathrm{C_{26}H_{30}D_{12}N_4F_2Ti}$: C, 61.40; H, 8.32; N, 11.02. Found C, 61.76; H, 8.73; N, 11.06.

Compound 5: Ti(NRAr_F)₂(NMe₂)(I). To a stirring yellow solution of $\mathrm{Ti(NRAr_F)_2(NMe_2)_2}$ (**4**, 1.91 g, 3.76 mmol) in THF (40 mL) was added MeI (5.63 g, 39.6 mmol). The reaction mixture slowly changed to a bright cherry red over 18 h. ^{1}H NMR was used to determine the extent of reaction by monitoring the disappearance of the dimethylamido peak at 3.075 ppm. The THF was removed in vacuo, and the red solids remaining were reconstituted in ether (10 mL). $\mathrm{[NMe_4]I}$ was removed by filtration through glass fibers, and the red solution was concentrated to a minimum amount. Two crops of crystals were collected and combined (**5**, 1.58 g, 2.67 mmol, 71%; mp 115−118 °C). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 6.933 (m, 1H, Ar), 6.830 (dd, 1H, Ar), 6.637 (m, 1H, Ar), 3.057 (s, 6H, $\mathrm{NMe_2}$), 2.057 (s, 6H, ArMe), 1.392 (s, 6H, $\mathrm{NC(CD_3)_2C}\mathit{H}_3$). ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$): δ 132.59 (s, para), 115.93 (d, $^2J_{\mathrm{CF}}$ = 23.2 Hz, ipso), ortho and meta broadened into base line, 63.62 (s, $\mathrm{N}\mathit{C}\mathrm{(CD_3)_2CH_3}$), 49.00 (s, $\mathrm{NMe_2}$), 30.106 (s, $\mathrm{C(CD_3)_2}\mathit{C}\mathrm{H_3}$), 29.589 (m, $\mathrm{C(}\mathit{C}\mathrm{D_3)_2CH_3}$), 20.652 (s, ArMe). Anal. Calcd for $\mathrm{C_{24}H_{24}D_{12}F_2N_3ITi}$: C, 48.74; H, 6.14; N, 7.10. Found: C, 48.98; H, 6.44; N, 6.98.

Compound 6: Ti(NRAr_F)₂(NMe₂)(CH₂SiMe₃). $\mathrm{Ti(NRAr_F)_2(NMe_2)(I)}$ (**5**, 0.5011 g, 0.8473 mmol) was dissolved in pentane (25 mL), and the solution was cooled to −30 °C. $\mathrm{LiCH_2SiMe_3}$ (0.85 mL, 1 M in pentane, 0.85 mmol) was added dropwise to the stirring solution. Precipitation of LiI with a concomitant color change to yellow-orange was observed over 3 h. LiI was removed by filtration through a medium frit. Volatile matter was removed from the filtrate in vacuo, and the resulting dark yellow oil was lyophilized with benzene (4 mL) providing a solid which was recrystallized from pentane (2 mL). Mustard yellow sheets were collected in two crops (**6**, 0.33 g, 0.60 mmol, 70%; mp 68−71 °C). ^{1}H NMR (250 MHz, $\mathrm{C_6D_6}$): δ 6.92 (m, 1H, Ar), 6.87 (d, 1H, Ar), 6.65 (m, 1H, Ar), 3.08 (s, 6H, $\mathrm{NMe_2}$), 2.12 (s, 6H, Ar*Me*), 1.31 (s, 6H, $\mathrm{NC(CD_3)_2C}\mathit{H}_3$), 1.19 (s, 2H, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$), 0.11 (s, 9H, $\mathrm{Si(CH_3)_3}$). ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$): δ 157.934 (d, J_{CF} = 242.4 Hz, C2), 135.863, 134.098, 132.502, 127.214, 115.894, 61.587 (s, $\mathrm{N}\mathit{C}\mathrm{(CD_3)_2CH_3}$ or $\mathit{C}\mathrm{H_2SiMe_3}$), 61.521 (s, $\mathrm{N}\mathit{C}\mathrm{(CD_3)_2CH_3}$ or $\mathit{C}\mathrm{H_2SiMe_3}$), 46.563 (s, $\mathrm{NMe_2}$), 30.262 (s, $\mathrm{NC(CD_3)_2}\mathit{C}\mathrm{H_3}$), 29.75 (m, $\mathrm{NC(}\mathit{C}\mathrm{D_3)_2CH_3}$), 20.769 (s, Ar*Me*), 3.408 (s, $\mathrm{SiMe_3}$). Anal. Calcd for $\mathrm{C_{28}H_{35}D_{12}N_3F_2SiTi}$: C, 60.95; H, 8.59; N, 7.62. Found: C, 61.18; H, 8.53; N, 7.37.

