Synthesis and Reactivity of d^0 Alkyl, Silyl, and Hydride Complexes of Titanium and Zirconium Featuring an Aryl-Substituted Tripodal Triamido Ligand Derived from *cis,cis*-1,3,5-Triaminocyclohexane

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Zirconium and titanium complexes containing the new chelating triamido ligand [*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]$^{3-}$ (**1**) are reported. The chloride complexes [*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]TiCl (**2**) and [*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrCl (**3**) were prepared by reaction of TiCl$_4$(THF)$_2$ and ZrCl$_4$, respectively, with [**1**]Li$_3$ (prepared in situ). The diethyl ether adduct of **3** (**3**·OEt$_2$) was crystallographically characterized. The alkyl complexes [*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrCH$_2$SiMe$_3$ (**4**) and [*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrCH$_2$Ph (**5**) were prepared by reaction of the triamine ([**1**]H$_3$) with Zr(CH$_2$SiMe$_3$)$_4$ and Zr(CH$_2$Ph)$_4$, respectively. The aryl complexes [*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrPh (**6**) and [*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrMes (**7**, Mes = 2,4,6-Me$_3$C$_6$H$_2$) were prepared by the reaction of **3** with PhLi and MesLi, respectively. Similarly, [*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]TiMe (**8**) was prepared by the reaction of **2** with MeMgBr. The alkyl and aryl complexes **4**−**8** did not react with hydrosilanes to give isolable silyl complexes. The titanium and zirconium silyl complexes [*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]TiSi(SiMe$_3$)$_3$ (**9**), [*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrSi(SiMe$_3$)$_3$ (**10**), [*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]TiSiHMes$_2$ (**11**), and [*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrSiHMes$_2$(THF) (**12**) were prepared by the reaction of the corresponding titanium and zirconium chloride complexes with either KSi(SiMe$_3$)$_3$ or LiSiHMes$_2$(THF)$_2$. Although the alkyl and aryl complexes **4**−**8** did not react appreciably with H$_2$ (1 atm), the silyl complexes **9** and **10** reacted with H$_2$ (1 atm) over the course of only a few minutes to give d^0 hydride products. Hydrogenolysis of **9** yielded the monohydride complex [*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]TiH (**13**), which was characterized in solution. Complex **13** readily inserted 1-hexene to give the hexyl insertion product [*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]TiHex (**14**). Hydrogenolysis of **10** yielded a mixture of monomeric and dimeric hydride products, [*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrH (**17a**) and {[*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrH}$_2$ (**17b**), both of which were characterized in solution. Upon addition of 1 equiv of PMe$_3$, a mixture of **17a** and **17b** reacted to give the adduct [*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrH(PMe$_3$) (**15**), which binds PMe$_3$ reversibly in solution. In the presence of 1-hexene, the mixture of **17a** and **17b** was readily converted to the hexyl insertion product, [*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrHex (**16**). The hydride species **13** and **17a**/**17b** undergo H/D exchange with D$_2$ but exhibit low reactivities toward hydrosilanes.

Introduction

Electron-deficient early-transition-metal complexes are known to mediate a number of bond-making and bond-breaking transformations and catalyze reactions such as olefin polymerization,[1−4] hydrogenation,[5−7] hydrosilylation,[8−11] alkane activation,[12−15] and dehydropolymerization.[16−19] In many of these processes, the activity of the catalyst is derived from electrophilicity

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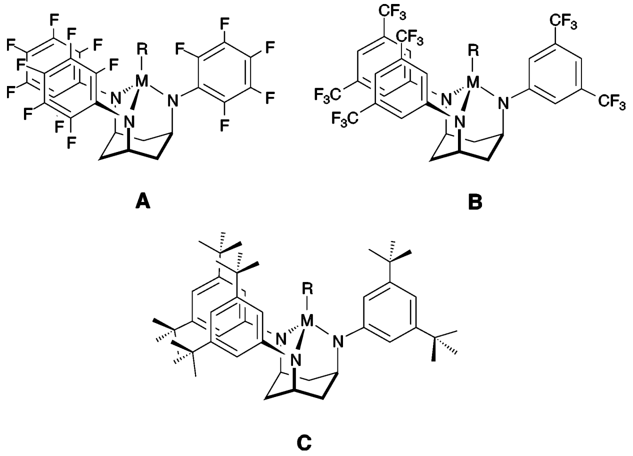
and coordinative unsaturation at the metal center, and these factors may be controlled via changes in the electronic and steric characteristics of the ancillary ligands.[4,20,21] Although much of the work involving electron-deficient early-metal complexes has featured cyclopentadienyl (Cp)-derived ligands, interest in furthering the utility of these catalytic processes has led to the development of new ancillary ligand systems capable of stabilizing electrophilic metal species in novel coordination environments.[2,22−24]

In this context, we have recently begun to study the reactivity of d^0 transition-metal silyl and hydride complexes supported by non-Cp ancillary ligands, especially those featuring imido and amido donor groups, as potential catalysts and catalyst precursors for the dehydropolymerization of silanes.[25−35] Previous work in our group has established that d^0, group 4 metal silyl and hydride complexes featuring Cp-derived ligands are among the best dehydropolymerization catalyst precursors known to date, and mechanistic studies have indicated that this dehydrocoupling chemistry occurs via σ-bond metathesis steps involving the activation of Si−H bonds by d^0 hydride species.[18,36−38] On the basis of these studies, we anticipated that complexes featuring non-Cp ligand systems might also represent interesting candidates for investigation.[38] Particular interest has focused on the development of new ligands that will allow access to monomer-stabilized d^0 hydride derivatives, while rendering the metal center coordinatively unsaturated and highly electrophilic.

Toward this end, we recently reported the synthesis and initial studies of a series of zirconium complexes containing the new chelating triamido ligands [*cis*,*cis*-1,3,5-$(C_6F_5N)_3C_6H_9]^{3-}$ and {*cis*,*cis*-1,3,5-$[3,5\text{-}(CF_3)_2C_6H_3\text{-}N]_3C_6H_9\}^{3-}$ (Chart 1, **A** and **B**), both of which are derived from *cis*,*cis*-1,3,5-triaminocyclohexane (tach).[35] In developing this ligand system we considered that a triamido ligand based on a cyclohexane framework might support particularly reactive early-transition-metal complexes, due in part to the rigidity of the constrained cyclohexane backbone and the small chelate bite angles, which should enforce a relatively “open” coordination sphere, leaving the electrophilic metal center accessible to small molecule reactants. We sought to employ sterically demanding, electron-withdrawing aryl substituents on the donor nitrogens in order to foster electrophilicity at the metal and suppress dimerization of the resulting complexes.

Chart 1. Examples of Aryl-Functionalized *cis*,*cis*-1,3,5-Triaminocyclohexane (tach)-Derived Ligand Architectures



Initial results indicated that tach derivatives functionalized with fluorinated arene substituents, such as C_6F_5 or $3,5\text{-}(CF_3)_2C_6H_3$ groups, could be readily prepared. The fluorinated ligands gave rise to highly Lewis acidic d^0 metal complexes that, in many cases, irreversibly coordinated additional electron-donating ligands such as diethyl ether or THF, ultimately rendering the metal centers less electrophilic. When reactive species such as hydrides were generated, the metal centers readily abstracted fluorine from the ligand periphery, thereby limiting the reactivity of these types of complexes. Similarly, these fluorinated ligand systems did not allow access to complexes that possess M−Si bonds.[35]

In this contribution, we report a synthetic route to new tach-derived ligands bearing sterically demanding, nonfluorinated aromatic substituents and investigations of several d^0 titanium and zirconium complexes thereof. These studies were based on the premise that elimination of fluorine from the ligand periphery would suppress previously observed ligand activation processes, providing access to new types of highly electrophilic d^0 transition-metal species featuring reactive M−R (R = H, silyl) σ-bonds. We specifically targeted a ligand system featuring bulky *tert*-butyl 3,5-substituents on the aryl functionalities (Chart 1, **C**), in anticipation that this ligand would provide a sterically protected, 3-fold symmetric “pocket” upon coordination to a transition metal. The steric properties of the ligand should therefore determine the characteristics of the metal reactive site by stabilizing monomeric species, such as metal hydrides, and by inhibiting intermolecular decomposition pathways, while leaving the metal center accessible to small molecule reactants.

Results and Discussion

Ligand Synthesis. Main-group and late-transition-metal complexes containing neutral derivatives of *cis*,*cis*-1,3,5-triaminocyclohexane (tach) have previously been

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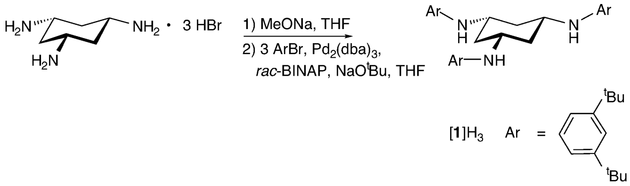
investigated for potential applications in the fields of radiopharmaceuticals and bioinorganic chemistry.[39−45] These tach derivatives have included triamines of the type *cis,cis*-1,3,5-$(ArCH_2NH)_3C_6H_9$ (Ar = phenyl or substituted phenyl, pyridyl) that can be prepared by condensation of *cis,cis*-1,3,5-triaminocyclohexane with an aldehyde, followed by an alkali metal hydride reduction. Additionally, *N,N′,N″*-trialkylated triamines of the type *cis,cis*-1,3,5-$(RNH)_3C_6H_9$ (R = Me, Et, ^nPr, neopentyl) have been prepared by a multistep route involving the nucleophilic substitution reaction of a *N,N′,N″*-tritosylamide tach derivative with a dialkyl sulfate, followed by deprotection of the resulting tosylamide.[44]

As these previously reported routes to *N,N′,N″*-trisubstituted tach derivatives are not amenable to the preparation of aryl-substituted triamines, we sought alternative synthetic routes. We initially employed nucleophilic aromatic substitution chemistry to access triamines functionalized with C_6F_5 or 3,5-$(CF_3)_2C_6H_3$ groups, directly from *cis,cis*-1,3,5-triaminocyclohexane in one synthetic step.[35] However, the preparation of tach derivatives containing nonfluorinated aryl substituents required an alternative methodology for forming the aromatic carbon−nitrogen bond. The Pd-catalyzed coupling reaction between an aryl bromide and an amine, developed by Buchwald and Hartwig, proved convenient, as it accomplishes the desired synthesis in one step.[46−51] Additionally, a large number of substituted aryl bromides are commercially available or readily prepared by literature procedures, making this a potentially general synthetic route for preparing aryl-substituted tach ligands. Schrock and co-workers have recently used a similar methodology to prepare aryl-substituted derivatives of triaminotriethylamine.[52,53]

