# Synthesis and Structure of (Triphenylsilyl)imido Complexes of Titanium and Zirconium

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Titanium and zirconium (triphenylsilyl)imido complexes are available through transimination from the *tert*-butylimido complexes with $H_2NSiPh_3$. The useful starting material $Ti(NSiPh_3)Cl_2(py)_2$ (**1**) is prepared in 88% yield by treatment of $Ti(NBu^t)Cl_2(py)_3$ with $H_2NSiPh_3$. Imido **1** is a dimer in the solid state with bridging chlorides; however, solution molecular weight studies indicate that **1** is a monomer in $CH_2Cl_2$. **1** reacts with 4,4′-di-*tert*-butyl-2,2′-bipyridine (bpy) to generate the pseudo-octahedral $Ti(NSiPh_3)(bpy)(py)Cl_2$ (**2**) in 74% recrystallized yield. Replacement of the chloride ligands of **1** with 2 equiv of Lidap, 1 equiv of Libap, or 1 equiv of Lipap afforded the pyrrolylimido complexes $Ti(NSiPh_3)(dap)_2$ (**3**), $Ti(NSiPh_3)(bap)Cl$ (**4**), and $Ti(NSiPh_3)(pap)Cl$ (**5**), respectively. The reaction of 2 equiv of neophyl (Nph) magnesium bromide with **1** provided $[Ti(\mu\text{-}NSiPh_3)(Nph)_2]_2$ (**6**) in 59% yield. The pseudo-octahedral complex $Ti(NSiPh_3)(dpma)(bpy)$ (**8**) was available through addition of $Li_2$dpma to **1**, forming $Ti(NSiPh_3)(dpma)(py)_2$ (**7**) followed by treatment with bpy. Alternatively, **8** was prepared by addition of bpy and $H_2NSiPh_3$ to $Ti(NMe_2)_2$(dpma). The zirconium *tert*-butylimido complex $Zr(NBu^t)(dpma)(bpy)$ (**9**) was available in 43% yield by treatment of $Zr(NMe_2)_2(py)$(dpma) with bpy and $H_2NBu^t$. Transimination on **9** with $H_2NSiPh_3$ provided the (triphenylsilyl)imido complex $Zr(NSiPh_3)(dpma)(bpy)$ (**10**) in 34% yield. In an unusual transformation, **10** reacts with excess sodium 2,6-dimethylphenoxide in THF to afford $[Na(bpy)][Zr(dpma)(OAr)_3]$ (**11**), where the Na coordinates to the bpy and both pyrrole rings of the dpma in an $\eta^5$ fashion. Compounds **1**, **5**, **6**, **8**, and **11** were structurally characterized.

## Introduction

Silylimido complexes are a mainstay of imido studies, and there are a large number of (trialkylsilyl)imido complexes known for the transition metals.[1] Most notably, terminal (trimethylsilyl)imido complexes are known for all the elements of groups 4−6.[1] In addition, Wolczanski and co-workers have prepared and studied the reaction chemistry of many (tri-*tert*-butylsilyl)imido complexes.[2] Surprisingly, (triarylsilyl)imido complexes of the transition metals have scarcely appeared in the literature, and there are none with titanium and zirconium.[3] Consequently, we sought, as a continuation of our interest in titanium imido reactivity,[4] to develop routes to these complexes.

The majority of silylimido complexes of the group 4 elements are the $NSiBu^t_3$ complexes of Wolczanski and co-workers, known to activate C−H bonds,[5] and several (trimethylsilyl)imido derivatives of titanium. The earliest report is by Bürger and Wannagat, who proposed the generation of $Me_3SiN{=}TiCl_2(pyridine)_2$ in 1963.[6,7] Dehnicke and co-workers reported the synthesis of an organometallic trimethylsilyl derivative.[8] Chirik and co-workers reported a cyclopentadienyl-supported (trimethylsilyl)imido complex,[9] and triazacyclononane derivatives were used by the Mountford group.[10] Benz-

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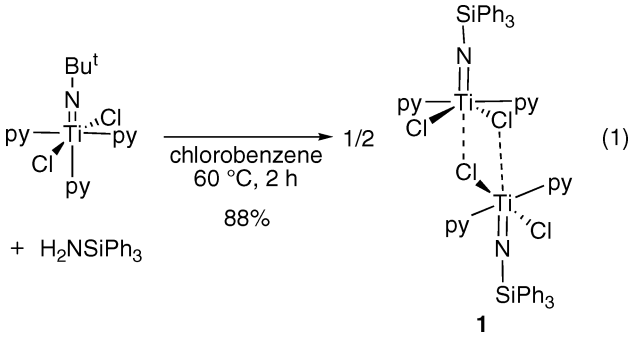
amidinatetitanium complexes were reported by Hagadorn and Arnold to generate (trimethylsilyl)imido complexes.[11] In addition, Woo and co-workers oxidized the formally titanium(II) porphyrin complex Ti(TTP)($\eta^2$-3-hexyne) with $Me_3SiN_3$ to generate $Me_3SiN{=}Ti(TTP)$.[12]

In this paper, we report that (triphenylsilyl)imido complexes of titanium and zirconium are readily prepared by transimination of *tert*-butylimido groups with readily available $H_2NSiPh_3$. Included among the new complexes reported is the simple, useful starting material $Ph_3SiN{=}TiCl_2(pyridine)_2$.

## Results and Discussion

(Triphenylsilyl)amine is commercially available or is readily prepared in high yield by the action of ammonia on a benzene solution of $ClSiPh_3$. Several methods for the generation of (triphenylsilyl)imido complexes of group 4 were explored. The reaction of $H_2NSiPh_3$ with $TiCl_4$ in the presence of pyridine (py) under conditions similar to those used to prepare Mountford's reagent, $Ti(NBu^t)Cl_2(py)_3$,[13] did not afford an isolable terminal imido complex. However, transimination[13b] by reaction of $Ti(NBu^t)Cl_2(py)_3$ with $H_2NSiPh_3$ in chlorobenzene (eq 1) provided the dichloride starting material $[Ti(NSiPh_3)Cl_2(py)_2]_2$ (**1**), which precipitates as a yellow crystalline solid during the reaction in 88% yield.




(1)

The transimination apparently proceeds to full conversion with no *tert*-butylimido complex remaining. A possible explanation for the greater stability of the silylimido is that the $SiPh_3$ group may stabilize the partial negative charge on the nitrogen of the imido, leading to its preferential formation.

The structure of **1** was determined by X-ray diffraction. An ORTEP representation of the structure is shown in Figure 1. In the solid state, the compound is dimeric, with equatorial chlorides of one imido complex coordinating trans to the imido group. The bridging chloride trans to the imido has a quite long Ti−Cl distance of 2.743(4) Å (Table 1). The Ti−Cl distance to the bridging chloride cis to the imide is lengthened at 2.444(4) Å relative to the terminal chloride at 2.357(4) Å. These distances are what would be expected, considering the known strong trans influence of imido substituents. The Ti=N bond distance is unremarkable at 1.714(8) Å, and the imido is linear, with a Ti=N−Si angle of 170.6(5)°. The pyridine rings on opposing titanium centers across the $Ti_2Cl_2$ ring are parallel; the arrangement and distance between the $\pi$-systems of 3.62 Å are suggestive of $\pi$-stacking interactions: cf. the interlayer distance in graphite of 3.35 Å.