Compound 11: Ti(NRAr)(I)₂(OAr′). $\mathrm{TiCl(NMe_2)_3}$ (1.64 g, 7.63 mmol) was dissolved in $\mathrm{Et_2O}$ (40 mL) and chilled to −35 °C. $\mathrm{Li(NRAr)(OEt_2)}$ (2.00 g, 7.60 mmol) was added as a solid, causing a color change to greenish brown in about 30 s. After 3 h, LiCl was removed by filtration and the solvent was removed from the filtrate in vacuo, yielding a thin dark brown oil (**9**, 2.81 g) which was judged to be ~95% pure by ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 6.66 (s, 1H, para), 6.58 (s, 2H, ortho), 2.91 (s, 18H, N*Me*₂), 2.28 (s, 6H, Ar*Me*), 1.16 (s, 3H, $\mathrm{NC(CD_3)_2C}\mathit{H}_3$). The oil was dissolved in fresh $\mathrm{Et_2O}$ (5 mL). To

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the solution was added a solution of 2,6-diisopropylphenol (1.35 g, 7.58 mmol) in Et_2O (5 mL). The resulting solution was stirred for 18 h, and then the solvent was removed in vacuo, yielding a thick dark brown oil (**10**, 4.29 g) which was judged to be ~95% pure by ^1H NMR (250 MHz, $CDCl_3$): δ 7.02 (d, 2H, OAr′ meta), 6.8 (t, 1H, OAr′ para), 6.68 (s, 1H, para), 6.59 (s, 2H, ortho), 3.45 (sep, 2H, $C\mathit{H}(CH_3)_2$), 3.04 (s, 12H, $N\mathit{Me}_2$), 2.25 (s, 6H, Ar*Me*), 1.19 (m, 15H, $NC(CD_3)_2C\mathit{H}_3$ and $C\mathit{H}(CH_3)_2$). The crude **10** was dissolved in THF (50 mL) at 30 °C. Methyl iodide (10.70 g, 75.4 mmol) was added, and the reaction mixture was stirred for 9 h. The reaction mixture gradually turned from dark brown to a blood-red color. THF was removed in vacuo, and the resulting solids were triturated three times with hexane. $[NMe_4]I$ was removed by filtration, volatile matter was removed in vacuo, and the resulting solid residue was recrystallized from ether to give bright red/purple faceted crystals. Second and third crops were collected from pentane as dark red crystals (**11**, 3.28 g, 4.96 mmol, 65% overall; mp 130−134 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 7.21 (br s, 1H, Aryl), 7.09 (br s, 2H, Aryl), 7.08 (s, 2H, Aryl), 7.07 (s, 1H, Aryl), 3.66 (m, 2H, $C\mathit{H}(CH_3)_2$), 2.38 (s, 6H, Ar*Me*), 1.33 (s, 3H, $C(CD_3)_2C\mathit{H}_3$), 1.27 (d, 12H, $CH(C\mathit{H}_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.33 (s), 139.19 (s), 138.37 (d), 133.33 (d), 132.00 (d), 131.94 (s), 124.04 (d), 123.19 (d), 69.88 (s, $N\mathit{C}(CD_3)_2CH_3$); 29.38 (q, $NC(CD_3)_2\mathit{C}H_3$), 28.9 (m, $NC(\mathit{C}D_3)_2CH_3$), 27.19 (d, $\mathit{C}H(CH_3)_2$), 23.86 (q, $CH(\mathit{C}H_3)_2$), 21.21 (q, Ar*Me*). Anal. Calcd for $C_{24}H_{29}D_6NOI_2Ti$: C, 43.59; H, 5.33; N, 2.12. Found: C, 43.98; H, 5.47; N, 1.92.

Alkylation of 11 with $LiCH_2SiMe_3$. To a stirring solution of $Ti(NRAr)(I)_2(OAr')$ (**11**, 0.3004 g, 0.4545 mmol) in hexane (10 mL) at −35 °C was added $LiCH_2SiMe_3$ (0.0428 g, 0.4546 mmol) in hexane (5 mL). The solution rapidly turned orange with the formation of a white precipitate. The reaction mixture was stirred for 20 min, at which time it was filtered. The filtrate was concentrated to a minimum volume. Microcrystals of $Ti(NRAr)(I)(OAr')(CH_2SiMe_3)$ were obtained in low yield, though ^1H NMR spectroscopy indicated quantitative reaction. ^1H NMR (250 MHz, $CDCl_3$): δ 7.1 (m, 6H, aryls), 3.72 (septet, 2H, $C\mathit{H}(CH_3)_2$), 2.39 (s, 6H, Ar*Me*), 2.24 (d, 1H, $C\mathit{H}aHbSiMe_3$), 1.38 (d, 6H, $CH(C\mathit{H}_3)_2$), 1.22 (m, 7H, $CHa\mathit{H}bSiMe_3$ and $CH(C\mathit{H}_3)_2$), 1.10 (s, 3H, $C(CD_3)_2C\mathit{H}_3$), −0.09 (s, 9H, $Si\mathit{Me}_3$).