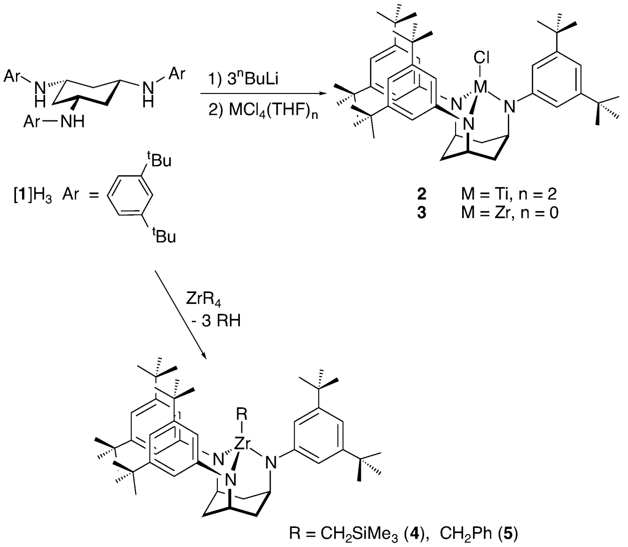
Treatment of *cis,cis*-1,3,5-triaminocyclohexane·3HBr with an excess of sodium methoxide in refluxing THF generated the free triamine, which was subsequently coupled with 3 equiv of 1-bromo-3,5-di-*tert*-butylbenzene[54] in the presence of 3 equiv of sodium *tert*-butoxide using $Pd_2(dba)_3$ (1 mol %) and BINAP as the catalyst (eq 1). The coupling reaction was carried out in THF due to the low solubility of free tach in toluene, the solvent most commonly employed for this type of reaction.[46−51] The desired *cis,cis*-1,3,5-tris{[(3,5-di-*tert*-butyl)phenyl]amino}cyclohexane ([**1**]H_3) was isolated as an off-white solid in 84% yield following extraction into diethyl ether and subsequent sublimation to remove traces of unreacted 1-bromo-3,5-di-*tert*-butylbenzene. The triamine was generally used without further purification; however it could be recrystallized from hexamethyldisiloxane.



(1)

Synthesis of Titanium and Zirconium Chloride Complexes. The reaction between $TiCl_4(THF)_2$ and 1 equiv of [**1**]Li_3 (prepared in situ) gave the titanium monochloride complex **2**, which was isolated as a dark red microcrystalline solid in 41% yield, following crystallization from pentane (Scheme 1). Similarly, the reaction between $ZrCl_4$ and 1 equiv of [**1**]Li_3 (prepared in situ) in diethyl ether gave the corresponding zirconium monochloride complex **3**, which was isolated as a yellow crystalline solid in 62% yield following extraction into toluene and crystallization from pentane. When the toluene extraction step was omitted from the workup of **3**, the diethyl ether adduct **3**·OEt_2 was isolated. The coordinated ether molecule can be removed by dissolving **3**·OEt_2 in toluene and subsequently removing the solvent under reduced pressure. Both **2** and **3** are highly soluble in pentane and aromatic hydrocarbon solvents, although both are slightly less soluble once isolated as crystalline solids. The room-temperature ^1H NMR spectra (benzene-d_6) of both **2** and **3** exhibit one set of aromatic resonances and one ^tBu peak, corresponding to apparent 3-fold symmetric complexes in solution.

Scheme 1



The solid-state structure of **3**·OEt_2 was determined by X-ray crystallography (Figure 1). The complex is monomeric in the solid state and exhibits approximate

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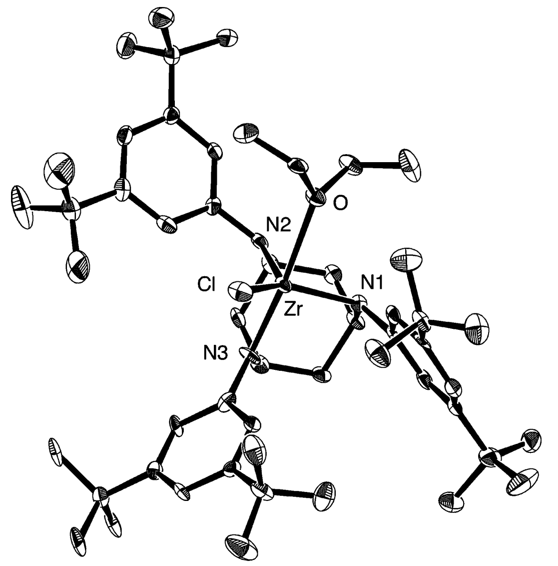

Figure 1. Crystallographically determined structure of **3**·OEt$_2$ depicted with 50% thermal ellipsoids; all hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Zr−Cl 2.455(2); Zr−O 2.409(4); Zr−N1 2.081(5); Zr−N2 2.018(5); Zr−N3 2.068(5); N1−Zr−N2 91.5(2); N2−Zr−N3 89.9(2); N1−Zr−N3 89.8(2); N3−Zr−O 174.5(2); Cl−Zr−N1 137.7(2); Cl−Zr−N2 129.9(2).

trigonal bipyramidal geometry about the Zr center with the chloride ligand in an equatorial site and the diethyl ether ligand in an axial site. The arms of the tach ligand take up the remaining axial and two equatorial sites. The geometry at each of the two nitrogen atoms in equatorial positions (N1 and N2) deviates slightly from planarity, with the sum of the angles about N1 totaling 345.6° and the angles about N2 totaling 353.9°, while the angles about the axial nitrogen atom (N3) sum to 359.0°. The chelate ligand bite angles (N1−Zr−N2, 91.5(2)°; N2−Zr−N3, 89.8(2)°; N1−Zr−N3 89.8(2)°) are significantly compressed, indicating the constrained nature of the tach chelating framework. The Zr atom is located 1.18 Å out of the plane defined by the three tach nitrogen atoms, and the average Zr−N distance is 2.06 Å.

Synthesis of Titanium and Zirconium Alkyl and Aryl Complexes. Zirconium alkyl complexes containing **1** were readily prepared by reaction of [**1**]H$_3$ with either Zr(CH$_2$SiMe$_3$)$_4$[55] to yield the zirconium trimethylsilylmethyl complex **4** or with Zr(CH$_2$Ph)$_4$[56,57] to yield the corresponding benzyl complex **5** (Scheme 1). In both cases, this reaction occurred readily at room temperature over the course of several hours in benzene solution to generate 3 equiv of the corresponding alkane. As monitored by ^{1}H NMR spectroscopy (room temperature, benzene-d_6), both reactions resulted in quantitative conversion to the monoalkyl products after 12 h (relative to an internal standard). This reactivity is in sharp contrast to that of the previously reported fluorinated tach derivatives, [*cis,cis*-1,3,5-(C$_6$F$_5$N)$_3$C$_6$H$_9$]H$_3$ and {*cis,cis*-1,3,5-[3,5-(CF$_3$)$_2$C$_6$H$_3$N]$_3$C$_6$H$_9$}H$_3$, neither of which reacted appreciably with zirconium tetraalkyl complexes even at temperatures up to 90 °C.[35]

The isolated complexes **4** and **5** are highly soluble in most common organic solvents, including benzene, toluene, diethyl ether, and pentane. The benzyl complex **5** could be crystallized in high yield by slow evaporation of a benzene solution at room temperature. Complex **4**, however, was isolated as an oily solid that resisted all crystallization attempts. Both **4** and **5** exhibit 3-fold symmetry in solution on the NMR time scale, as indicated by the presence of only one ^{t}Bu resonance in their ^{1}H NMR spectra at room temperature (benzene-d_6). For **4**, the diastereotopic Zr-bound methylene protons are observed as a pair of doublets at 0.13 and 0.08 ppm ($^2J_{HH}$ = 3 Hz for each resonance; $^1J_{CH}$ = 105 Hz), while for **5**, the Zr−CH$_2$ group is observed as a singlet at 2.96 ppm ($^1J_{CH}$ = 131 Hz). The low CH coupling constant measured for the diastereotopic methylene protons of the −CH$_2$SiMe$_3$ ligand of complex **4** suggests that these may be involved in an α-agostic interaction with the coordinatively and electronically unsaturated metal center.[58] A similar α-agostic interaction has previously been observed for the related complex, [*cis,cis*-1,3,5-(C$_6$F$_5$N)$_3$C$_6$H$_9$]ZrCH(SiMe$_3$)$_2$, which features perfluorinated phenyl groups as the substituents on the tach ligand nitrogen donors.[35] By comparison, complex **5** does not exhibit a similarly low CH coupling constant for the benzylic protons, possibly as a result of the preferential coordination of the benzyl ligand in either an η^2 or η^3 configuration.

Alternatively, alkyl and aryl derivatives of the metal chloride species **2** and **3** could be prepared readily via salt metathesis. The zirconium phenyl (**6**) and mesityl (**7**) derivatives were prepared by reaction of **3** with 1 equiv of PhLi or MesLi, respectively, in toluene at room temperature (Scheme 2). Both complexes were isolated as yellow, microcrystalline solids and are stable indefinitely at room temperature in the solid state. The ZrPh group of complex **6** was identified by the ^{1}H NMR multiplets observed at 7.69 ppm (2 H) and 7.02 ppm (3 H), corresponding to the *ortho*- and coincident *meta*- and *para*-protons, respectively. The ZrMes group of complex **7** exhibits a ^{1}H NMR resonance at 6.59 ppm corresponding to the two aromatic protons, as well as two singlets at 2.24 (6 H) and 2.10 ppm (3 H) corresponding to the *ortho*- and *para*-methyl groups, respectively. Similarly, the titanium methyl complex, **8**, was prepared by reaction of **2** with 1 equiv of MeMgBr in toluene solution (Scheme 2). The crude methyl complex, **8**, was isolated as a red solid (>90% pure) and appears to be thermally stable at room temperature in the solid state. Analytically pure **8** was obtained by crystallization from diethyl ether at low temperature (−35 °C), which afforded thin red needles in low yield (10%), due to the high solubility of **8**. The TiMe group of complex **8** was identified by a ^{1}H NMR resonance at 2.07 ppm and a ^{13}C NMR signal at 61.7 ppm ($^1J_{CH}$ = 118 Hz).