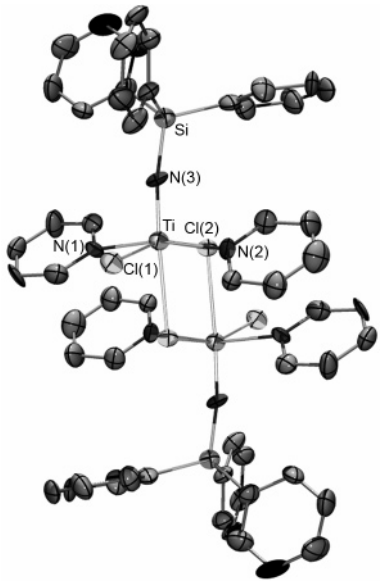



**Figure 1.** ORTEP representation of the structure of $[Ti(NSiPh_3)Cl_2(py)_2]_2$ (**1**) from X-ray diffraction. The molecule resides on a crystallographic inversion center.

**Table 1. Selected Bond Distances (Å) and Angles (deg) from the X-ray Diffraction Study on $[Ti(NSiPh_3)Cl_2(py)_2]_2$ (1)**

| | | | |
|---|---|---|---|
| Ti−N(3) | 1.716(7) | Ti−N(2) | 2.219(8) |
| Ti−N(1) | 2.232(8) | Ti−Cl(1) | 2.355(3) |
| Ti−Cl(2) | 2.443(3) | Ti−Cl(2′) | 2.755(3) |
| Ti−N(3)−Si | 171.1(5) | | |
| N(3)−Ti−N(1) | 96.7(3) | N(2)−Ti−N(1) | 167.8(3) |
| Cl(1)−Ti−Cl(2) | 160.7(1) | N(3)−Ti−Cl(2′) | 174.7(3) |
| Cl(2)−Ti−Cl(2′) | 76.5(1) | Cl(1)−Ti−Cl(2′) | 84.3(1) |
| N(3)−Ti−N(1) | 95.5(3) | | |

While complex **1** is a dimer in the solid state, solution molecular weight measurements in $CH_2Cl_2$ are more consistent with a monomer formulation in that solvent.

The *tert*-butylimido analog of **1** has been extensively used in the synthesis of new imido complexes.[14] Consequently, we explored the chloride metathesis chemistry and pyridine replacement reactions of **1**.

Addition of 4,4′-di-*tert*-butyl-2,2′-bipyridine (bpy) to dimeric **1** results in the loss of one pyridine ligand and formation of monomeric, pseudo-octahedral $Ti(NSiPh_3)Cl_2(bpy)(py)$ (**2**) (eq 2).

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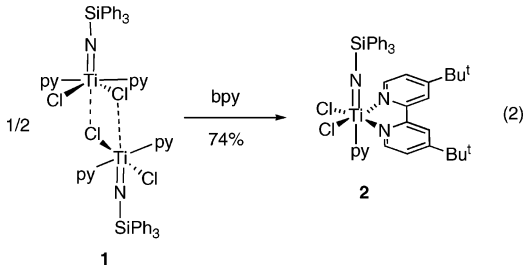


A few metathesis reactions with the dichloride starting material **1** were explored (Scheme 1). Three pyrrolyl ligands are shown in Scheme 1. Reaction of **1** with 2 equiv of Li(dap), where dap[15] is α-((dimethylamino)-methyl)pyrrolyl, generates the five-coordinate complex $Ti(NSiPh_3)(dap)_2$ (**3**). Reaction with 1 equiv of Li(bap), where bap is α,α′-bis((dimethylamino)methyl)pyrrolyl, results in the formation of $Ti(NSiPh_3)Cl(bap)$ (**4**). Similarly, reaction with 1 equiv of Li(pap), where pap is α,α′-bis(piperidin-1-ylmethyl)pyrrolyl, affords $Ti(NSiPh_3)$-Cl(pap) (**5**).

The structure of $Ti(NSiPh_3)(Cl)(pap)$ (**5**) was determined by X-ray diffraction (Figure 2, Table 2). The complex is best described as square pyramidal with the imido nitrogen occupying the axial site. The pap ligand is tridentate in this case, which is not always the case with the 2,5-disubstituted pyrrolyl ligands pap and bap.[16]

As shown in Scheme 1, reaction of **1** with neophyl (Nph) magnesium chloride provides the dimeric complex $[Ti(\mu\text{-}NSiPh_3)(Nph)_2]_2$ (**6**). Attempts to convert dimeric **6** into a monomeric, terminal imido complex by addition of bpy were unsuccessful. Addition of methylalumoxane to either **1** or **6** did not provide a catalyst capable of polymerizing 1-hexene.[17]

The solid-state structure of $[Ti(\mu\text{-}NSiPh_3)(Nph)_2]_2$ (**6**) was also determined by X-ray diffraction (Figure 3, Table 3). As shown, the complex is a dimer that resides on a crystallographically imposed inversion center. The imido group bridges are chemically identical, with Ti−N(imido) distances that are identical within error, 1.917(4) and 1.923(4) Å, which as would be expected is substantially longer than the Ti−N distances of ∼1.70 Å found for the terminal (triphenylsilyl)imido complexes. Each pseudo-tetrahedral titanium center also bears two neophyl groups with Ti−C distances of 2.064(4) and 2.100(5) Å.

Metathesis on $[Ti(NSiPh_3)Cl_2(py)_2]_2$ (**1**) with $Li_2$dpma, where dpma[18] is *N*,*N*-di(pyrrolyl-α-methyl)-*N*-methylamine, was also investigated (Scheme 2). Addition of $Li_2$dpma to $^1/_2$ equiv of $[Ti(NSiPh_3)Cl_2(py)_2]_2$ (**1**) results in the formation of $Ti(NSiPh_3)(dpma)(py)_2$ (**7**) in 36% yield. It is currently unknown whether **7** has a cis or trans geometry with respect to the pyridine ligands; both geometries have precedents in other Ti(imido)-$(dpma)L_2$ complexes.[18] Treatment of **7** with bpy provided $Ti(NSiPh_3)(dpma)(bpy)$ (**8**) in 76% yield. A shorter, alternative procedure to obtain **8** (Scheme 2) involves the action of $H_2NSiPh_3$ on a solution of $Ti(NMe_2)_2(dpma)$