Alkylation of 11 with $LiCH_2CMe_2Ph$. $Ti(NRAr)(I)_2(OAr')$ (**11**, 1.04 g, 1.57 mmol) was dissolved in hexane (25 mL) and chilled to −30 °C. Lithium neophyl (0.2205 g, 1.573 mmol) was added, causing a rapid color change to a light red-brown. After 15 min of stirring, LiI was removed as a grey solid by filtration of the mixture through a sintered glass frit. The filtrate was concentrated to dryness in vacuo, leaving a thick orange-red oil. The oil was lyophilized (benzene) and subsequently crystallized from pentane to give red-orange waxy crystals of $Ti(NRAr)(I)(OAr')(CH_2CMe_2Ph)$ (0.5161 g, 49.3%; mp 75−77 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 7.3 (br s, 1H, ortho), 7.05 (m, 9H, aryls), 6.7 (br s, 1H, ortho), 3.82 (sep, 2H, $C\mathit{H}(CH_3)_2$), 2.41 (br s, 6H, Ar*Me*), 2.35 (d, 1H, $C\mathit{H}aHbC(CH_3)_2Ph$), 2.07 (d, 1H, $CHa\mathit{H}bC(CH_3)_2Ph$), 1.36 (d, 6H, $CH(C\mathit{H}_3)_2$), 1.32 (s, 3H, $CHaHbC(C\mathit{H}_3)_2Ph$), 1.24 (s, 3H, $CHaHbC(C\mathit{H}_3)_2Ph$), 1.09 (s, 3H, $C(CD_3)_2C\mathit{H}_3$).

Compound 12: $Ti(NR'Ar)(NMe_2)_3$. $TiCl(NMe_2)_3$ (1.50 g, 6.97 mmol) was dissolved in THF (50 mL) and chilled to −35 °C. $Li(NR'Ar)(OEt_2)$ (2.27 g, 6.98 mmol) was added as a powder. The solution changed color rapidly from brown to a darker, green-brown. The reaction mixture was stirred for 12 h, and then the solvent was removed in vacuo. The mixture was reconstituted using pentane (~50 mL) and filtered through a frit, giving a yellow-brown filtrate from which volatile material was removed in vacuo, leaving a thin oil. Lyophilization twice from benzene to remove residual THF, followed by recrystallization from pentane (8 mL), afforded a green-brown powder (**12**, 2.445 g, 5.76 mmol, 82.6%; mp 32.5-33.5 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 7.21 (d, 2H), 7.06 (t, 2H), 6.95 (t, 1H), 6.29 (s, 1H), 5.96 (s, 2H), 2.77 (s, 18H, $N\mathit{Me}_2$), 1.88 (s, 6H, Ar*Me*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.056, 148.716, 136.578, 127.64, 126.44, 125.48, 124.09, 123.57. 45.09, 30.64, 21.46. MS (70 eV): *m/z* (%) 424 (0.9) [M^+]. Anal. Calcd for $C_{23}H_{32}D_6N_4Ti$: C, 65.08; H, 9.02; N, 13.20. Found: C, 65.29; H, 9.02; N, 13.17.