Synthesis of Titanium and Zirconium Silyl and Hydrosilyl Complexes. A majority of previously reported metal silyl complexes feature low-valent, electron-

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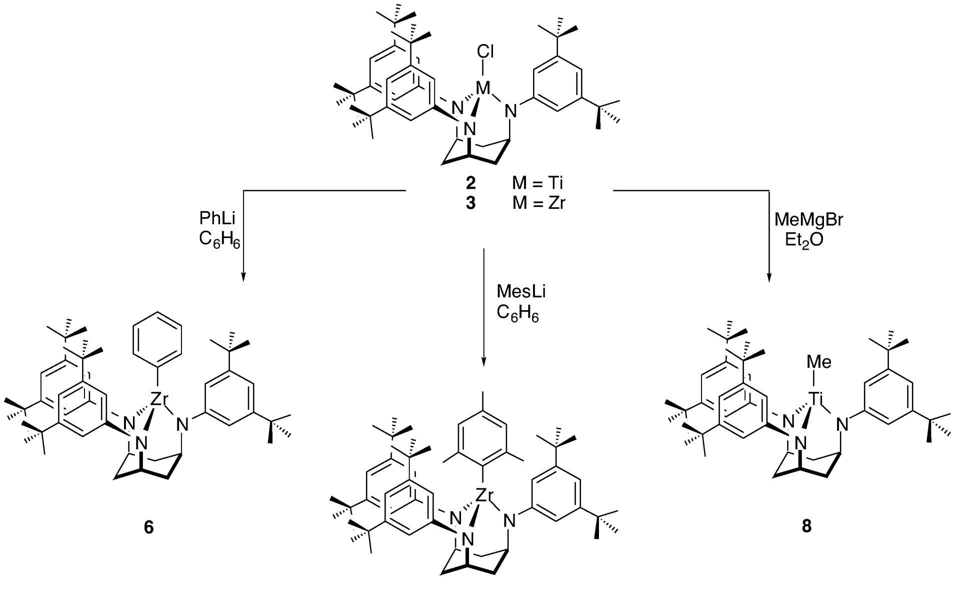
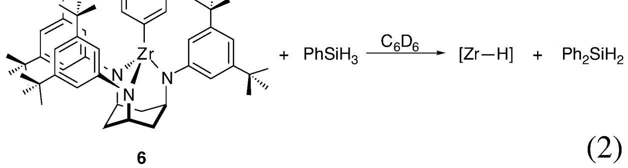
Scheme 2



rich late transition metals, largely due to the availability of convenient synthetic routes based on the facile oxidative addition of Si−H bonds.[59] By comparison, the chemistry of d^0 early-transition-metal silyl complexes is relatively new and synthetic routes are somewhat less straightforward. Syntheses typically involve either nucleophilic displacement of halide by a silyl anion reagent or σ-bond metathesis activation of Si−H bonds. Only a handful of d^0 transition-metal silyl complexes free of cyclopentadienyl ancillary ligands have been reported.[29,30,60−66]

Attempts to prepare tach-containing titanium and zirconium silyl complexes by a σ-bond metathesis pathway involving treatment of the alkyl or aryl derivatives (complexes **4**−**8**) with hydrosilanes did not lead to appreciable formation of the desired silyl species. For example, reactions of the alkyl complexes **4**, **5**, or **8** with a large excess (10 equiv) of $PhSiH_3$ (temperatures up to 90 °C in benzene-d_6 monitored over the course of a week) led to formation of an insignificant amount of PhH_2SiSiH_2Ph, and no trace of a metal hydride or hydrosilyl product was observed by ^1H NMR spectroscopy. No reaction was observed between $PhSiH_3$ and complex **7** under similar conditions. The phenyl derivative **6** reacted over the course of 12 h with 1 equiv of $PhSiH_3$ at 80 °C in benzene-d_6 solution to produce 1 equiv of Ph_2SiH_2 (eq 2). A zirconium hydride resonance was observed in the ^1H NMR spectrum of this reaction mixture at 10.65 ppm; however, this species did not form cleanly and appeared to decompose under the reaction conditions. Under the same conditions, treatment of **6** with excess $PhSiH_3$ (10 equiv) led to formation of 1 equiv of Ph_2SiH_2 and unreacted $PhSiH_3$.



6

(2)

Silyl and hydrosilyl complexes featuring the tach-derived ligand **1**, including rare examples of isolable Ti(IV) silyls, were accessible via reaction of the corresponding metal chloride complexes with silyl anion reagents (Scheme 3). Treatment of either **2** or **3** with $KSi(SiMe_3)_3$[67] or $(THF)_2LiSiHMes_2$[68] in benzene solution resulted in clean formation of the corresponding d^0 silyl complexes [**1**]$TiSi(SiMe_3)_3$ (**9**), [**1**]$ZrSi(SiMe_3)_3$ (**10**), [**1**]$TiSiHMes_2$ (**11**), and [**1**]$ZrSiHMes_2(THF)$ (**12**), isolated in 89, 86, 53, and 36% yields, respectively (Scheme 3). As monitored by ^1H NMR spectroscopy (room temperature, benzene-d_6), these reactions were observed to quantitatively proceed to the silyl products within minutes (relative to an internal standard). Complexes **9** and **10** were isolated as solids upon lyophilization from benzene; however, neither could be induced to crystallize (both complexes are highly soluble in aromatic and aliphatic hydrocarbon solvents). By comparison, complexes **11** and **12** crystallized from pentane solutions at −30 °C, but due to their high solubility in hydrocarbon solvents, low isolated yields were observed.

Complexes **9** and **10** were identified by ^1H NMR resonances at 0.05 and 0.12 ppm, respectively, corresponding to the $SiMe_3$ groups of the metal-bound silyl ligand. The ^{29}Si NMR spectra of **9** and **10** contain two resonances, consistent with the two silicon environ-

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(59) For examples, see: (a) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Wiley: New York, 1991; pp 245, 309. (b) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.

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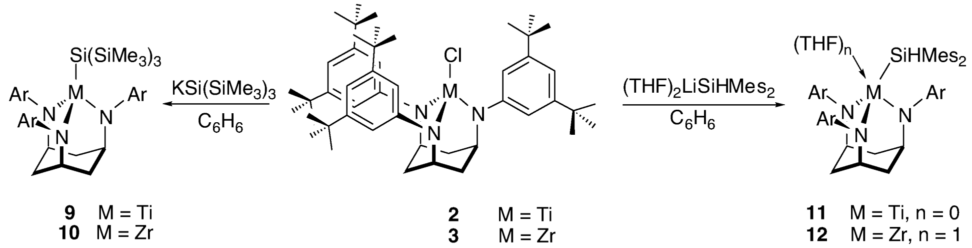
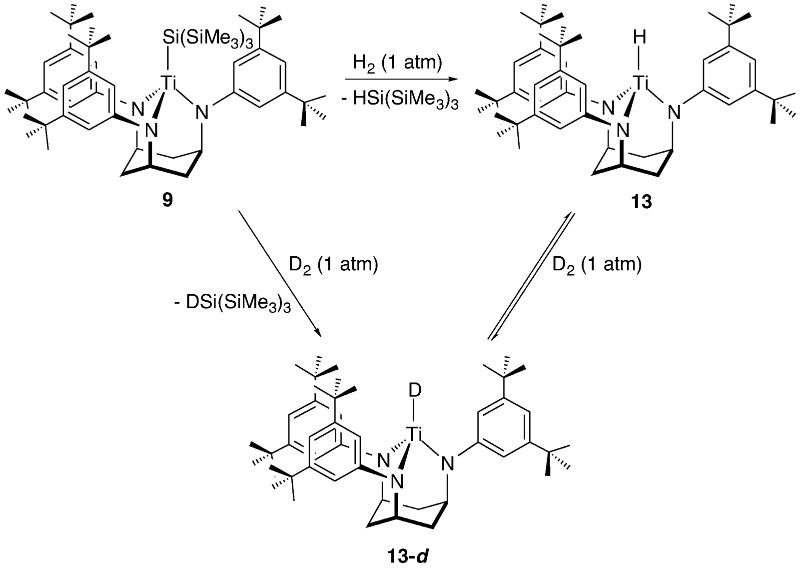
Scheme 3



Scheme 4



ments of the silyl ligand; the resonance corresponding to the $SiMe_3$ groups is observed at −4.4 ppm for **9** and −5.1 ppm for **10**, while the resonance corresponding to the metal-bound silicon is observed upfield at −75.3 ppm for **9** and −100.6 ppm for **10**. Complexes **11** and **12** exhibit characteristic ^1H NMR resonances at 5.25 ppm (**11**) and 5.19 ppm (**12**) corresponding to the Si−H group of the silyl ligand. For both the Ti and Zr hydrosilyl complexes, the mesityl methyl groups are observed as two singlets in a 2:1 ratio, corresponding to the *ortho*- and *para*-methyl substituents, respectively. The ^{29}Si NMR spectra of complexes **11** and **12** each contain only one resonance at −36.6 ($^1J_{SiH} = 147$ H) and −33.0 ($^1J_{SiH} = 135$ Hz), respectively, corresponding to the metal-bound hydrosilyl ligand. The Si−H coupling constant for **11** falls within the range predicted for transition-metal silyl complexes (143−219 Hz), while that of **12** is fairly low, suggesting the possibility of a weak interaction of the Si−H bond with the electrophilic metal center.[59b] Although silyl complexes **9** and **10** are stable to ambient light, the hydrosilyl complexes **11** and **12** are somewhat light sensitive, necessitating their storage in the dark. Monitoring benzene-d_6 solutions of either **11** or **12** exposed to ambient lab light over the course of a day by ^1H NMR spectroscopy revealed the formation of H_2SiMes_2, but no metal-containing products could be identified.

Hydrogenolysis of Zirconium and Titanium Complexes. Complexes **4**−**8** did not react appreciably with H_2 (1 atm) in benzene-d_6 at temperatures up to 90 °C. By comparison, the silyl complexes **9** and **10** reacted over the course of only a few minutes with H_2 at room temperature in benzene solution, consistent with previous observations that hydrogenolysis of d^0 M−Si bonds is rapid compared to the corresponding reactions of d^0 M−C bonds.[68−70]

Complex **9** reacted cleanly with H_2 (1 atm), resulting in quantitative formation (by ^1H NMR spectroscopy in benzene-d_6 solvent) of $HSi(SiMe_3)_3$ and a Ti(IV) monohydride complex, [**1**]TiH (**13**, Scheme 4). The hydride complex (**13**) exhibited 3-fold symmetry at room temperature by ^1H NMR spectroscopy (benzene-d_6), and a hydride resonance was observed at 10.73 ppm, the downfield shift being characteristic of hydride ligands on a highly electrophilic metal center[71] surrounded by hard donor groups (cf. $[(Me_3SiNCH_2CH_2)_3N]TiH$, δ 8.29;[72] $(2,6\text{-}^iPr_2C_6H_3O)_3TiH(PMe_3)$, δ 8.5[73]). When D_2 reacted with **9** to give **13-*d***, the aforementioned titanium hydride resonance was no longer observed in the ^1H NMR spectrum (Scheme 4). Upon exposure of a benzene solution of **13** to D_2 at room temperature, a peak was observed at 10.7 ppm in the ^2H NMR spectrum within 5 min of mixing, indicating that H/D exchange occurs readily (Scheme 4). The infrared spectrum of **13** (generated in situ, benzene-d_6 solution) exhibits a large number of interfering bands in the region of 1580−800 cm^{-1}. However, the difference spectrum obtained from **13** and the analogous deuteride complex, [**1**]TiD (**13-*d***), exhibits bands of medium to weak intensity at

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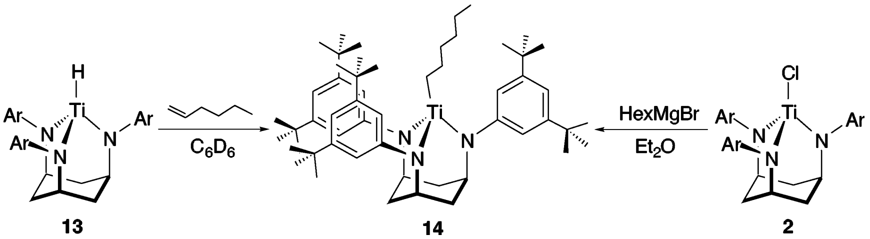
Scheme 5



1458 and 1015 cm^{-1}, which we tentatively assign as ν(Ti−H) and ν(Ti−D), respectively.