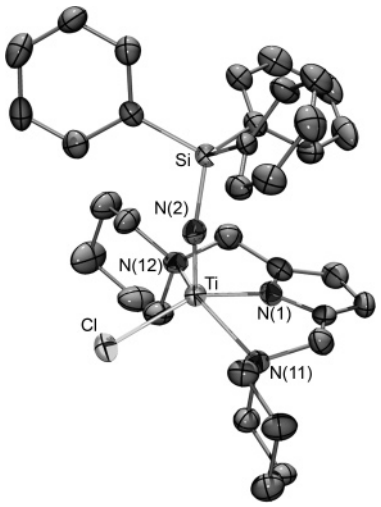


**Figure 2.** ORTEP representation of the structure of $Ti(NSiPh_3)(Cl)(pap)$ (**5**) from X-ray diffraction.

**Scheme 1. Metathesis Reactions on 1 with Monoanionic Ligands**

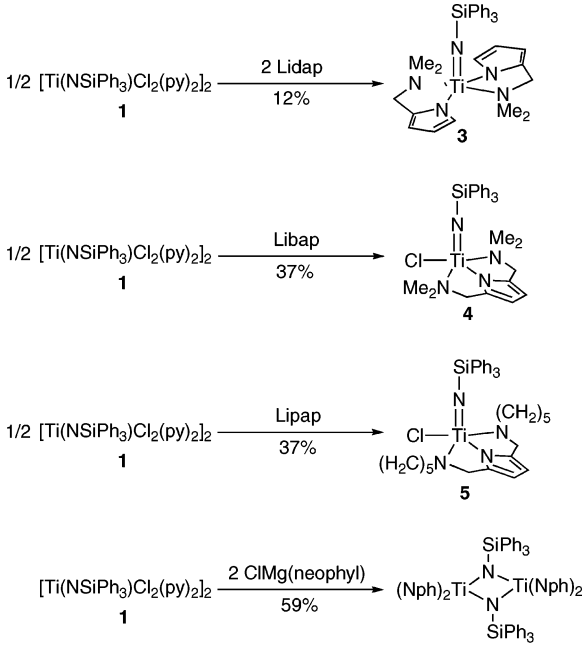


**Table 2. Selected Bond Distances (Å) and Angles (deg) from the X-ray Diffraction Study on $Ti(NSiPh_3)(Cl)(pap)$ (5)**

| | | | |
|---|---|---|---|
| Ti−N(2) | 1.698 (6) | Ti−N(1) | 1.995(6) |
| Ti−N(11) | 2.248(6) | Ti−N(12) | 2.274(6) |
| Ti−Cl | 2.333(2) | | |
| Ti−N(2)−Si | 156.5(4) | N(2)−Ti−N(1) | 106.6(3) |
| N(2)−Ti−N(11) | 106.4(2) | N(1)−Ti−N(11) | 73.7(2) |
| N(1)−Ti−N(12) | 73.1(2) | N(11)−Ti−N(12) | 139.7(2) |
| N(2)−Ti−Cl | 145.1(2) | Cl−Ti−N(12) | 97.5(2) |

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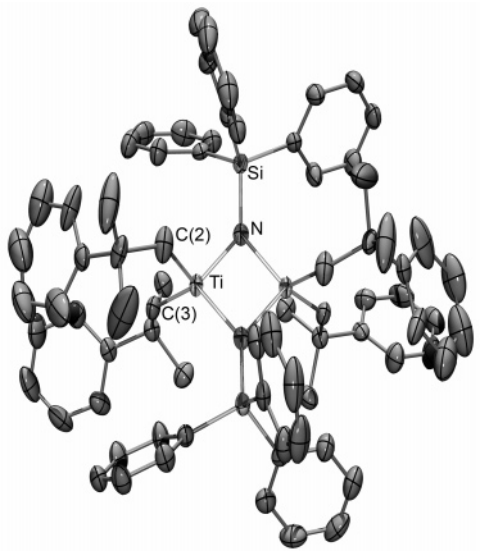
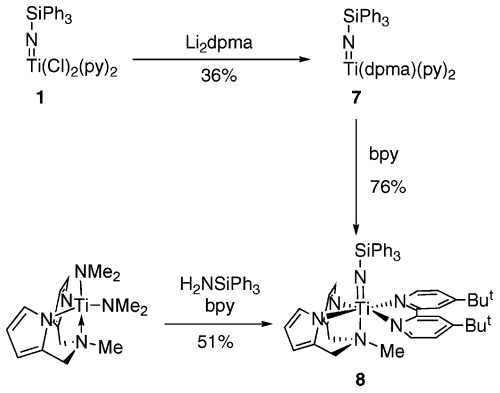



**Figure 3.** ORTEP representation of the structure of $[Ti(\mu\text{-}NSiPh_3)(Nph)_2]_2$ (**6**) from X-ray diffraction. The molecule resides on a crystallographic inversion center.

**Table 3. Selected Bond Distances (Å) and Angles (deg) from the X-ray Diffraction Study on $[Ti(\mu\text{-}NSiPh_3)(Nph)_2]_2$ (6)**

| | | | |
|---|---|---|---|
| Ti−N | 1.923(4) | Ti−N′ | 1.917(4) |
| Ti−C(3) | 2.064(4) | Ti−C(2) | 2.100(5) |
| Ti−N−Si | 133.6(2) | Ti−N−Ti′ | 93.4(2) |
| C(2)−Ti−C(3) | 110.1(2) | N−Ti−C(2) | 115.0(2) |
| N−Ti−C(3) | 119.3(2) | | |

**Scheme 2. Two Routes to $Ti(NSiPh_3)(dpma)(bpy)$ (8)**

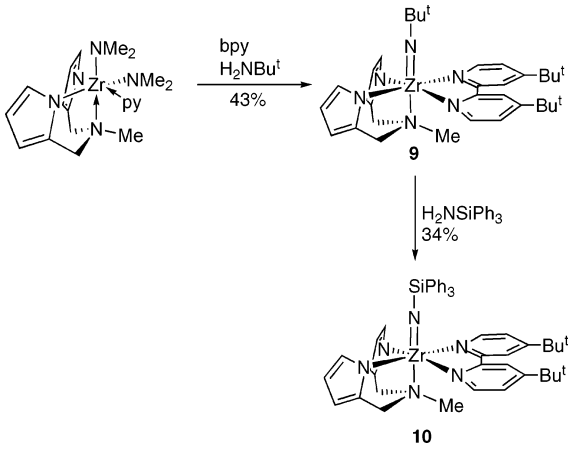



and bpy, which afforded **8** in 51% yield. Complex **8** was also structurally characterized (see the Supporting Information for details).

The addition of various primary amines to alkynes, hydroamination, is catalyzed by $Ti(NMe_2)_2(dpma)$.[18] In these reactions, titanium imido complexes are likely intermediates. Considering the formation and isolation of an imido complex on addition of $H_2NSiPh_3$ to $Ti(NMe_2)_2(dpma)$ shown above, we were somewhat surprised to find that the reaction of 1-hexyne and $H_2NSiPh_3$ in the presence of this titanium complex did not afford the expected hydroamination product. It is currently unknown if it is steric and/or electronic factors that result in this lack of reactivity.

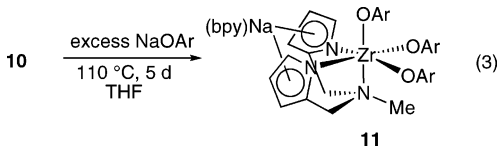
Access to zirconium (triphenylsilyl)imido complexes was accomplished through transimination on a *tert*-butylimido complex as well. The new imido $Zr(NBu^t)$-

**Scheme 3. Synthetic Route to $Zr(NSiPh_3)(dpma)(bpy)$ (10)**




(bpy)(dpma) (**9**) was synthesized by addition of *tert*-butylamine to a solution of $Zr(dpma)(py)(NMe_2)_2$[18a] and bpy in 43% yield. Treatment of **9** with $H_2NSiPh_3$ afforded silylimido $Zr(NSiPh_3)(dpma)(bpy)$ (**10**) in 34% isolated yield (Scheme 3). As with the synthesis of $[Ti(NSiPh_3)Cl_2(py)_2]_2$ (**1**) (vide supra), attempts to circumvent the transimination procedure and avoid the formation of *tert*-butylimido **9** were unsuccessful. In other words, addition of $H_2NSiPh_3$ to a solution of $Zr(dpma)(py)(NMe_2)_2$ and bpy did not provide observable quantities of **10**.