Compound 13: $Ti(NR'Ar)(NMe_2)_2(OAr'')$. $Ti(NR'Ar)(NMe_2)_3$ (**12**, 1.4274 g, 3.3622 mmol) was dissolved in Et_2O (20 mL), and the solution was cooled to −35 °C in a round bottom flask. 2,6-Di-*tert*-butylphenol (0.6937 g, 3.362 mmol) was dissolved in Et_2O (10 mL), cooled to −35 °C and then added to the solution. The green-brown reaction mixture changed to a reddish orange color after 3 h. ^1H NMR spectroscopy at this point revealed the presence of a considerable amount of unreacted **12**. After 19.5 h reaction time, the solvent was removed in vacuo to give a bright cherry-red foam. The foam was redissolved in pentane (ca. 3 mL), resulting in crystallization of the desired product as an orange powder at room temperature. A second crop of powder resulted upon cooling a concentrated solution for several days at −35 °C (**13**, 1.626 g, 2.776 mmol, 82.6%; mp 130−131 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 7.593 (d, 2H, $J = 7.58$ Hz), 7.3450 (t, 2H, $J = 7.56$ Hz), 7.25 (t, 3H, $J = 7.8$ Hz), 6.799 (t, 1H, $J = 7.8$ Hz), 6.5057 (s, 1H, para), 6.4372 (s, 2H, ortho), 3.0153 (s, 12H, $N\mathit{Me}_2$), 1.9116 (s, 6H, Ar*Me*), 1.4842 (s, 18H, $C(C\mathit{H}_3)_3$)). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.565 (s), 150.438 (s), 146.383 (s), 140.229 (s), 138.920 (s), 127.922 (d), 126.513 (d), 125.745 (d), 125.254 (d), 124.379 (d), 120.755 (d), 119.236 (d), 65.8920 (s, $N\mathit{C}(CD_3)_2C_6H_5$), 47.9519 (q, $N\mathit{Me}_2$), 35.4817 (s, $\mathit{C}(CH_3)_3$), 31.6 (m, CD_3), 31.0918 (q, $C(\mathit{C}H_3)_3$), 21.5033 (q, Ar*Me*). MS (70 eV): *m/z* (%) 585 (0.5) [M^+]. Anal. Calcd for $C_{35}H_{47}D_6N_3OTi$: C, 71.77; H, 9.12; N, 7.17. Found: C, 72.25; H, 8.94; N, 6.75.

Compound 14: $Ti(NR'Ar)(NMe_2)(OAr'')(I)$. $Ti(NR'Ar)(NMe_2)_2(OAr'')$ (**13**, 0.7363 g, 1.257 mmol) was dissolved in Et_2O (45 mL), and the solution was cooled to −35 °C in a round bottom flask. Methyl iodide (1.92 g, 13.5 mmol) was added, the flask was stoppered, and the reaction mixture was stirred overnight. Monitoring by ^1H NMR spectroscopy indicated almost no conversion to product at that point in time. It was thought that MeI was escaping from the stoppered flask. The reaction mixture was transferred to a glass bomb, additional MeI was added, and the reaction mixture was stirred (and monitored by ^1H NMR) for 48 h. A large amount of white precipitate formed, but there was no noticeable color change. The solvent was then removed in vacuo, the product was extracted with pentane, and Me_4NI was removed with a medium frit. The solution was concentrated down to about 4 mL, when small microcrystals became apparent in the solution. Cooling overnight at −35 °C yielded a cake of orange microcrystalline powder (**14**, 0.7952 g, 1.189 mmol, 94.6 %; mp 57−59 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 7.4 (tm, $J \sim 5.4$ Hz, 2H), 7.331 (d, $J = 7.8$ Hz, 2H), 7.237 (dm, $J \sim 4.2$ Hz, 3H), 6.912 (t, $J = 7.8$ Hz, 1H), 6.850 (s, 1H, para), 6.408 (s, 2H, ortho), 2.859 (s, 6H, $N\mathit{Me}_2$), 2.180 (s, 6H, Ar*Me*), 1.620 (s, 18H, $C(C\mathit{H}_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.424, 144.226, 142.433, 138.998, 137.546, 129.049, 128.891, 127.820, 127.145, 126.979, 125.765, 120.894, 68.955 ($N\mathit{C}(CD_3)_2C_6H_5$), 49.836 ($N\mathit{Me}_2$), 35.730 ($\mathit{C}(CH_3)_3$), 32.414 ($C(\mathit{C}H_3)_3$), 31.0 ($\mathit{C}D_3$), 21.101 (Ar*Me*). MS (70 eV): *m/z* (%) 667.9 (0.19) [M^+]. Anal. Calcd for $C_{33}H_{41}D_6IN_2OTi$: C, 59.29; H, 7.09; N, 4.19. Found: C, 58.98; H, 7.34; N, 3.88.