Although **13** forms cleanly and quantitatively on an NMR tube scale, preparative-scale attempts to isolate this complex resulted in impure mixtures of the desired Ti−H complex (ca. 60%), $HSi(SiMe_3)_3$, which is a side product in the hydrogenolysis reaction, and additional unidentified impurities. Due to its considerable solubility in common solvents, including hexane, pentane, and hexamethyldisiloxane, **13** could not be isolated away from these byproducts. However, by analogy with the related actinide hydride complexes $[(Me_3Si)_2N]_3MH$ (M = U, Th),[74,75] **13** is formulated as a pseudotetrahedral monomer.

Complex **13** (generated in situ in benzene-d_6) readily inserts 1-hexene to give the corresponding *n*-hexyl derivative, [**1**]TiHex (**14**) (Scheme 5). This complex could also be prepared independently via the reaction of **2** with HexMgBr in pentane (Scheme 5). When excess 1-hexene (10 equiv) was added to a benzene solution of **13**, 1 equiv reacted immediately at room temperature to give **14**, and no further reaction was observed under these conditions. When this reaction mixture was heated to 90 °C, the excess 1-hexene was consumed over the course of 12 h and converted to a mixture of internal olefins, as confirmed by ^{1}H NMR spectroscopy and GC−MS analysis. The reaction of **13** (generated in situ in benzene-d_6) with ethylene (1 atm) resulted in a complicated mixture of products which included trace amounts (<10%) of 1-hexene (identified by ^{1}H NMR spectroscopy and GC−MS). The amount of 1-hexene produced did not build up when higher pressures of ethylene were employed (up to 700 psi in a Parr pressure reactor) or with heating of the reaction mixture up to 90 °C, and only an insignificant amount of polyethylene formation was observed. No appreciable reaction was observed between **13** and excess $PhSiH_3$ (10 equiv) in benzene-d_6 solution at temperatures up to 85 °C, although **13** does begin to undergo thermal decomposition under these conditions.

Although the reaction of the zirconium silyl complex **10** with H_2 (1 atm) also resulted in quantitative formation of $HSi(SiMe_3)_3$, the ^{1}H NMR spectrum of the reaction mixture is significantly more complicated than in the hydrogenolysis of the titanium analogue **9**. In the reaction of **10**, three hydride resonances are observed at 10.31 ppm (singlet), 9.63 ppm (doublet, $^2J_{HH} = 4$ Hz), and 5.66 ppm (doublet, $^2J_{HH} = 4$ Hz) in the approximate ratio of 1:2:2 (cyclohexane-d_{12} solution). Coupling between the resonances at 9.63 and 5.66 ppm was confirmed by the presence of off-diagonal correlation peaks in the two-dimensional ^{1}H,^{1}H-TOCSY NMR spectrum. Treatment of the hydrogenolysis product mixture (**17a**/**17b**, vide infra) with D_2 (1 atm) in benzene solution resulted in exchange of deuterium into all three hydride positions within minutes at room temperature. Deuterium incorporation into the C−H positions of the ligand ^{t}Bu substituents was also observed by ^{2}H NMR spectroscopy.

Addition of 1 equiv of PMe_3 to the mixture of products resulting from hydrogenolysis of **10** in benzene-d_6 solution resulted in the formation of one hydride species exhibiting apparent 3-fold symmetry and a single hydride resonance at 11.12 ppm by ^{1}H NMR spectroscopy (Scheme 6). Similarly, when the hydrogenolysis was carried out in the presence of 1 equiv of PMe_3, this same hydride species, [**1**]ZrH(PMe_3) (**15**), was formed cleanly, accompanied by 1 equiv of $HSi(SiMe_3)_3$. A broad resonance is observed at −57.8 ppm in the ^{31}P NMR spectrum of **15** (benzene-d_6); however, no evidence of ^{31}P−^{1}H coupling was observed for the hydride ligand down to −80 °C, suggesting that in benzene solution the phosphine ligand is dissociating from the metal center in a rapid equilibrium. Indeed, placing the reaction mixture under vacuum results in complete dissociation of PMe_3 and regeneration of the initial mixture of hydride products, thus prohibiting the isolation of **15**.

When 1 equiv of 1-hexene was added as a trapping agent to the product mixture of zirconium hydrides (**17a**/**17b**), the corresponding zirconium hexyl insertion product (**16**) formed cleanly and quantitatively as the only product (Scheme 6). Although **16** could not be prepared cleanly by the reaction of **3** with HexMgBr, it was characterized in solution by comparison with the titanium analogue **14**. As in the case of **13**, when an excess of 1-hexene (10 equiv) was added to a benzene-d_6 solution of **17a**/**17b**, 1 equiv reacted immediately to form **16**. Upon subsequent heating at 85 °C over the course of 14 h, the remaining 1-hexene were converted to a mixture of internal olefins, as confirmed by ^{1}H NMR and GC−MS analysis. The reaction of the zirconium hydride product mixture (**17a**/**17b**) with ethylene (1 atm) resulted in a complicated mixture of products from which no metal-containing species could be unambiguously identified. No evidence for polyethylene formation was observed.

On the basis of these data, the resonance at 10.31 ppm in the ^{1}H NMR spectrum of the zirconium hydrogenolysis product mixture is assigned to a monomeric Zr−H species (**17a**, Scheme 6), while the two doublets at 9.63 and 5.66 ppm are assigned to an unsymmetrical dimeric species featuring one bridging Zr−H ligand and one terminal Zr−H (**17b**, Scheme 6). The resonance at

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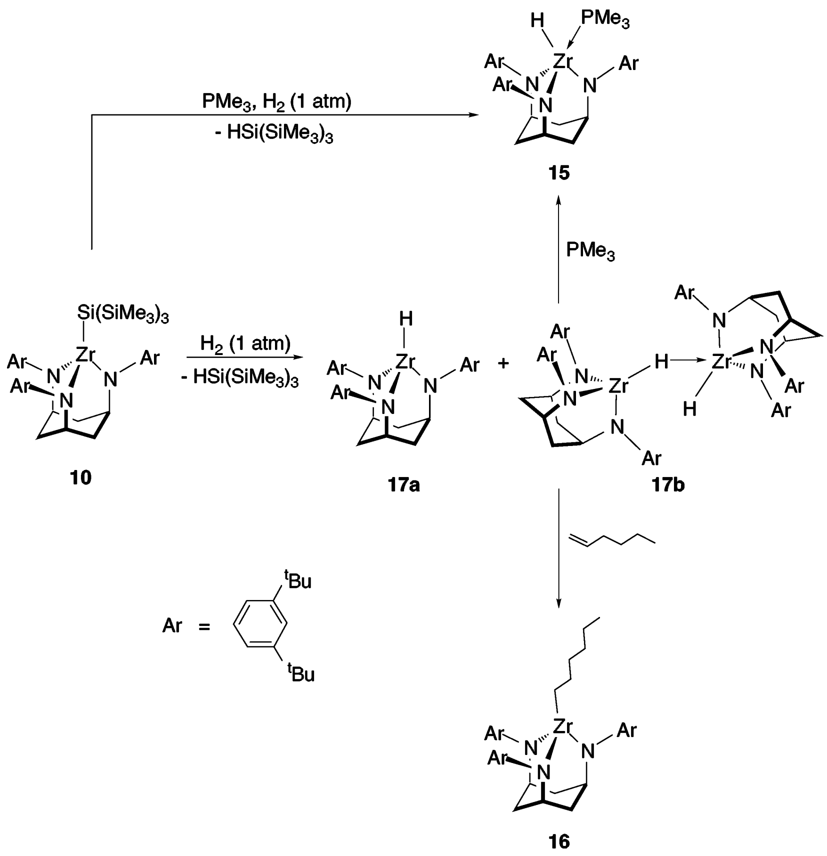
Scheme 6



9.63 ppm is assigned to the terminal hydride ligand of the dimer, while the upfield shifted resonance at 5.66 ppm is assigned to the bridging hydride, as the ^{1}H NMR chemical shifts of hydride ligands that bridge between two metal centers are characteristically observed at higher field than those of terminally bonded hydrides.[76] These hydride ^{1}H NMR shifts are in agreement with previously reported NMR shifts for related d^0 zirconium hydride complexes (cf. (^{t}Bu$_3$SiNH)$_3$ZrH, δ 9.60;[77] {HC-[SiMe$_2$(4-MeC$_6$H$_4$)N]$_3$}ZrH, δ 8.06[78]). The Zr–H IR stretches for **15** and **17** are obscured by a large number of interfering bands in the region of ca. 1580–800 cm^{-1}.

Attempts to observe evidence for chemical exchange between **17a** and **17b** by a 2D EXSY NMR experiment proved inconclusive, as no off-diagonal cross-peaks of significant intensity were observed for correlation of the hydride resonances assigned to these two species.[79] Further attempts to probe the dynamic characteristics of the two hydride complexes by variable-temperature ^{1}H NMR spectroscopy (in either toluene-d_8 or methylcyclohexane-d_{14} solvents) did not indicate coalescence of the hydride resonances assigned to **17a** and **17b** in the temperature range 193–353 K, although broadening of these resonances was observed at both the high- and low-temperature limits. In addition, an interesting solvent effect on the monomer/dimer ratio was observed in toluene-d_8 versus methylcyclohexane-d_{14} solution. While a room-temperature methylcyclohexane-d_{14} solution of freshly generated **17a**/**17b** featured a monomer/dimer ratio of approximately 0.43, a toluene-d_8 solution of the same concentration (based on the amount of **10** hydrogenated) exhibited a monomer/dimer ratio of 1.4 (by ^{1}H NMR spectroscopy, relative to an internal standard of ferrocene), suggesting that solvent may play a role in the equilibrium distribution of these two species.

As in the case of **13**, preparative-scale attempts to isolate **17a** and **17b** resulted in impure mixtures of the Zr–H complexes (ca. 70%), HSi(SiMe$_3$)$_3$, and additional unidentified impurities. Due to the considerable solubility of both **17a** and **17b** in common aromatic and aliphatic hydrocarbon solvents, neither of these complexes could be isolated from the crude product mixture.