In a very unusual reaction, addition of an excess of sodium 2,6-dimethylphenoxide to **10** results in the loss of the imido ligand entirely to form the triaryloxide zirconate complex [(bpy)Na][$Zr(OAr)_3(dpma)$] (**11**) (eq 3).




The complex was structurally characterized (Figure 4, Table 4), and the sodium is bound to the bpy ligand and, in a bis-$\eta^5$ fashion, to the two pyrrolyl substituents of

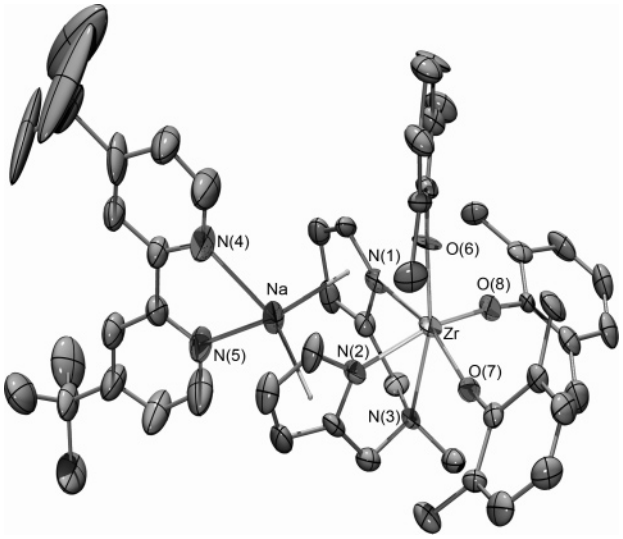



**Figure 4.** ORTEP representation of the structure of [(bpy)Na][$Zr(OAr)_3(dpma)$] (**11**) from X-ray diffraction.

**Table 4. Selected Bond Distances (Å) and Angles (deg) from the X-ray Diffraction Study on [(bpy)Na][Zr(OAr)$_3$(dpma)] (11)**

| | | | |
|---|---|---|---|
| Zr−O(6) | 1.945(9) | Zr−O(7) | 1.983(11) |
| Zr−O(8) | 2.005(11) | Zr−N(1) | 2.291(14) |
| Zr−N(2) | 2.211(13) | Zr−N(3) | 2.468(3) |
| Na−N(4) | 2.397(17) | Na−N(5) | 2.374(17) |
| O(6)−Zr−O(7) | 99.7(4) | O(6)−Zr−O(8) | 103.0(4) |
| O(7)−Zr−N(8) | 95.5(4) | O(6)−Zr−N(2) | 97.5(5) |
| O(7)−Zr−N(2) | 91.1(5) | O(8)−Zr−N(2) | 157.0(4) |
| N(2)−Zr−N(1) | 78.9(5) | N(1)−Zr−N(3) | 74.4(4) |

the dpma. The zirconium is pseudo-octahedral, with the aryloxide ligands facially occupying three sites. The reaction was run at 110 °C for 5 days in THF. Attempts to run the reaction under milder conditions afforded the same product at slower rates without observed intermediates. The binding of the pyrrolyl ligands to the sodium does not effect the Zr−N(pyrrolyl) bonding, as judged by the metrical parameters from X-ray diffraction. The Zr−N(pyrrolyl) distances in **10** average 2.25(1) Å, which is very similar to the distances in Zr(NMe$_2$)$_2$(NHMe$_2$)(dpma) of 2.232(4) Å.[18a] The average Na−centroid distance in the pyrrole ring is 2.53 Å, with a centroid−Na−centroid angle of 107°.

## Concluding Remarks

(Triphenylsilyl)imido complexes of titanium and zirconium are readily available from transimination of the *tert*-butylimido derivatives. For example, the useful starting material [Ti(NSiPh$_3$)Cl$_2$(py)$_2$]$_2$ (**1**) is prepared in 88% yield from Mountford's reagent, Ti(NSiPh$_3$)Cl$_2$(py)$_3$, and H$_2$NSiPh$_3$. Halide replacement on **1** with Grignard and lithium reagents often occurs smoothly to afford new imido complexes. As a result, this chemistry offers a new inlet into (triarylsilyl)imido complexes that will likely provide some variability in steric and electronic control at the imido substituent through the use of different substitution patterns on readily prepared Ar$_3$SiNH$_2$ starting materials.

## Experimental Section

**General Considerations.** All manipulations of air-sensitive compounds were carried out in an MBraun drybox under a purified nitrogen atmosphere. Anhydrous ether was purchased from Columbus Chemical Industries Inc. and freshly distilled from purple sodium benzophenone ketyl. Toluene was purchased from Spectrum Chemical Mfg. Corp. and purified by refluxing over molten sodium under nitrogen for at least 2 days. Pentane (Spectrum Chemical Mfg. Corp.), tetrahydrofuran (JADE Scientific), and benzene (EM Science) were distilled from purple sodium benzophenone ketyl. Dichloromethane (EM Science) and acetonitrile (Spectrum Chemical) were distilled from calcium hydride. Deuterated solvents were dried over purple sodium benzophenone ketyl (C$_6$D$_6$) or phosphoric anhydride (CDCl$_3$) and distilled under nitrogen. $^1$H and $^{13}$C NMR spectra were recorded on Inova-300 or VXR-500 spectrometers. $^1$H and $^{13}$C assignments were confirmed when necessary with the use of two-dimensional $^1$H−$^1$H and $^{13}$C−$^1$H correlation NMR experiments. All spectra were referenced internally to residual protio solvent ($^1$H) or solvent ($^{13}$C) resonances. Chemical shifts are quoted in ppm and coupling constants in Hz, and common coupling constants are not provided. The gaseous ammonia was 99.99% anhydrous NH$_3$ purchased from AGA Gas, Inc. H$_2$dpma, Zr(dpma)(py)(NMe$_2$)$_2$, and Ti(NMe$_2$)$_2$(dpma) were prepared as previously described.[18a] Ti(NBu$^t$)Cl$_2$(py)$_3$,[13] Hbap,[19] Hdap,[19] and Hpap[19] were prepared using the literature procedures. Ph$_3$SiCl was purchased from Aldrich Chemical Co. and was used as received.

**General Considerations for X-ray Diffraction.** Crystals grown from concentrated solutions at −35 °C were moved quickly from a scintillation vial to a microscope slide containing Paratone N. Samples were selected and mounted on a glass fiber in wax and Paratone. The data collections were carried out at a sample temperature of 173 K on a Bruker AXS platform three-circle goniometer with a CCD detector. The data were processed and reduced utilizing the program SAINT-PLUS supplied by Bruker AXS. The structures were solved by direct methods (SHELXTL v5.1, Bruker AXS) in conjunction with standard difference Fourier techniques. Structural parameters for **1**, **5**, **6**, **8**, and **11** are given in Table 5.