Compound 17: $Ti(NR'Ar)(\mathit{O}\text{-}2,6\text{-}C_6H_3[^tBu][CMe_2CH_2])(I)$. A solution of **14** (1.3206 g, 1.9752 mmol) in pentane (40 mL) was chilled to −40 °C. Neopentyllithium (0.1543 g, 1.9761 mmol) was added as a solution in ether. The reaction mixture changed from red to yellow over ca. 5 min. The solution was stirred 18 h, and the yellow-brown solution was then filtered to remove lithium iodide. A proton NMR spectrum of the crude product indicated a relatively clean conversion to the desired neopentyl complex **15**, but attempts to crystallize this species proved futile. The ether was removed in vacuo, and THF (40 mL) was added. The mixture was heated at 65 °C for 2 h. A proton NMR spectrum of an aliquot taken at this time indicated ca. 50% conversion to the cyclometalated dimethylamide compound **16**. Further heating at 65 °C resulted in clean production of **16**. THF was removed in vacuo, and ether (60 mL) and MeI (2.90 g, 20.4 mmol, 10.3 equiv) were added. No reaction occurred at room temperature according to the ^{1}H NMR spectrum of an aliquot, so the mixture was heated to 70 °C for 21 h. Precipitate was observed, but no color change was evident. The ^{1}H NMR spectrum of an aliquot showed no resonance attributable to a dimethylamide function. The solvent was removed from the mixture in vacuo. The solid residue thus obtained was extracted with pentane, $[Me_4N]I$ was removed by filtration from the extract, and the filtrate was concentrated. Crystals were obtained after storing the filtrate overnight at −35 °C (**17**, 0.7668 g, 1.230 mmol, 62.3%; mp 102-103 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, J = 7.59 Hz, 2H), 7.393 (t, J = 7.04 Hz, 2H), 7.295 (t, J = 6.7 Hz, 1H), 7.174 (d, J = 7.71 Hz, 1H), 7.0235 (d, J = 7.71 Hz, 1H), 6.90 (s, 1H, para), 6.879 (t, $J \sim 10$ Hz, 1H), 6.708 (s, 2H, ortho), 2.202 (s, 6H, Ar*Me*), 1.470 (d, J = 11.7 Hz, 1H, C*H*$_2$-a), 1.320 (s, 9H, $C(CH_3)_3$), 0.9836 (s, 6H, $C(CH_3)_2Ar$), 0.833 (d, J = 11.7 Hz, C*H*$_2$-b). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.818, 146.038, 143.338, 139.764, 139.345, 136.051, 130.326, 129.281, 127.914, 126.766, 124.759, 124.577, 122.270, 122.070, 65.842, 46.410, 35.304, 32.578, 32.046, 30.603, 28.2, 25.455, 21.202. 15.259. Anal. Calcd for $C_{31}H_{34}D_6INOTi$: C, 59.72; H, 6.47; N, 2.25. Found: C, 60.19; H, 6.98; N, 1.92.

Compound 19: $Ti(NR'Ar)_2Cl_2$. $TiCl_3(THF)_3$ (1.00 g, 2.70 mmol) and TMEDA (1.94 g, 16.7 mmol) were added to THF (100 mL) to form a bright blue solution. $Li(NR'Ar)(OEt_2)$ (1.76 g, 5.41 mmol) was added, causing the solution to become olive-green. The solvent was removed from the mixture in vacuo, the solid residue was extracted with ether, and the extract was filtered. Yellow green crystals consisting of ate complex **18** were collected from the concentrated filtrate at −35 °C (2.28 g). A large excess of $CDCl_3$ (1.48 g) was added to an olive-green ether solution of **18** (0.17 g). The solution turned blood-red. Integration of the ^{1}H NMR spectrum of an aliquot indicated the presence of 3 equiv of TMEDA per titanium. The solvent was removed in vacuo, and the crude product thus obtained was extracted with benzene. The extract was filtered through glass fibers and evaporated to dryness yielding a dark red microcrystalline powder (0.10 g). The red solid was recrystallized by vapor diffusion of pentane into toluene followed by cold storage overnight; mp 155−160 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (d, 2H, aryl ortho), 7.28 (m, 4H, aryl meta, para), 6.56 (s, 2H, para), 5.62 (s, 4H, ortho), 1.93 (s, 12H, ArMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.700, 143.119, 137.286, 128.699, 127.812, 126.841 (may be 2 carbons), 123.475, 71.2 ($NC(CD_3)_2Ar$), 28.7 (CD_3), 21.094 (Ar*Me*). Anal. Calcd for $C_{34}H_{28}D_{12}Cl_2N_2Ti$: C, 67.22; H, 6.64; N, 4.61. Found: C, 67.00; H, 6.69; N, 4.28.