The reactivity of tach-supported zirconium hydride species with hydrosilanes was probed by reacting benzene-d_6 solutions of freshly generated **15** and **17a**/**17b** with excess (10 equiv) PhSiH$_3$ and PhMeSiH$_3$. Little reactivity was observed with either of these silanes at temperatures ranging from 25 to 90 °C. For both **15** and **17a**/**17b**, traces of PhH$_2$SiSiH$_2$Ph (<5%) were observed by ^{1}H NMR spectroscopy upon heating benzene-d_6 solutions containing the metal hydride and 10 equiv of PhSiH$_3$ at 90 °C over the course of 36 h. In similar reactions with 10 equiv of PhMeSiH$_2$, traces (<10%) of silane redistribution products (Ph$_2$MeSiH, Ph$_2$SiH$_2$, Me$_2$SiH$_2$, MeSiH$_3$) were observed by ^{1}H NMR spectroscopy after heating the reaction mixtures at 90 °C over the course of 36 h. Both **15** and **17a**/**17b** undergo thermal decomposition under these reaction conditions.

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(79) Benzene-d_6, 298 K, mixing times ranging from 0.3 to 0.7 s. These mixing times were selected based on the T_1 values of 0.72, 0.50, and 0.37 found for the terminal monomeric, terminal dimeric, and bridging hydride ligands, respectively, of **17a** and **17b**.

Concluding Remarks

In this contribution, a new triamido ligand derived from *cis,cis*-1,3,5-triaminocyclohexane (tach) and containing nonfluorinated aromatic substituents on the donor nitrogen atoms was introduced. This ligand system provides several advantages over its fluorinated counterparts, [*cis,cis*-1,3,5-($C_6F_5N)_3C_6H_9$]$^{3-}$ and {*cis,cis*-1,3,5-[3,5-($CF_3)_2C_6H_3N]_3C_6H_9$}$^{3-}$, including a ligand periphery that is substantially less prone to activation by electrophilic d^0 transition metals. Titanium and zirconium alkyl, aryl, and rare examples of d^0 silyl and hydrosilyl complexes featuring this nonfluorinated ligand can be readily prepared and isolated. Although the alkyl and aryl derivatives proved unreactive toward σ-bond metathesis reactions with H_2 and hydrosilanes, the silyl complexes readily undergo hydrogenolysis of the M−Si bond to produce M−H species. By analogy with previously studied d^0 metal silyl complexes featuring Cp-derived ligands, this M−Si bond cleavage likely occurs by a concerted σ-bond metathesis type pathway.[37,69,70]

In preliminary reactivity studies, the titanium and zirconium hydride species, which have been characterized in solution, appear unreactive in σ-bond metathesis activations of Si−H bonds, although they readily undergo H/D exchange with D_2 and insert 1-hexene to form the corresponding hexyl complexes. Several factors may be responsible for the observed limited σ-bond metathesis reactivity, including a high degree of ionicity in the metal−nitrogen bonding, leading to contracted vacant metal orbitals that are therefore less effective at mediating σ-bond metathesis transformations. This effect has been previously suggested in yttrium benzamidinate complexes that exhibited a low tendency to engage in σ-bond metathesis reactions.[80−82] Previous observations with group 4 complexes supported by Cp-derived ligands have also indicated that steric factors can play a significant role in σ-bond metathesis reactivity with silanes.[37] Thus, steric crowding at the metal center, potentially as a result of dimer formation or coordination of additional donor functionalities, may also result in the low observed reactivity with hydrosilanes. Significantly smaller molecules such as H_2 and D_2 are able to access the metal much more readily, leading to the observed hydrogenolysis of M−Si bonds and H/D exchange at the metal hydride position.

Additional scrambling of deuterium into the ^{t}Bu arene substituents on the ligand was observed in the reaction of **17a**/**17b** with D_2, but not in the related reaction of **13** with D_2. By analogy with the related deuterium incorporation into the R substituent of the cyclopentadienyl zirconium species η^5-($C_5Me_4R)_2ZrH_2$ (R = Me, Et, CH_2CMe_3),[83] the likely mechanism for this process involves intramolecular σ-bond metathesis between an alkyl C−H bond and a Zr−D bond. Due to geometric constraints, it is difficult to envision an intramolecular pathway that would facilitate this reactivity for a monomeric hydride species such as **13** or **17a**. However, in the case of a dimeric hydride such as **17b**, the ^{t}Bu substituents should come in close proximity with the metal center, thereby facilitating the H/D exchange at this position.

Experimental Section

General Procedures. All experiments were conducted under nitrogen in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Dry, oxygen-free solvents were used unless otherwise indicated. Pentane was pretreated with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, and saturated $NaHCO_3$ solution, then dried over $MgSO_4$, stored over 4 Å molecular sieves, and distilled from potassium/benzophenone ketyl under a nitrogen atmosphere. Diethyl ether and THF were distilled under nitrogen from sodium/benzophenone ketyl. Toluene and benzene were pretreated with concentrated H_2SO_4, followed by saturated $NaHCO_3$ solution, and then dried over $MgSO_4$. Toluene was then distilled from molten sodium under a nitrogen atmosphere. Benzene was distilled from molten potassium under a nitrogen atmosphere. Benzene-d_6 and toluene-d_8 were degassed via three freeze−pump−thaw cycles and dried over 4 Å molecular sieves. Methylene chloride-d_2 was dried over CaH_2. All NMR data were recorded at room temperature, unless otherwise noted, using either a Bruker AMX, AM, or DRX spectrometer. ^{1}H NMR spectra were referenced internally by the residual solvent proton signal relative to tetramethylsilane. ^{13}C NMR spectra were referenced internally by the ^{13}C signal of the NMR solvent relative to tetramethylsilane. ^{29}Si NMR spectra were referenced relative to an external standard of tetramethylsilane. In some cases, distortionless enhancement by polarization transfer (DEPT) was used to assign the ^{13}C NMR resonances as CH_3, CH_2, CH, or C, and ^{1}H-coupled and decoupled insensitive nuclei enhanced by polarization transfer (INEPT) were used to identify ^{29}Si resonances, $^1J_{SiH}$ values, and $^1J_{CH}$ values. Heteronuclear multiple quantum coherence (HMQC) was used to identify ^{1}H−^{13}C coupling. Infrared spectra were recorded between NaCl plates using a Mattson FTIR spectrometer at a resolution of 4 cm^{-1}. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. The compounds *cis,cis*-1,3,5-triaminocyclohexane·3HBr,[40] 3,5-^{t}Bu$_2C_6H_3$Br,[54] $TiCl_4(THF)_2$,[84] $Zr(CH_2Ph)_4$,[56,57] $Zr(CH_2SiMe_3)_4$,[55] $LiCH_2SiMe_3$,[85] $KSi(SiMe_3)_3$,[67] and $(THF)_2$Li-SiHMes$_2$[68] were prepared according to literature procedures.

***cis,cis*-1,3,5-(3,5-^{t}Bu$_2C_6H_3NH)_3C_6H_9$ ([1]H_3).** A 1 L Schlenk flask containing a magnetic stirbar was charged with *cis,cis*-1,3,5-triaminocyclohexane·3HBr (4.0 g, 10.76 mmol) and NaOMe (17.3 g, 320 mmol). Dry THF (500 mL) was added, and the flask was adapted with a reflux condenser. The resulting slurry was refluxed for 18 h with stirring. The contents were then cooled to room temperature, and the reaction mixture was filtered under nitrogen via cannula. The pale yellow filtrate solution was collected in a 500 mL Schlenk flask, and the solvent was removed under reduced pressure, leaving behind an off-white semicrystalline residue. The flask was then charged with 3,5-^{t}Bu$_2C_6H_3$Br (8.7 g, 32.3 mmol), $Pd_2(dba)_3$ (0.1 g, 0.11 mmol), *rac*-BINAP (0.19 g, 0.3 mmol), NaO^{t}Bu (3.10 g, 32.28 mmol), and THF (200 mL). The reaction mixture was heated to 70 °C under a nitrogen atmosphere for 20 h with stirring. It was then cooled to room temperature, and the THF was removed under reduced pressure. The remaining residue was taken up in ca. 200 mL of diethyl ether and extracted with 3 × 200 mL of water. The organic fraction was then washed with saturated NaCl solution (100 mL), dried over anhydrous

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magnesium sulfate, and filtered. The solvent was removed on the rotary evaporator to afford an off-white solid. Traces of unreacted 3,5-^{t}Bu$_2$C$_6$H$_3$Br were removed by sublimation (0.01 Torr, 70 °C) to give [**1**]H$_3$ as an off-white solid (6.3 g, 84% yield) that was used without further purification. IR (Nujol mull, cm^{-1}): 3402 (NH). ^{1}H NMR (benzene-d_6, 500 MHz): δ 6.99 (br m, 3 H, p-H$_{\text{arom}}$), 6.58 (d, 6 H, $^3J_{\text{HH}} = 1.5$ Hz, o-H$_{\text{arom}}$), 3.51 (br m, 3 H, NCH), 3.09 (br s, 3 H, NH), 2.59 (br m, 3 H, CH_2), 1.34 (s, 54 H, CMe_3), 0.65 (br m, 3 H, CH_2). ^{13}C{^{1}H} NMR (benzene-d_6, 125.76 MHz): δ 151.9 (m-C^tBu), 147.0 (CNH), 112.4 (p-CH), 108.5 (o-CH), 49.5 (CHN), 41.1 (CH$_2$), 34.9 (CMe$_3$), 31.8 (CH$_3$). Anal. Calcd for C$_{48}$H$_{75}$N$_3$: C, 83.06; H, 10.89; N, 6.02. Found: C, 82.88; H, 10.86; N, 5.71.

[*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]TiCl (2). A solution of ^{n}BuLi (1.47 mL, 1.6 M in hexanes, 2.36 mmol) was added to a precooled (−30 °C) solution of [**1**]H$_3$ (0.55 g, 0.79 mmol) in Et$_2$O (15 mL). The resulting homogeneous solution was allowed to stand at room temperature for 4 h. The reaction mixture was then cooled to −30 °C, and TiCl$_4$(THF)$_2$ (0.26 g, 0.79 mmol) was added as a solid. The color of the solution changed immediately from orange to dark red. The reaction mixture was allowed to stir at room temperature for 16 h, after which the solvent was removed under vacuum. The resulting dark red residue was extracted into pentane (3 × 5 mL), and each extract was filtered through Celite. The extracts were combined, and the solvent was removed under vacuum. The remaining dark red residue was redissolved in ca. 1 mL of pentane, and the solution was refrigerated at −30 °C to afford dark red microcrystals of **2** (0.25 g, 41% yield). ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.17 (t, 3 H, $J_{\text{HH}} = 2$ Hz, p-H$_{\text{arom}}$), 7.08 (d, 6 H, $J_{\text{HH}} = 2$ Hz, o-H$_{\text{arom}}$), 4.37 (br m, 3 H, CHN), 2.12 (br m, 3 H, CH_2), 1.71 (br m, 3 H, CH_2), 1.30 (s, 54 H, CMe_3). ^{13}C{^{1}H} NMR (benzene-d_6, 125.76 MHz): δ 152.0 (m-C^tBu), 150.4 (CN), 117.0 (p-CH), 113.4 (o-CH), 60.2 (CHN), 35.5 (CMe$_3$), 35.1 (CH$_2$), 31.6 (CH$_3$). Anal. Calcd for C$_{48}$H$_{72}$ClN$_3$Ti: C, 74.44; H, 9.37; N, 5.43. Found: C, 74.55; H, 9.59; N, 5.00.