**Synthesis of H$_2$NSiPh$_3$.** A solution of 16 g of Ph$_3$SiCl (54.3 mmol) in 250 mL of anhydrous benzene was placed in a 500 mL round-bottom flask equipped with a mechanical stirrer, a water-cooled condenser, and a gas inlet tube. The system was kept under dry nitrogen through a gas adapter fixed to the top of the condenser. The gas inlet tube extended ~1 cm below the surface of the stirred reaction mixture. The gas inlet tube was connected to a tank of ammonia through an empty trap (in case of accidental backup of solution) and to an oil-filled bubbler through a glass T-tube. An external ice−water bath was used to keep the temperature of the reaction mixture below 30 °C. A slow stream of ammonia was passed into the reaction flask, and a precipitate of ammonium chloride appeared during addition. The gas flow was continued for 6 h. Then, the reaction mixture was refluxed for 3 h to remove excess ammonia. The reaction mixture was cooled to room temperature and taken into a glovebox. The precipitate was removed by filtration through a fritted funnel. The solid residue was washed with small portions equaling ~100 mL of C$_6$H$_6$, and the filtrates were combined. The volatiles of the mixture were removed in vacuo to yield a white solid. The solid was recrystallized from benzene/pentane to yield (triphenylsilyl)amine as a white solid. Yield: 13.9 g (93%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.79 (6H, m, 2,6-Si(C$_6$H$_5$)$_3$), 7.65 (3H, m, 4-Si(C$_6$H$_5$)$_3$), 7.53 (6H, m, 3,5-Si(C$_6$H$_5$)$_3$), 1.41 (2H, s, $H_2$NSi)). $^{13}$C NMR (CDCl$_3$): $\delta$ 135.2 (2,6-C$_6$H$_5$), 135.1 (3,5-C$_6$H$_5$), 129.6 (1-C$_6$H$_5$), 127.8 (4-C$_6$H$_5$).

**Synthesis of [Ti(NSiPh$_3$)Cl$_2$py$_2$]$_2$ (1).** To an orange solution of Ti(NBu$^t$)Cl$_2$py$_3$ (1.770 g, 4.15 mmol) in 20 mL of chlorobenzene was added H$_2$NSiPh$_3$ (1.142 g, 4.15 mmol) in 5 mL of chlorobenzene in a threaded thick-walled reaction vessel. The vessel was capped with a Teflon stopper and removed from the drybox. The reaction mixture was heated in a 60 °C oil bath for 2 h. During heating, a yellow solid precipitated from solution. The solid was collected by filtration and dried under reduced pressure. Yield: 2.012 g (88%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 9.02 (4 H, m, 2-C$_5$H$_5$N), 7.69 (4 H, m, 3-C$_5$H$_5$N), 7.36−7.22 (17 H, m, Si(C$_6$H$_5$)$_3$ and 4-C$_5$H$_5$N). $^{13}$C NMR (CDCl$_3$): $\delta$ 151.3 (4-C$_5$H$_5$N), 138.8 (3-C$_5$H$_5$N), 135.4 (4-C$_5$H$_5$N), 129.3 (1-C$_6$H$_5$), 127.7 (2-C$_6$H$_5$ and 3-C$_6$H$_5$), 124.3 (4-C$_6$H$_5$).

**Synthesis of Ti(NSiPh$_3$)Cl$_2$(Bu$^t$-bpy)(py) (2).** To a yellow solution of Ti(NSiPh$_3$)Cl$_2$py$_2$ (**1**; 1.116 g, 2.03 mmol) in 10 mL of CH$_2$Cl$_2$ was added Bu$^t$-bpy (545 mg, 2.03 mmol) in 5 mL of CH$_2$Cl$_2$. After the mixture was stirred at room temperature for 16 h, volatiles of the reaction mixture were removed in vacuo to yield a yellow solid. The solid was recrystallized from CH$_2$Cl$_2$. Yield: 1.107 g (74%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 9.63 (2H, d, 6,6′-bpy), 7.88 (2H, s, 3,3′-bpy), 7.53 (2H, d, 5,5′-bpy), 7.41 (6H, m, 2,6-Si(C$_6$H$_5$)$_3$), 7.25 (3H, m, 4-Si(C$_6$H$_5$)$_3$), 7.14 (6H, m, 3,5-Si(C$_6$H$_5$)$_3$), 1.42 (18H, s, Bu$^t$). $^{13}$C NMR (CDCl$_3$): $\delta$ 164.6 (2,2′-bpy), 152.9 (6,6′-bpy), 152.2 (4,4′-bpy), 136.8 (1-C$_6$H$_5$), 134.0 (3,3′-bpy), 128.5 (5,5′-bpy), 127.1 (2-C$_6$H$_5$), 122.8 (3-C$_6$H$_5$), 117.4 (4-C$_6$H$_5$), 35.4 (*C*(CH$_3$)$_3$-bpy), 30.3 (C(*C*H$_3$)$_3$-

(19) Kim, H.; Elsenbaumer, R. L. *Tetrahedron Lett.* **1998**, *39*, 1087.

**Table 5. Structural Parameters for $[Ti(NSiPh_3)(py)_2Cl_2]_2$ ($1\cdot CH_2Cl_2$), $Ti(NSiPh_3)(pap)Cl$ ($5\cdot C_7H_8$), $[Ti(Nph)_2(\mu\text{-}NSiPh_3)]_2$(6), $Ti(NSiPh_3)(bpy)(dpma)$ ($8\cdot CH_2Cl_2$), and $[Na(bpy)][Zr(dpma)(OAr)_3]$ ($11\cdot C_7H_8$)**

| | 1 | 5 | 6 | 8 | 11 |
|---|---|---|---|---|---|
| formula | $C_{29}H_{27}Cl_4N_3SiTi_2$ | $C_{41}H_{49}ClN_4SiTi$ | $C_{38}H_{41}NSiTi$ | $C_{48}H_{54}Cl_2N_6SiTi$ | $C_{60}H_{72}N_5NaO_3Zr$ |
| formula wt | 645.33 | 709.28 | 587.71 | 861.86 | 1025.44 |
| space group | $P2_1/c$ | $P2_1/c$ | $C2/c$ | $P2_1/c$ | $P\bar{1}$ |
| $a$ (Å) | 9.100(2) | 11.880(3) | 25.633(4) | 12.3148(18) | 12.468(3) |
| $b$ (Å) | 18.062(5) | 19.005(4) | 11.2928(17) | 17.191(3) | 15.019(3) |
| $c$ (Å) | 18.337(4) | 17.779(4) | 22.587(4) | 22.176(4) | 13.703(3) |
| α (deg) | | | | | 84.293(7) |
| $\beta$ (deg) | 102.342(5) | 92.182(4) | 99.0.119(3) | 98.280(4) | 86.841(5) |
| $\gamma$ (deg) | | | | | 75.727(5) |
| $V$ (Å$^3$) | 2944.4(12) | 4011.2(16) | 6455.5(17) | 4645.6(12) | 3506.0(19) |
| $Z$ | 4 | 4 | 8 | 4 | 2 |
| $\mu$ (mm$^{-1}$) | 0.719 | 0.342 | 0.329 | 0.364 | 0.201 |
| $D_{calcd}$ (g cm$^{-3}$) | 1.433 | 1.174 | 1.209 | 1.232 | 0.971 |
| total no. of rflns | 1322 | 33 445 | 26 453 | 16 689 | 29 851 |
| no. of unique rflns ($R_{int}$) | 4212 (0.295) | 5774 (0.081) | 4666 (0.1518) | 6401 (0.1256) | 10 139 (0.351) |
| extinction | 0.0004(5) | 0.010(2) | 0.00019(16) | 0.00126(10) | none |
| $R(F_o)$ ($I > 2\sigma$) | 0.0756 | 0.0965 | 0.0615 | 0.0481 | 0.1396 |
| $R_w(F_o^2)$ ($I > 2\sigma$) | 0.1381 | 0.3098 | 0.1572 | 0.0668 | 0.3590 |