Compound 20: $(ArRN)_2Ti(\mu\text{-}Cl)_2Li(TMEDA)$. $TiCl_3(THF)_3$ (1.00 g, 2.70 mmol) was slurried in THF (100 mL). TMEDA (1.92 g, 6.13 eq) was added, generating a blue solution. A solution of $Li(NRAr)(OEt_2)$ (1.43 g, 5.44 mmol) in THF (50 mL) was added to the $TiCl_3(THF)_3$/TMEDA mixture, causing a rapid color change to bright green. After 5 min, the shade of green changed to olive. Volatile material was removed in vacuo, and the residual oil was triturated twice with pentane. The residue was then extracted with pentane, and the extract was filtered to remove LiCl. The filtrate was stored at −30 °C overnight, giving bright green needles (**20**, 0.93 g, 56.9%; mp 137−138 °C). ^{2}H NMR (46 MHz, C_6H_6): δ 3.809; $\Delta\nu_{1/2}$ = 18.5 Hz. μ_{eff} (300 MHz, C_6D_6, 25 °C) = 2.22 μ_B. UV−vis (hexane): λ_{max} (ϵ) 780 nm (188 M^{-1} cm^{-1}). EPR (298 K, toluene): g = 1.95. EPR (103 K, toluene): g_1 = 1.980; g_2 = 1.964; g_3 = 1.930; this spectrum is approximately axial with broad linewidths (~25 G) that merge g_1 and g_2 into one feature. Anal. Calcd for $C_{30}H_{40}D_{12}Cl_2N_2LiTi$: C, 59.40; H, 8.64; N, 9.24. Found: C, 58.97; H, 8.44; N, 8.46.

Reaction of 20 with Chloroform. A small amount of $(ArRN)_2Ti(\mu\text{-}Cl)_2Li(TMEDA)$ (**20**) was added to $CDCl_3$, giving a red solution. A ^{1}H NMR spectrum of the solution was consistent with clean formation of $Ti(NRAr)_2Cl_2$. ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.877 (s, 2H, para), 6.363 (s, 4H, ortho), 2.262 (s, 12H, Ar*Me*), 1.263 (s, 6H, $C(CD_3)_2CH_3$), 2.389 (s, 4H, TMEDA methylene), 2.20 (s, 12H, TMEDA methyl).

Compound 21: $Ti(NRAr)_2(CH[SiMe_3]_2)$. A solution of **20** (1.1385 g, 1.8770 mmol) in pentane (50 mL) was cooled to −35 °C prior to treatment with $LiCH(SiMe_3)_2$ (0.3123 g, 1.877 mmol), which was added as a solid. The reaction mixture adopted a dark green color. The reaction mixture was stirred for 15 min and then filtered to remove LiCl (0.1348 g, 3.186 mmol, 1.7 equiv). The dark green filtrate was concentrated to ca. 20 mL and stored at −35 °C. Dark green blocklike crystals were obtained in two crops (**21**, 0.7755 g, 1.356 mmol, 72.3%; mp 134−135 °C). ^{2}H NMR (46 MHz, C_6H_6): δ 3.968; $\Delta\nu_{1/2}$ 17.9 Hz. μ_{eff} (300 MHz, C_6D_6, 25 °C) = 2.21 μ_B. UV−vis (ether): λ_{max} (ϵ) = 663 nm (407 M^{-1} cm^{-1}). EPR (298 K, toluene): g = 1.95. EPR (95 K, toluene): g_1 = 1.997; g_2 = 1.962; g_3 = 1.918. Anal. Calcd for $C_{31}H_{43}D_{12}N_2Si_2Ti$: C, 65.10; H, 9.69; N, 4.90. Found: C, 65.36; H, 9.76; N, 4.67.

SQUID Magnetic Measurements on $Ti(NRAr)_2(CH[SiMe_3]_2)$ (21). Measurements were made using a Quantum Design SQUID magnetometer. The magnetometer uses the MPMSR2 software (Magnetic Property Measurement System Revision 2). Data were recorded at a field strength of 5000 G. Gel caps (Gelatin Capsule No. 4 Clear), and straws were ordered from Quantum Design, Inc. Samples of **21** for magnetic measurements were prepared in the drybox as described above. The solid compound was placed into a preweighed gel cap, and a preweighed plug of Parafilm was inserted above it to keep it in place. The mass of the **21** sample was then ascertained by weighing the loaded gel cap. The loaded gel cap was mounted in a straw, and the straw was placed in an N_2-filled vessel for transport to the magnetometer. The straw was placed on the end of a rod for insertion into the magnetometer. The field and temperature were adjusted to 5000 G and 5 K, respectively. Once the temperature had equilibrated and the field was stable, the sample was centered. This was done by running a full length DC scan, adjusting the position automatically and then recentering using a DC centering scan. During the run, measurements were taken over the following temperature ranges with the indicated increments: 5−10 K (one data point every 1 K), 12−20 K (one data point every 2 K), 23−50 (one data point every 3 K), 55−100 (one data point every 5 K), 110−200 (one data point every 10 K), 220-300 (one data point every 20 K). The run required approximately 5 h.