[*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrCl (3). A solution of ^{n}BuLi (1.47 mL, 1.6 M in hexanes, 2.36 mmol) was added to a precooled (−30 °C) solution of [**1**]H$_3$ (0.55 g, 0.79 mmol) in Et$_2$O (15 mL). The resulting homogeneous solution was allowed to stand at room temperature for 4 h. The reaction mixture was then cooled to −30 °C, and ZrCl$_4$ (0.18 g, 0.79 mmol) was added as a solid. The color of the solution changed from orange to light yellow-orange. The reaction mixture was allowed to stir at room temperature for 16 h, after which the solvent was removed under vacuum. The resulting dark yellow residue was extracted into pentane (3 × 5 mL), and each extract was filtered through Celite. The extracts were combined, and the solvent was removed under vacuum. Recrystallization of the remaining dark yellow residue from ca. 1 mL of pentane at −30 °C afforded **3**·OEt$_2$ as a yellow crystalline solid in minimal yields due its high solubility in pentane. To obtain solvent-free **3**, the pentane extracts were combined, and upon removal of the pentane under vacuum, toluene (ca. 5 mL) was added to the remaining residue. The toluene was removed under vacuum to afford a yellow solid that was recrystallized from a minimum amount of pentane (ca. 7 mL) to give **3** as fine yellow crystals (0.40 g, 62% yield). ^{1}H NMR (methylene chloride-d_2, 500 MHz): δ 7.35 (s, 3 H, p-H$_{\text{arom}}$), 6.93 (s, 6 H, o-H$_{\text{arom}}$), 4.36 (br m, 3 H, CHN), 2.04 (m, 6 H, CH_2), 1.29 (s, 54 H, CMe_3). ^{13}C{^{1}H} NMR (methylene chloride-d_2, 125.76 MHz): δ 152.5 (m-C^tBu), 150.3 (CN), 115.3 (p-CH), 112.7 (o-CH), 56.4 (CHN), 35.3 (CH$_2$), 35.1 (CMe$_3$), 31.6 (CH$_3$). Anal. Calcd for C$_{48}$H$_{72}$ClN$_3$Zr: C, 70.50; H, 8.87; N, 5.14. Found: C, 70.85; H, 8.93; N, 4.71.

[*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrCH$_2$SiMe$_3$ (4). A benzene solution (5 mL) of Zr(CH$_2$SiMe$_3$)$_4$ (0.081 g, 0.18 mmol) was added to a benzene solution (5 mL) of [**1**]H$_3$ (0.13 g, 0.18 mmol) at room temperature. The resulting orange solution was left to stand at room temperature over the course of 12 h. The solvent was removed under vacuum to afford **5** as a yellow-orange oily solid that resisted all crystallization attempts (0.14 g, > 90% pure). Alternatively, **5** could also be prepared by reacting **3** (0.15 g, 0.18 mmol) with LiCH$_2$SiMe$_3$ (0.017 g, 0.18 mmol) in ca. 5 mL of pentane at room temperature. After 2 h at room temperature, the reaction mixture was filtered through Celite, and the solvent was removed under vacuum to afford **4** as a yellow-orange oily solid in comparable yield (0.13 g, >90% pure). ^{1}H NMR (benzene-d_6, 500 MHz): δ 7.15 (m, overlaps with residual C$_6$H$_6$ peak, 3 H, p-H$_{\text{arom}}$), 6.89 (br s, 6 H, o-H$_{\text{arom}}$), 4.15 (br m, 3 H, CHN), 2.04 (br m, 3 H, CH_2), 1.58 (br m, 3 H, CH_2), 1.33 (s, 54 H, CMe_3), 0.13 (d, 1 H, ZrCH_2-Si, $^2J_{\text{HH}} = 3$ Hz), 0.08 (d, 1 H, ZrCH_2Si, $^2J_{\text{HH}} = 3$ Hz), −0.10 (br s, 9 H, CH$_2$SiMe_3). ^{13}C{^{1}H} NMR (benzene-d_6, 125.76 MHz): δ 152.9 (m-C^tBu), 149.2 (CN), 115.7 (p-CH), 113.6 (o-CH), 56.4 (ZrCH$_2$, $^1J_{\text{CH}} = 105$ Hz), 55.9 (CHN), 35.1 (CH$_2$), 34.9 (CMe$_3$), 31.7 (CMe_3), 2.1 (SiMe_3).

[*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrCH$_2$Ph (5). A benzene solution (5 mL) of Zr(CH$_2$Ph)$_4$ (0.16 g, 0.36 mmol) was added to a benzene solution (5 mL) of [**1**]H$_3$ (0.25 g, 0.36 mmol) at room temperature. The resulting orange solution was left to stand at room temperature over the course of 12 h. The reaction mixture was concentrated to ca. 2 mL volume under vacuum. Crystallization by slow evaporation of this solution at room temperature afforded analytically pure **5** as an orange solid (0.30 g, 94% yield). ^{1}H NMR (benzene-d_6, 500 MHz): δ 7.17 (m, 3 H, p-H$_{\text{arom}}$), 6.79 (m, 2 H, m-H$_{\text{Bn}}$), 6.75 (d, 6 H, $J_{\text{HH}} = 2$ Hz, o-H$_{\text{arom}}$), 6.67 (m, 1 H, p-H$_{\text{Bn}}$), 6.55 (d, 2 H, $J_{\text{HH}} = 7$ Hz, o-H$_{\text{Bn}}$), 4.08 (br m, 3 H, CHN), 2.96 (s, 2 H, ZrCH_2), 1.95 (br m, 3 H, CH_2), 1.56 (br m, 3 H, CH_2), 1.36 (s, 54 H, CMe_3). ^{13}C{^{1}H} NMR (benzene-d_6, 125.76 MHz): δ 152.7 (m-C^tBu), 151.5 (CN), 140.7 (ZrCH$_2$$C$), 130.6 ($o$-$CH_{\text{Bn}}$), 127.0 ($m$-$CH_{\text{Bn}}$), 123.7 ($p$-$CH_{\text{Bn}}$), 115.5 ($p$-$C$H), 113.7 ($o$-$C$H), 65.9 (Zr$CH_2$, $^1J_{\text{CH}} = 131$ Hz), 57.1 (CHN), 35.0 (CH$_2$), 34.9 (CMe$_3$), 31.8 (CH$_3$). Anal. Calcd for C$_{55}$H$_{79}$N$_3$Zr: C, 75.63; H, 9.12; N, 4.81. Found: C, 75.73; H, 9.55; N, 4.61.

[*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrPh (6). Solid PhLi (0.009 g, 0.10 mmol) was added to a room-temperature benzene solution of **3** (0.085 g, 0.10 mmol). The reaction mixture was allowed to stand at room temperature for 1 h, and was then filtered through Celite. The solvent was removed under vacuum to afford **6** as a yellow solid (0.081 g, 91% yield). ^{1}H NMR (benzene-d_6, 300 MHz): δ 7.72 (br d, 2 H, o-H$_{\text{Ph}}$), 7.10 (s, 3 H, p-H$_{\text{arom}}$), 7.02 (m, 3 H, m-H$_{\text{Ph}}$, p-H$_{\text{Ph}}$), 6.84 (s, 6 H, o-H$_{\text{arom}}$), 4.41 (br s, 3 H, CHN), 2.18 (br m, 3 H, CH_2), 1.79 (br m, 3 H, CH_2), 1.22 (s, 54 H, CMe_3). ^{13}C{^{1}H} NMR (benzene-d_6, 100.62 MHz): δ 152.5 (m-C^tBu), 150.3 (CN), 133.2 (C$_{\text{Ph}}$), 129.7 (C$_{\text{Ph}}$), 128.6 (C$_{\text{Ph}}$), 128.5 (C$_{\text{Ph}}$), 115.2 (p-CH), 112.9 (o-CH), 55.0 (CHN), 35.6 (CMe$_3$), 35.0 (CH$_2$), 31.6 (CH$_3$). Anal. Calcd for C$_{54}$H$_{77}$N$_3$Zr: C, 75.47; H, 9.03; N, 4.89. Found: C, 75.81; H, 9.02; N, 4.92.

[*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrMes (7). Solid MesLi (0.031 g, 0.24 mmol) was added to a room-temperature benzene solution of **3** (0.20 g, 0.24 mmol). The reaction mixture was allowed to stand at room temperature for 3 h and was then filtered through Celite. The solvent was removed under vacuum, and the residue was dissolved in ca. 2 mL of pentane. The pentane solution was refrigerated at −30 °C overnight to afford **7** as a pale yellow microcrystalline solid (0.12 g, 55% yield). ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.11 (m, 3 H, p-H$_{\text{arom}}$), 6.89 (d, 6 H, $J_{\text{HH}} = 2$ Hz, o-H$_{\text{arom}}$), 6.59 (s, 2 H, m-H$_{\text{Mes}}$) 4.28 (br m, 3 H, CHN), 2.24 (s, 6 H, o-CH_3), 2.12 (br m, 3 H, CH_2), 2.10 (s, 3 H, p-CH_3), 1.68 (br m, 3 H, CH_2), 1.21 (s, 54 H, CMe_3). ^{13}C{^{1}H} NMR (benzene-d_6, 125.76 MHz): δ 152.6 (m-C^tBu), 150.6 (CN), 145.2 (ZrC), 142.3 (o-C$_{\text{Mes}}$), 139.2 (p-C$_{\text{Mes}}$), 127.6 (m-CH$_{\text{Mes}}$), 115.3 (p-CH), 113.9 (o-CH), 55.5 (CHN), 35.2 (CMe$_3$), 35.0 (CH$_2$), 31.6 (o-CH$_3$), 31.5 (CH$_3$), 21.4 (p-CH$_3$). Anal. Calcd for C$_{57}$H$_{83}$N$_3$Zr: C, 75.94; H, 9.28; N, 4.66. Found: C, 75.73; H, 9.55; N, 4.61.