bpy). Anal. Found (calcd) for $C_{36}H_{39}N_3Cl_2SiTi$: C, 64.98 (65.38); H, 6.15 (5.90); N, 6.23 (6.36).

**Synthesis of $[Ti(NSiPh_3)(neophyl)]_2$ (6).** To a near-frozen solution of $Ti(NSiPh_3)Cl_2py_2$ (**1**; 550 mg, 1.00 mmol) in 10 mL of $Et_2O$ was added a solution of $ClMgCH_2C(Me)_2Ph$ (4 mL, 2.00 mmol, 0.5 M solution in $Et_2O$) dropwise. After it was stirred at room temperature for 16 h, the resulting orange solution was filtered to remove a white solid. Volatiles were removed from the solution in vacuo, yielding the product, which was recrystallized from $CH_2Cl_2$/pentane. Yield: 350 mg (59%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.78 (6H, d, 2,6-Si($C_6H_5$)$_3$), 7.45 (3H, m, 4-Si($C_6H_5$)$_3$), 7.36 (6H, m, 3,5-Si($C_6H_5$)$_3$), 7.12 (4H, m, 3,5-C($C_6H_5$)), 7.07 (2H, m, 4-C($C_6H_5$)), 6.87 (4H, d, 2,6-C($C_6H_5$)), 2.13 (4H, s, C$H_2$C(Me)$_2$Ph), 0.92 (12H, s, $CH_2C(Me)_2Ph$). $^{13}$C NMR ($CDCl_3$): $\delta$ 136.8 (2-$C_6H_5$), 135.5 (1-$C_6H_5$), 130.2 (4-$C_6H_5$), 128.2 (6-$C_6H_5$), 125.5 (5-$C_6H_5$), 111.4 ($CH_2C(Me)_2Ph$), 32.6 ($CH_2C(Me)_2Ph$), 31.6 ($CH_2C(Me)_2Ph$). Anal. Found (calcd) for $C_{76}H_{82}N_2Si_2Ti_2$: C, 77.64 (76.82); H, 6.98 (6.97); N, 2.38 (2.41).

**Synthesis of $Ti(NSiPh_3)(dpma)(py)_2$ (7).** To a near-frozen solution of $Ti(NSiPh_3)Cl_2py_2$ (**1**; 932 mg, 1.69 mmol) in 20 mL of toluene was added $Li_2$dpma (340 mg, 1.69 mmol) in 10 mL of toluene dropwise. After it was stirred at room temperature for 48 h, the resulting dark yellow solution was filtered to remove a white solid. Volatiles were removed from the reaction in vacuo, yielding the solid crude product, which was recrystallized from toluene at −35 °C to provide a yellow solid. Yield: 405 mg (36%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.10 (2 H, d, 2-$C_5H_5N$), 7.87 (2 H, d, 4-$C_5H_5N$), 7.73 (2 H, app s, 3-$C_4H_3N$), 7.65 (2 H, m, 3-$C_5H_5N$), 7.31−7.10 (19 H, m, Si($C_6H_5$)$_3$, 2-$C_5H_5N$, and 3-$C_5H_5N$), 6.29 (2 H, m 4-$C_4H_3N$), 5.99 (2 H, m, 5-$C_4H_3N$), 3.41 (4 H, s, $C_4H_3NCH_2N(CH_3)$), 1.69 (3 H, s, $C_4H_3NCH_2N(CH_3)$). $^{13}$C NMR ($CDCl_3$): $\delta$ 151.3 (2-$C_5H_5N$), 150.6 (2-$C_5H_5N$), 139.7 (3-$C_5H_5N$), 138.3 (3-$C_5H_5N$), 137.6 (2-$C_4H_3N$), 135.1 (4-$C_5H_5N$), 130.1 (1-$C_6H_5$), 128.3 (2-$C_6H_5$), 127.1 (5-$C_4H_3N$), 124.8 (3-$C_6H_5$), 59.6 ($C_4H_3NCH_2N(CH_3)$), 45.1 ($C_4H_3NCH_2N(CH_3)$). Anal. Found (calcd) for $C_{39}H_{38}N_6SiTi$: C, 69.76 (70.28); H, 5.71 (5.71); N, 12.38 (12.61).

**Synthesis of $Ti(NSiPh_3)(dpma)(bpy)$ (8). Method A.** To a mixture of $Ti(NMe_2)_2$(dpma) (200 mg, 0.62 mmol) and Bu$^t$-bpy (166 mg, 0.62 mmol) in chlorobenzene (5 mL) was added $H_2NSiPh_3$ (170 mg, 0.62 mmol) in chlorobenzene (5 mL). The Schlenk flask was taken out of the drybox and heated under $N_2$ at 60 °C. After the mixture was heated for 16 h, the volatiles were removed in vacuo, resulting in a yellow solid, which was washed with pentane. Yield: 245 mg (51%).

**Method B.** To a yellow solution of $Ti(NSiPh_3)(dpma)(py)_2$ (**7**; 199 mg, 0.3 mmol) in 5 mL of toluene was added 4,4′-di-*tert*-butyl-2,2′-dipyridyl (80 mg, 0.3 mmol) in toluene (5 mL). The reaction mixture was stirred for 16 h, after which time volatiles were removed in vacuo. The resulting yellow solid was recrystallized from $CH_2Cl_2$/pentane at −35 °C to provide the product as yellow crystals. Yield: 177 mg (76%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.90 (2 H, s, 3,3′-[Bu$^t$-bpy]), 7.69 (2 H, s, 5-$C_4H_3N$), 7.41 (8 H, m, 2-$C_6H_5$ and 5,5′-[Bu$^t$-bpy]), 7.35 (2 H, s, 6,6′-[Bu$^t$-bpy]), 7.20 (4 H, m, 4-$C_6H_5$), 7.09 (6 H, m, 3-$C_6H_5$), 6.13 (2 H, s, 4-$C_4H_3N$), 5.93 (2 H, s, 3-$C_4H_3N$), 3.75 (2 H, d, $^2J$ = 13.7 Hz, $C_4H_3NCH_2N$), 3.07 (2 H, d, $^2J$ = 13.7 Hz, $C_4H_3NCH_2N$), 1.45 (3 H, s, $C_4H_3NCH_2N(CH_3)$), 1.42 (18 H, s, C(C$H_3$)$_3$-[Bu$^t$-bpy]). $^{13}$C NMR ($CDCl_3$): $\delta$ 164.4 (2,2′-[Bu$^t$-bpy]), 152.6 (4.4′-[Bu$^t$-bpy]), 151.5 (6.6′-[Bu$^t$-bpy]), 139.1 (2-$C_4H_3N$), 136.9 (1-$C_6H_5$), 136.1 (2-$C_6H_5$), 132.0 (4-$C_6H_5$), 128.1 (5.5′-[Bu$^t$-bpy]), 127.0 (3-$C_6H_5$), 123.7 (5-$C_4H_3N$), 116.9 (3,3′-[Bu$^t$-bpy]), 107.1 (4-$C_4H_3N$), 102.6 (3-$C_4H_3N$), 58.0 ($C_4H_3NCH_2N$), 44.2 ($C(CH_3)_3$-[Bu$^t$-bpy]), 35.4 ($C_4H_3NCH_2N(CH_3)$), 30.3 (C($CH_3$)$_3$-[Bu$^t$-bpy]). Anal. Found (calcd) for $C_{47}H_{52}N_6SiTi$: C, 72.66 (72.64); H, 6.87 (6.70); N, 10.53 (10.82).