The data for **21** fit the Curie−Weiss law in the temperature range 5−300 K (R = 0.999 99). The calculated curve (Figure 1) is the best least-squares fit of the observed susceptiblity data to the equation $\chi_M(\text{obs}) = ((\mu^2)/(7.997584(T - \theta))) - C$. The value of μ obtained in this manner was 1.66 μ_B, to be compared with the spin-only value for one unpaired electron, 1.73 μ_B. In the least-squares fit, carried out using the general curve-fitting routine included with the program Kaleidagraph, both θ and C were treated as variable parameters. The obtained value of θ, the Weiss constant, was −0.194 74 K. The value of the constant C, included to represent the sum of all temperature-independent contributions to the total observed susceptibility, including the diamagnetic correction and TIP, was −0.000 241 39.

X-ray Structure of $Ti(NRAr)_2(CH[SiMe_3]_2)$ (21). A crystal of approximate dimensions 0.50 × 0.23 × 0.20 mm was obtained from a chilled ether solution. The crystal was mounted on a glass fiber. Data were collected at −86 °C on an Enraf-Nonius CAD-4 difractometer with graphite-monochromated Mo Kα radiation. A total of 4774 reflections were collected to a 2θ value of 44.9°, 4446 of which were unique (R_{int} = 0.098); equivalent reflections were merged. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically, except C26, which was refined isotropically. The final cycle of least-squares refinement was based on 2735 observed reflections ($I > 3.00\sigma(I)$) and 320 variable parameters and converged (largest parameter shift was 0.01 times its esd) with $R = 0.075$ and $R_w = 0.065$. A final difference Fourier map showed no chemically significant features. Crystal data are $a = 10.644(2)$ Å, $b = 10.844(2)$ Å, $c = 16.718(4)$ Å, $V = 1713(2)$ Å^3, $\alpha = 100.48(3)°$, $\beta = 95.86(3)°$, $\gamma = 113.11(3)°$, space group $P\bar{1}$ (No. 2), $Z = 2$, $M_r = 571.92$ for $C_{31}H_{43}D_{12}N_2Si_2Ti$, and ρ(calcd) = 1.109 g/cm^3. See Tables 1 and 2 and Figure 2 for metrical parameters and an ORTEP diagram; complete data tables have been deposited as Supporting Information.

Compound 23: (μ-NCPhCPhN)[Ti(NRAr)$_2$(CH[SiMe$_3$]$_2$)]$_2$. Ti(NRAr)$_2$[CH(SiMe$_3$)$_2$] (**21**, 0.4257 g, 0.7444 mmol) was dissolved in ether (20 mL), and the solution was cooled to −35 °C. Benzonitrile (100 mL, 0.7534 mmol) was added over approximately 5 min, eliciting a rapid color change to deep dark blue, a color we attribute to formation of paramagnetic adduct **22**. ^{2}H NMR (46 MHz): δ 4.671, 1.86; $\Delta\nu_{1/2} = 20$ Hz, 17 Hz. The 1.86 ppm peak, attributable to diamagnetic **23**, emerged noticeably over a 10 min period. After stirring 17 h, an orange powder which had precipitated was collected on a frit (**23**, 0.4212 g, 0.6130 mmol, 82%). The powder was essentially insoluble in pentane and ether but could be recrystallized from hot THF; mp 180 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ 8.039 (br s, 2H, para), 7.28 (m, 8H, ortho/meta), 6.587 (s, 4H, paras), 6.397 (br s, 8H, orthos), 2.159 (s, 24H, Ar*Me*), 1.439 (s, 2H, C*H*[SiMe$_3$]$_2$), 1.210 (s, 12H, C(CD$_3$)$_2$C*H*$_3$), 0.443 (s, 36H, Si*Me*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 173.115 (s, *C*=N), 148.112 (s), 143.462 (s), 135.773 (s), 129.878 (d), 129.441 (d), 128.037 (d), 127.458 (d), 127.140 (d), 77.206 (d, *C*H(SiMe$_3$)$_2$), 62.380 (s, *C*(CD$_3$)$_2$CH$_3$), 30.628 (q, C(CD$_3$)$_2$*C*H$_3$), 30.065 (m, C(*C*D$_3$)$_2$CH$_3$), 21.408 (q, Ar*Me*), 6.181 (q, SiMe$_3$). Anal. Calcd for $C_{76}H_{96}D_{24}N_6Si_4Ti_2$: C, 67.61; H, 8.96; N, 6.22. Found: C, 68.05; H, 9.26; N, 6.13.