[*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]TiMe (8). A solution of MeMgBr (3.0 M in Et$_2$O, 0.077 mL, 0.23 mmol) was added to a precooled toluene solution (5 mL, −30 °C) of **2** (0.18 g, 0.23 mmol). The resulting red reaction mixture was allowed to warm to room temperature over the course of 3 h with stirring. The solvent was removed under vacuum, and the residue was extracted into ca. 20 mL of pentane. The pentane extracts were filtered through Celite, and the solvent was removed under vacuum to afford crude **6** as a red solid (0.14 g, >90% pure). Analytically pure **8** was obtained in 10% yield by recrystallization of the crude **6** from Et_2O solution at −30 °C. ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.12 (m, 3 H, *p*-H$_{arom}$), 7.03 (d, 6 H, J_{HH} = 2 Hz, *o*-H$_{arom}$), 4.30 (br m, 3 H, C*H*N), 2.14 (br m, 3 H, C*H*$_2$), 2.06 (s, 3 H, Ti*Me*), 1.67 (br m, 3 H, C*H*$_2$), 1.29 (s, 54 H, C*Me*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 125.76 MHz): δ 152.1 (*m*-*C*^{t}Bu), 150.0 (*C*N), 115.9 (*p*-*C*H), 113.0 (*o*-*C*H), 61.7 (Ti*Me*, $^{1}J_{CH}$ = 118 Hz), 57.9 (*C*HN), 35.9 (*C*H$_2$), 35.1 (*C*Me$_3$), 31.7 (*C*H$_3$). Anal. Calcd for $C_{49}H_{75}N_3Ti$: C, 78.05; H, 10.03; N, 5.57. Found: C, 77.90; H, 10.25; N, 5.38.

[*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]TiSi(SiMe$_3$)$_3$ (9). Solid KSi(SiMe$_3$)$_3$ (0.028 g, 0.097 mmol) was added to a room-temperature benzene solution (ca. 5 mL) of **2** (0.075 g, 0.097 mmol). The resulting dark red reaction mixture was allowed to stir at room temperature for 30 min. The solution was filtered through Celite, and the solvent was removed under vacuum to afford **9** as a red-orange solid which resisted all crystallization attempts (0.085 g, > 90% pure). The conversion of **2** to **9** was quantitative by ^{1}H NMR spectroscopy. ^{1}H NMR (benzene-d_6, 500 MHz): δ 7.51 (s, 3 H, *p*-H$_{arom}$), 7.36 (s, 6 H, *o*-H$_{arom}$), 3.61 (br m, 3 H, C*H*N), 2.24 (br m, 3 H, C*H*$_2$), 1.49 (s, 54 H, C*Me*$_3$), 1.26 (br m, 3 H, C*H*$_2$), 0.05 (s, 27 H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 125.76 MHz): δ 152.4 (*m*-*C*^{t}Bu), 151.6 (*C*N), 122.2 (*o*-*C*H), 121.7 (*p*-*C*H), 66.8 (*C*HN), 35.2 (*C*Me$_3$), 34.7 (*C*H$_2$), 31.8 (C*Me*$_3$), 4.8 (Si*Me*$_3$). ^{29}Si NMR (benzene-d_6, 99.36 MHz): δ −4.4 (*Si*Me$_3$), −75.3 (*Si*SiMe$_3$).

[*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrSi(SiMe$_3$)$_3$ (10). KSi(SiMe$_3$)$_3$ (0.076 g, 0.28 mmol) was added as a solid to a room-temperature solution of **3** (0.23 g, 0.28 mmol) in 7 mL of benzene. The reaction mixture was allowed to stir at room temperature for 15 min. The solution was then filtered through Celite, and the solvent was removed under vacuum to afford **10** as an analytically pure yellow powder (0.25 g, 86%). ^{1}H NMR (benzene-d_6, 500 MHz): δ 7.89 (s, 3 H, *p*-H$_{arom}$), 7.20 (s, 6 H, *o*-H$_{arom}$), 3.75 (br m, 3 H, C*H*N), 2.09 (br m, 3 H, C*H*$_2$), 1.44 (s, 54 H, C*Me*$_3$), 1.31 (br m, 3 H, C*H*$_2$), 0.12 (s, 27 H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 125.76 MHz): δ 152.7 (*m*-*C*^{t}Bu), 149.0 (*C*N), 120.9 (*o*-*C*H), 120.4 (*p*-*C*H), 62.1 (*C*HN), 35.2 (*C*Me$_3$), 35.1 (*C*H$_2$), 31.8 (C*Me*$_3$), 5.1 (Si*Me*$_3$). ^{29}Si NMR (benzene-d_6, 99.36 MHz): δ −5.1 (*Si*Me$_3$), −100.6 (*Si*SiMe$_3$) Anal. Calcd for $C_{57}H_{99}N_3Si_4Zr$: C, 66.47; H, 9.69; N, 4.08. Found: C, 66.13; H, 9.64; N, 4.06.

[*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]TiSiH(Mes)$_2$ (11). Solid Mes$_2$SiHLi(THF)$_2$ (0.14 g, 0.32 mmol) was added to a room-temperature benzene solution (ca. 10 mL) of **2** (0.25 g, 0.32 mmol). The resulting dark red solution was allowed to stir at room temperature for 2 h in the dark. The solvent was removed under vacuum, and the residue was extracted into ca. 7 mL of pentane. The pentane extracts were filtered through Celite, and the filtrate was concentrated under vacuum to ca. 2 mL volume. The solution was refrigerated at −30 °C overnight to afford **11** as a dark red microcrystalline solid (0.16 g, 53% yield). IR (Nujol mull, cm^{-1}): 2054 (SiH). ^{1}H NMR (benzene-d_6, 500 MHz): δ 7.54 (s, 3 H, *p*-H$_{arom}$), 7.09 (s, 6 H, *o*-H$_{arom}$), 6.60 (s, 4 H, *m*-H$_{arom}$), 5.25 (s, 1 H, Si*H*), 3.97 (br m, 3 H, C*H*N), 2.35 (br m, 3 H, C*H*$_2$), 2.07 (s, 6 H, *p*-C*H*$_3$), 2.01 (s, 12 H, *o*-CH$_3$), 1.43 (br m, 3 H, C*H*$_2$), 1.26 (s, 54 H, C*Me*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 125.76 MHz): δ 152.9 (*m*-*C*^{t}Bu), 150.0 (*C*N), 144.6 (*o*-*C*Me), 138.4 (*p*-*C*Me), 136.8 (*C*Si), 129.0 (*m*-*C*H), 118.4 (*o*-*C*H), 117.9 (*p*-*C*H), 62.8 (*C*HN), 35.1 (*C*H$_2$), 34.7 (*C*Me$_3$), 31.6 (C*Me*$_3$), 24.4 (*m*-C*Me*), 21.0 (*o*-C*Me*). ^{29}Si NMR (benzene-d_6, 99.36 MHz): δ −36.6 (Zr*Si*, $^{1}J_{SiH}$ = 147 Hz) Anal. Calcd for $C_{66}H_{95}N_3SiTi$: C, 78.76; H, 9.51; N, 4.18. Found: C, 78.48; H, 9.93; N, 4.07.

[*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrSiH(Mes)$_2$(THF) (12). Solid Mes$_2$SiHLi(THF)$_2$ (0.13 g, 0.32 mmol) was added to a room-temperature benzene solution (ca. 10 mL) of **3** (0.26 g, 0.32 mmol). The resulting dark yellow solution was allowed to stir at room temperature for 2 h in the dark. The solvent was removed under vacuum, and the remaining residue was extracted into ca. 5 mL of pentane. The pentane extracts were filtered through Celite and concentrated to ca. 1 mL volume. The solution was refrigerated at −30 °C overnight, to afford **12** as a yellow microcrystalline solid (0.13 g, 36% yield). IR (Nujol mull, cm^{-1}): 2079 (SiH). ^{1}H NMR (benzene-d_6, 500 MHz): δ 7.17 (s, 3 H, *p*-H$_{arom}$), 6.95 (s, 6 H, *o*-H$_{arom}$), 6.73 (s, 4 H, *m*-H$_{arom}$), 5.19 (s, 1 H, Si*H*), 4.13 (br m, 3 H, C*H*N), 3.77 (br m, 4 H, OC*H*$_2$), 2.60 (s, 12 H, *o*-C*H*$_3$), 2.14 (s, 6 H, *p*-C*H*$_3$), 2.09 (br m, 3 H, C*H*$_2$), 1.57 (br m, 3 H, C*H*$_2$), 1.35 (s, 54 H, C*Me*$_3$), 0.99 (br m, 4 H, OCH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, 125.76 MHz): δ 153.1 (*C*N), 151.4 (*m*-*C*^{t}Bu), 144.4 (*o*-*C*Me), 140.5 (*p*-*C*Me), 136.1 (*C*Si), 128.9 (*m*-*C*H), 115.3 (*p*-*C*H), 114.8 (*o*-*C*H), 72.3 (O*C*H$_2$CH$_2$), 63.0 (*C*HN), 35.0 (*C*H$_2$), 34.2 (*C*Me$_3$), 31.8 (C*Me*$_3$), 26.1 (*o*-C*Me*), 25.5 (OCH$_2$*C*H$_2$), 21.1 (*p*-C*Me*). ^{29}Si NMR (benzene-d_6, 99.36 MHz): δ −33.0 (Zr*Si*, $^{1}J_{SiH}$ = 135 Hz). Anal. Calcd for $C_{70}H_{103}N_3SiOZr$: C, 74.94; H, 9.25; N, 3.75. Found: C, 74.90; H, 9.43; N, 3.73.

[*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]TiH (13). A J-Young NMR tube was charged with a benzene-d_6 solution (0.06 mL) of **9** (10 mg, 0.010 mmol). The solution was degassed via three freeze−pump−thaw cycles, and H_2 (1 atm) was introduced. The dark red reaction mixture was shaken and allowed to stand at room temperature for 10 min. Compound **13** and 1 equiv of HSi(SiMe$_3$)$_3$ were observed as the only products by ^{1}H NMR spectroscopy (99% relative to internal standard). IR (benzene-d_6 solution, cm^{-1}): 1458 (TiH). ^{1}H NMR (benzene-d_6, 300 MHz): δ 10.73 (s, 1 H, TiH), 7.19 (s, 3 H, *p*-H$_{arom}$), 6.80 (s, 6 H, *o*-H$_{arom}$), 4.32 (br m, 3 H, C*H*N), 2.53 (s, 1 H, *H*Si(SiMe$_3$)$_3$), 2.31 (br m, 3 H, C*H*$_2$), 1.82 (br m, 3 H, C*H*$_2$), 1.32 (s, 54 H, C*Me*$_3$), 0.25 (s, 27 H, HSi(Si*Me*$_3$)$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 125.76 MHz): δ 153.0 (*m*-*C*^{t}Bu), 151.6 (*C*N), 112.8 (*p*-*C*H), 108.9 (*o*-*C*H), 56.7 (*C*HN), 35.2 (*C*H$_2$), 35.0 (*C*Me$_3$), 31.7 (C*Me*$_3$), 1.9 (HSi(Si*Me*$_3$)$_3$).

[*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]TiD (13-*d*). A procedure essentially identical to that used to prepare **13** (substituting D_2 for H_2) yielded a dark red solution of **13-*d***. Selected data: IR (benzene-d_6 solution, cm^{-1}): 1015 (TiD).