**Synthesis of $Ti(NSiPh_3)(dap)_2$ (3).** To a near-frozen solution of $Ti(NSiPh_3)Cl_2py_2$ (**1**; 410 mg, 0.75 mmol) in 10 mL of toluene was added Lidap (194 mg, 1.49 mmol) in toluene (10 mL) dropwise. After it was stirred at room temperature for 24 h, the resulting dark yellow solution was filtered to remove a white solid. Volatiles were removed from the solution under reduced pressure to yield the crude product, which was recrystallized from $CH_2Cl_2$/pentane. Yield: 51 mg (12%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.52−7.26 (15 H, m, Si($C_6H_5$)$_3$), 7.08 (2 H, s, 5-$C_4H_3N$), 6.36 (2 H, m, 4-$C_4H_3N$), 6.18 (2 H, s, 3-$C_4H_3N$), 4.58 (2 H, d, $^2J$ = 13.3 Hz, $C_4H_3NCH_2N(CH_3)_2$), 3.62 (2 H, d, $^2J$ = 13.3 Hz, $C_4H_3NCH_2N(CH_3)_2$), 2.87 (6 H, s, $C_4H_3NCH_2N(CH_3)_2$), 2.55 (6 H, s, $C_4H_3NCH_2N(CH_3)_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ 136.7 (2-$C_4H_3N$), 135.4 (1-$C_6H_5$), 129.2 (4-$C_6H_5$), 127.8 (2-$C_6H_5$), 125.9 (5-$C_4H_3N$), 108.6 (4-$C_4H_3N$), 105.5 (3-$C_4H_3N$), 61.87 ($C_4H_3NCH_2N$ $(CH_3)_2$), 50.0 ($C_4H_3NCH_2N(CH_3)_2$), 45.8 ($C_4H_3NCH_2N(CH_3)_2$). Anal. Found (calcd) for $C_{32}H_{37}N_5SiTi$: C, 67.52 (67.69); H, 6.79 (6.52); N, 12.07 (12.34).

**Synthesis of $Ti(NSiPh_3)(bap)(Cl)$ (4).** To a near-frozen solution of $Ti(NSiPh_3)(Cl)_2(py)_2$ (**1**; 782 mg, 1.42 mmol) in 10 mL of toluene was added Libap (266 mg, 1.42 mmol) in toluene (10 mL) dropwise. After it was stirred at room temperature for 24 h, the resulting pink solution was filtered to remove a white solid. Volatiles were removed in vacuo to yield a pink solid. The solid was recrystallized from $CH_2Cl_2$/pentane at −35 °C. Yield: 279 mg (37%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.63−7.59 (6 H, m, Si($C_6H_5$)$_3$), 7.35−7.27 (9 H, m, Si($C_6H_5$)$_3$), 5.96 (2 H, s, $C_4H_2N$), 4.23 (2 H, d, $^2J$ = 13.2 Hz, $C_4H_2NCH_2N(CH_3)_2$), 3.50 (2 H, d, $^2J$ = 13.2 Hz, $C_4H_2NCH_2N(CH_3)_2$), 2.75 (6 H, s, $C_4H_2NCH_2N(CH_3)_2$), 2.46 (6 H, s, $C_4H_2NCH_2N(CH_3)_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ 137.3 (2-$C_4H_2N$), 135.2 (1-$C_6H_5$), 134.4 (4-$C_6H_5$), 129.0 (2-$C_6H_5$), 127.6 (3-$C_6H_5$), 103.5 (3-$C_4H_2N$), 65.2 ($C_4H_2NCH_2N$ $(CH_3)_2$), 50.0 ($C_4H_2NCH_2N(CH_3)_2$), 48.4

($C_4H_2NCH_2N(CH_3)_2$). Anal. Found (calcd) for $C_{28}H_{33}N_4ClSiTi$: C, 62.15 (62.65); H, 6.26 (6.15); N, 10.47 (10.44).

**Synthesis of Ti(NSiPh$_3$)(pap)(Cl) (5).** To a yellow solution of $Ti(NSiPh_3)(Cl)_2(py)_2$ (**1**; 616 mg, 1.12 mmol) in toluene (10 mL) cooled to nearly freezing was added Lipap (299 mg, 1.12 mmol) in 10 mL of toluene dropwise. After it was stirred at room temperature for 24 h, the resulting pink solution was filtered to remove a white solid. Volatiles were removed in vacuo. The solid was recrystallized from $CH_2Cl_2$/pentane at −35 °C to provide pink crystals. Yield: 254 mg (37%). $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 7.66 (3 H, m, Si($C_6H_5$)$_3$), 7.27−7.16 (12 H, m, Si($C_6H_5$)$_3$), 5.13 (2 H, s, $C_4H_2N$), 3.30 (4 H, s, $C_4H_2NCH_2N$-($C_5H_{10}$)), 2.24 (8 H, s, 2-N($C_5H_{10}$)), 1.48−1.41 (8 H, m, 3-N($C_5H_{10}$)), 1.31−1.22 (4 H, m, 4-N($C_5H_{10}$)). $^{13}$C NMR ($C_6D_6$): $\delta$ 136.9 (2-$C_4H_2N$), 135.8 (1-$C_6H_5$), 135.2 (4-$C_6H_5$), 129.0 (2-$C_6H_5$), 127.4 (3-$C_6H_5$), 106.9 (2-$C_4H_2N$), 104.1 (3-$C_4H_2N$), 54.3 ($C_4H_2NCH_2N(C_5H_{10})$), 26.1 (2-N($C_5H_{10}$)), 24.6 (3-N($C_5H_{10}$)), 23.1(4-N($C_5H_{10}$)). Anal. Found (calcd) for $C_{34}H_{41}N_4ClSiTi$: C, 66.21 (66.20); H, 7.04 (6.65); N, 9.40 (9.08).