Compound 25: Ti(NRAr)$_2$(CH[SiMe$_3$]$_2$)(N$_3$). Ti(NRAr)$_2$(CH[SiMe$_3$]$_2$) (**21**, 0.7124 g, 1.245 mmol) was dissolved in pentane (40 mL). *tert*-Butyl nitrile (575 mL, 5.20 mmol, 4 equiv) was added, causing a color change to a light green, presumably corresponding to adduct **24**. Trimethylsilyl azide (230 mL, 1.733 mmol, 1.4 equiv) was then added, and the solution was stirred overnight (after about 2 h the solution had adopted an orange-yellow color). Volatile material was removed in vacuo, and the waxy solid thus obtained was recrystallized from pentane to give a light orange powder (**25**, 0.2852 g, 0.4645 mmol, 37%; mp 147−148 °C (dec. with bubbling)). ^{1}H NMR (300 MHz, C_6D_6): δ 6.839 (br s, 4H, ortho), 6.708 (s, 2H, para), 2.50 (s, 1H, C*H*(SiMe$_3$)$_2$), 2.213 (s, 12H, Ar*Me*), 1.251 (s, 6H, C(CD$_3$)$_2$C*H*$_3$), 0.222 (s, 18H, Si*Me*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 146.815 (s, ipso), 137.629 (s, meta), 128.247 (d, J = 157.3 Hz), 128.201 (d, J = 157.4 Hz), 98.1749 (d, J = 90.85 Hz, *C*H(SiMe$_3$)$_2$), 63.6716 (s, *C*(CD$_3$)$_2$CH$_3$), 30.3523 (q, J = 125.9 Hz, C(CD$_3$)$_2$*C*H$_3$), 29.8439 (m, C(*C*D$_3$)$_2$CH$_3$), 21.3200 (q, J = 126.4 Hz, Ar*Me*), 4.2006 (q, J = 118.2 Hz, Si*Me*$_3$). IR (16 scans, 2.0 cm^{-1}, THF): ν(N$_3$) 2107 cm^{-1}. Anal. Calcd for $C_{31}H_{43}D_{12}N_5Si_2Ti$: C, 60.64; H, 9.03; N, 11.41. Found: C, 60.75; H, 9.07; N, 11.05.

Compound 26: Ti(NRAr)$_2$(CH[SiMe$_3$]$_2$)(I). Ti(NRAr)$_2$(CH[SiMe$_3$]$_2$) (**21**, 0.4034 g, 0.7054 mmol) was dissolved in benzene (5 mL). Iodine (0.0900 g, 0.3546 mmol, 0.5 equiv) was slurried in benzene (5 mL), and the slurry was added to the solution of **21**. The reaction mixture adopted a dark orange-red color. Volatile material was removed from the reaction mixture in vacuo, giving a light orange powder. Crystals were obtained from a concentrated ether solution (**26**, 0.3329 g, 0.4764 mmol, 67.5%; mp 175−176 °C). ^{1}H NMR (300 MHz, C_6D_6): δ 6.938 (br d, J = 71.9 Hz, 4H, ortho), 6.710 (s, 2H, para), 3.466 (s, 1H, C*H*(SiMe$_3$)$_2$), 2.184 (s, 12H, Ar*Me*), 1.404 (s, 6H, C(CD$_3$)$_2$C*H*$_3$), 0.393 (s, 18H, Si*Me*$_3$). ^{13}C NMR (125 MHz, CDCl$_3$): δ 145.972 (s, ipso), 137.682 and 137.085 (s, meta), 128.594 and 127.971 (d, ortho and meta), 112.023 (d, para), 104.010 (d, J = 90.6 Hz, *C*H(SiMe$_3$)$_2$), 65.306 (s, N*C*(CD$_3$)$_2$CH$_3$), 30.394 (q, NC(CD$_3$)$_2$*C*H$_3$), 30.074 (m, NC(*C*D$_3$)$_2$CH$_3$), 21.274 (q, Ar*Me*), 5.857 (q, Si*Me*$_3$). Anal. Calcd for $C_{31}H_{43}D_{12}IN_2Si_2Ti$: C, 53.28; H, 7.93; N, 4.01. Found: C, 53.66; H, 7.90; N, 3.84.

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Supporting Information Available: Tables of positional and thermal equivalent parameters, anisotropic thermal parameters, intramolecular distances, bond angles, and torsion angles for Ti(NRAr)$_2$(CH[SiMe$_3$]$_2$) (**21**) (12 pages). Ordering information is given on any current masthead page.

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