[*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]TiC$_6$H$_{13}$ (14). An Et_2O solution of HexMgBr (0.053 mL, 2.0 M, 0.11 mmol) was added to a precooled (−30 °C) solution of **2** (0.083 g, 0.11 mmol) in pentane (ca. 10 mL). The dark red reaction mixture was allowed to warm to room temperature over the course of 2 h and was then filtered through Celite. The solvent was removed under vacuum to afford **14** as a dark red solid (0.072 g, 82% yield). Alternatively, **14** could also be generated by addition of 1 equiv of neat 1-hexene to a benzene-d_6 solution of **13**. ^{1}H NMR (benzene-d_6, 500 MHz): δ 7.16 (s, 3 H, *p*-H$_{arom}$), 6.99 (s, 6 H, *o*-H$_{arom}$), 4.24 (br m, 3 H, C*H*N), 2.44 (br m, 2 H, TiC*H*$_2$), 2.12 (br m, 3 H, CHNC*H*$_2$), 1.78 (br m, 2 H, (C*H*$_2$)$_4$), 1.63 (br m, 3 H, CHNC*H*$_2$), 1.33 (s, 54 H, C*Me*$_3$), 1.27 (br m, 4 H, (C*H*$_2$)$_4$), 1.01 (br m, 2 H, (C*H*$_2$)$_4$), 0.74 (t, 3 H, CH$_2$C*H*$_3$, J_{HH} = 6 Hz). ^{13}C{^{1}H} NMR (benzene-d_6, 100.62 MHz): δ 152.1 (*m*-*C*^{t}Bu), 151.1 (*C*N), 115.9 (*p*-*C*H), 113.6 (*o*-*C*H), 84.8 (Ti*C*H$_2$, $^{1}J_{CH}$ = 119 Hz), 58.3 (*C*HN), 35.9 (*C*Me$_3$), 35.1 (CHN*C*H$_2$), 34.4 ((*C*H$_2$)$_4$), 34.0 ((*C*H$_2$)$_4$), 31.7 (C*Me*$_3$), 27.5 ((*C*H$_2$)$_4$), 22.7 ((*C*H$_2$)$_4$), 14.2 (CH$_2$*C*H$_3$). Anal. Calcd for $C_{54}H_{85}N_3Ti$: C, 78.70; H, 10.40; N, 5.10. Found: C, 78.26; H, 10.68; N, 5.00.

[*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]ZrH(PMe$_3$) (15). A J-Young NMR tube was charged with a benzene-d_6 solution (0.06 mL) of **10** (0.030 g, 0.029 mmol). The solution was degassed via three freeze−pump−thaw cycles, and H_2 (1 atm) was introduced. The reaction mixture was shaken and allowed to stand at room temperature for 10 min, over the course of which the solution changed color from yellow to dark orange-red. The solution was degassed once again via one freeze−

pump−thaw cycle, and neat PMe_3 (3 μL, 2.2 mg, 0.029 mmol) was added to the reaction mixture. The solution was shaken, and over the course of ca. 5 min the color changed from dark orange-red to yellow-orange. Compound **15** and 1 equiv of $HSi(SiMe_3)_3$ were observed as the only products by ^1H NMR spectroscopy (99% relative to internal standard). ^1H NMR (benzene-d_6, 400 MHz): δ 11.12 (s, 1 H, ZrH), 7.04 (s, 3 H, p-H_{arom}), 6.67 (s, 6 H, o-H_{arom}), 4.35 (br m, 3 H, CHN), 2.53 (s, 1 H, HSi(SiMe$_3$)$_3$), 2.23 (br m, 3 H, CH_2), 1.82 (br m, 3 H, CH_2), 1.36 (s, 54 H, CMe_3), 0.68 (br s, 9 H, PMe_3), 0.25 (s, 27 H, HSi(SiMe_3)$_3$). $^{13}C\{^1H\}$ NMR (toluene-d_8, 125.76 MHz): δ 152.9 (m-C^tBu), 150.1 (CN), 113.8 (p-CH), 109.6 (o-CH), 54.5 (CHN), 35.2 (CH$_2$), 34.7 (CMe$_3$), 31.8 (CMe_3), 15.6 (PMe_3), 1.9 (HSi(SiMe_3)$_3$). $^{31}P\{^1H\}$ NMR (toluene-d_8, 202.46 MHz): δ −57.8 (br, Zr-PMe$_3$).

[*cis,cis*-1,3,5-(3,5-$^tBu_2C_6H_3N)_3C_6H_9]ZrC_6H_{13}$ (16). A J-Young NMR tube was charged with a benzene-d_6 solution (0.06 mL) of **10** (0.030 g, 0.029 mmol). The solution was degassed via three freeze−pump−thaw cycles, and H_2 (1 atm) was introduced. The reaction mixture was shaken and allowed to stand at room temperature for 10 min, over the course of which the solution changed color from yellow to dark orange-red. The solution was degassed once again via one freeze−pump−thaw cycle, and neat 1-hexene (3.6 μL, 2.5 mg, 0.029 mmol) was added to the reaction mixture. The solution was shaken, and over the course of ca. 5 min the color changed from dark orange-red to yellow. Compound **16** and 1 equiv of $HSi(SiMe_3)_3$ were observed as the only products by ^1H NMR spectroscopy (99% relative to internal standard). ^1H NMR (benzene-d_6, 400 MHz): δ 7.12 (br m, 3 H, p-H_{arom}), 6.80 (br d, 6 H, o-H_{arom}, $J_{HH} = 1$ Hz), 4.26 (br m, 3 H, CHN), 2.53 (s, 1 H, HSi(SiMe$_3$)$_3$), 2.11 (br m, 3 H, CHNCH_2), 1.70 (br m, 5 H, CHNCH_2 and (CH_2)$_4$), 1.52 (br m, 2 H, ZrCH_2), 1.33 (s, 54 H, CMe_3), 1.25 (br m, 4 H, (CH_2)$_4$), 1.03 (br m, 2 H, (CH_2)$_4$), 0.75 (t, 3 H, CH$_2$CH_3, $J_{HH} = 7$ Hz), 0.25 (s, 27 H, HSi(SiMe_3)$_3$). $^{13}C\{^1H\}$ NMR (benzene-d_8, 100.62 MHz): δ 152.8 (m-C^tBu), 149.7 (CN), 115.1 (p-CH), 111.7 (o-CH), 61.7 (ZrCH$_2$, $^1J_{CH} = 118$ Hz), 54.8 (CHN), 35.4 (CMe$_3$), 35.1 (CHNCH$_2$), 34.7 ((CH$_2$)$_4$), 33.8 ((CH$_2$)$_4$), 31.7 (CMe_3), 25.5 ((CH$_2$)$_4$), 22.4 ((CH$_2$)$_4$), 14.0 (CH$_2$$CH_3$), 1.9 (HSi(Si$Me_3$)$_3$).

Hydrogenolysis of 10: Formation of [*cis,cis*-1,3,5-(3,5-$^tBu_2C_6H_3N)_3C_6H_9]ZrH$ (17a) and $\{$[*cis,cis*-1,3,5-(3,5-$^tBu_2C_6H_3N)_3C_6H_9]ZrH\}_2$ (17b). A J-Young NMR tube was charged with a cyclohexane-d_{12} solution (0.06 mL) of **10** (0.010 g, 0.01 mmol). The solution was degassed via three freeze−pump−thaw cycles, and H_2 (1 atm) was introduced. The reaction mixture was shaken and allowed to stand at room temperature for 10 min, over the course of which the solution changed color from yellow to dark orange-red. The only products observed by ^1H NMR (relative to an internal standard) were 1 equiv of $HSi(SiMe_3)_3$ and a mixture of **17a** and **17b**, in a 1:2 ratio. Selected data: ^1H NMR (cyclohexane-d_{12}, 500 MHz): δ 10.31 (s, 1 H, Zr$H_{monomer}$), 9.63 (br d, 1 H, $^2J_{HH} = 4$ Hz, Zr$H_{dimer,terminal}$), 5.66 (br d, 1 H, $^2J_{HH} = 4$ Hz, Zr$H_{dimer,bridging}$).

X-ray Structure Determination. Crystallographic data for complex **3**·OEt_2 are summarized in Table 1. Crystals suitable for X-ray diffraction were obtained from a concentrated pentane solution at −30 °C. X-ray diffraction measurements were made on a Siemens SMART diffractometer equipped with a CCD area detector, using graphite-monochromated Mo Kα (λ = 0.71069 Å) radiation. The crystal was mounted on a quartz fiber using Paratone N hydrocarbon oil. A hemisphere of data was collected using ω scans of 0.3°. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the measured positions of reflections in the range $3.5° < 2\theta < 45°$. The frame data were integrated using the program SAINT. An empirical absorption correction based on measurements of multiply redundant data was performed using the program SADABS. Equivalent reflections were merged. The data were corrected for Lorentz and polarization effects. The structure was solved using the teXsan crystallographic software package of Molecular Structure Corp., using direct methods, and expanded with Fourier techniques. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in geometrically calculated positions but not refined. The function minimized in the full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme was based on counting statistics and included a p factor to downweight the intense reflections.

Table 1. Crystallographic Data for Compound 3·OEt_2

empirical formula	$C_{52}H_{82}N_3ZrClO$
fw	891.91
cryst color, habit	yellow plate
cryst size (mm)	0.25 × 0.18 × 0.04
cryst syst	triclinic
space group	$P\bar{1}$(#2)
a (Å)	11.6761(3)
b (Å)	12.7217(4)
c (Å)	19.1575(7)
α (deg)	93.904(1)
β (deg)	106.820(1)
γ (deg)	110.368(1)
V (Å^3)	2508.0(1)
no. of orientation reflns (2θ range)	3617 (3.5−45.0°)
Z value	2
D_{calc} (g/cm^3)	1.181
F_{000}	960.00
μ(Mo Kα) (cm^{-1})	3.10
diffractometer	SMART
radiation	Mo Kα (λ = 0.71069 Å) graphite monochromated
temperature (°C)	−133
scan type	ω (0.3° per frame)
scan rate	20.0 s per frame
$2\theta_{max}$ (deg)	46.5
no. reflns measured	total: 11 554 unique: 7040
R_{int}	0.058
transmn factors	$T_{max} = 0.98$ $T_{min} = 0.44$
structure solution	direct methods (SIR92)
no. of observations	4041 ($I > 3.00\sigma(I)$)
no. of variables	523
reflns/param ratio	7.73
residuals: R; R_w; R_{all}	0.054; 0.056; 0.099
goodness of fit	1.46
max. shift/error in final cycle	0.00
max. and min. peaks in final diff map (e$^-$/Å^3)	1.03; −1.47

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Supporting Information Available: Summaries of crystallographic data, bond distances and angles, atomic coordinates, and anisotropic displacement parameters for **3**·OEt_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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