**Synthesis of Zr(NBu$^t$)(dpma)(bpy) (9).** To a solution of Zr(dpma)(py)($NMe_2$)$_2$ (1.39 g, 3.12 mmol) and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (836 mg, 3.11 mmol) in toluene (10 mL) cooled to nearly freezing was added $H_2NBu^t$ (228 mg, 3.12 mmol) in toluene (5 mL) dropwise. After the mixture was stirred at room temperature overnight, an orange solid precipitated from the solution. The solid was collected by filtration and dried in vacuo. Yield: 819 mg (43%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.10 (2 H, d, 3,3′-[Bu$^t$-bpy]), 7.98 (2 H, s, 6,6′-[Bu$^t$-bpy]), 7.68 (2 H, m, 5-$C_4H_3N$), 7.47 (2 H, m, 5,5′-[Bu$^t$-bpy]), 6.27 (2 H, m, 4-$C_4H_3N$), 6.04 (2 H, s, 3-$C_4H_3N$), 3.85 (2 H, d, $^2J$ = 13.8 Hz, $C_4H_3NCH_2N$), 3.20 (2 H, d, $^2J$ = 13.6 Hz, $C_4H_3NCH_2N$), 1.64 (3 H, s, $C_4H_3NCH_2N(CH_3)$), 1.47 (18 H, s, C($CH_3$)$_3$-[Bu$^t$-bpy]), 1.00 (9 H, s, NC($CH_3$)$_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ 164.4 (2,2′-[Bu$^t$-bpy]), 153.0 (4,4′-[Bu$^t$-bpy]), 151.6 (6,6′-[Bu$^t$-bpy]), 136.8 (2-$C_4H_3N$), 130.7 (5,5′-[Bu$^t$-bpy]), 123.1 (5-$C_4H_3N$), 117.5 (3,3′-[Bu$^t$-bpy]), 107.3 (4-$C_4H_3N$), 104.3 (3-$C_4H_3N$), 57.6 ($C_4H_3NCH_2N$), 43.5 ($C(CH_3)_3$-[Bu$^t$-bpy]), 35.4 ($C_4H_3NCH_2N$-($CH_3$)), 34.2 (TiN$C(CH_3)_3$), 30.6 (TiNC($CH_3$)$_3$), 30.3 (C($CH_3$)$_3$-[Bu$^t$-bpy]). Anal. Found (calcd) for $C_{33}H_{46}N_6Zr$: C, 63.55 (64.16); H, 7.55 (7.45); N, 13.17 (13.61).

**Synthesis of Zr(NSiPh$_3$)(dpma)(bpy) (10).** To an orange solution of Zr(NBu$^t$)(dpma)(bpy) (**9**; 433 mg, 0.70 mmol) in 10 mL of $CH_2Cl_2$ was added a colorless solution of $H_2NSiPh_3$ (193 mg, 0.70 mmol) in $CH_2Cl_2$ (5 mL). The reaction mixture was stirred for 16 h, after which volatiles were removed in vacuo to give a yellow solid. The solid was recrystallized from $CH_2Cl_2$/pentane at −35 °C. Yield: 194 mg (34%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.90 (2 H, s, 3,3′-[Bu$^t$-bpy]), 7.73 (2 H, s, 5-$C_4H_3N$), 7.48 (8 H, m, 2-$C_6H_5$ and 5,5′-[Bu$^t$-bpy]), 7.38 (2 H, s, 6,6′-[Bu$^t$-bpy]), 7.23−7.03 (10 H, m, 4-$C_6H_5$ and 3-$C_6H_5$), 6.14 (2 H, s, 4-$C_4H_3N$), 5.99 (2 H, s, 3-$C_4H_3N$), 3.85 (2 H, d, $^2J$ = 13.7 Hz, $C_4H_3NCH_2N$), 3.18 (2 H, d, $^2J$ = 13.7 Hz, $C_4H_3NCH_2N$), 1.40 (3 H, s, $C_4H_3NCH_2N(CH_3)$), 1.39 (18 H, s, C($CH_3$)$_3$-[Bu$^t$-bpy]). $^{13}$C NMR ($CDCl_3$): $\delta$ 165.4 (2,2′-[Bu$^t$-bpy]), 153.1 (4,4′-[Bu$^t$-bpy]), 151.4 (6,6′-[Bu$^t$-bpy]), 149.1 (2-$C_4H_3N$), 142.1 (1-$C_6H_5$), 137.1 (2-$C_6H_5$), 135.1 (4-$C_6H_5$), 130.7 (5.5′-[Bu$^t$-bpy]), 127.4 (3-$C_6H_5$), 126.7 (5-$C_4H_3N$), 117.8 (3,3′-[Bu$^t$-bpy]), 108.1 (4-$C_4H_3N$), 105.2 (3-$C_4H_3N$), 57.6 ($C_4H_3NCH_2N$), 43.9 ($C(CH_3)_3$-[Bu$^t$-bpy]), 35.6 ($C_4H_3NCH_2N(CH_3)$), 30.6 (C($CH_3$)$_3$-[Bu$^t$-bpy]). Anal. Found (calcd) for $C_{47}H_{52}N_6SiZr$: C, 68.35 (68.80); H, 6.41 (6.34); N, 10.20 (10.25).

**Synthesis of [(bpy)Na][Zr[O-(2,6-MeC$_6$H$_3$)]$_3$(dpma)] (11).** To a yellow solution of Zr(NSiPh$_3$)(dpma)(bpy) (**10**; 2.93 g, 3.57 mmol) in 20 mL of THF was added NaO(2,6-$Me_2C_6H_3$) (1.55 g, 10.72 mmol) in THF (10 mL). The reaction vessel was removed from the box in a sealed vessel and heated to 110 °C in an oil bath. After the mixture was heated to 110 °C for 5 days, the flask was cooled and brought inside the box. Volatiles were removed in vacuo to yield a light yellow solid. The solid was recrystallized from toluene/pentane at −35 °C. Yield: 1.62 g (49%). $^1$H NMR (300 MHz, $C_6D_6$)**:** $\delta$ 8.18 (2H, s, 6,6′-[Bu$^t$-bpy]), 8.07 (6 H, m, 3-(2,6-$MeC_6H_3$)), 7.50 (3,3′-[Bu$^t$-bpy]), 7.40 (2 H, s, 5-$C_4H_3N$), 6.97 (3 H, m, 4-(2,6-$MeC_6H_3$)), 6.72 (2 H, s, 5,5′-[Bu$^t$-bpy]), 5.87 (2 H, s, 4-$C_4H_3N$), 5.68 (2 H, s, 3-$C_4H_3N$), 3.86 (2 H, d, $^2J$ = 14.6 Hz, $C_4H_3NCH_2N$), 3.21 (2 H, d, $^2J$ = 14.4 Hz,$C_4H_3NCH_2N$), 2.37 (18 H, s, Me-(2,6-$MeC_6H_3$)), 2.06 (3 H, s, $C_4H_3NCH_2N(CH_3)$), 0.96 (18 H, s, C($CH_3$)$_3$-[Bu$^t$-bpy]). $^{13}$C NMR ($C_6D_6$): $\delta$ 161.8 (2,2′-[Bu$^t$-bpy]), 161.3 (*ipso*-2,6-$MeC_6H_3$), 155.2 (4,4′-[Bu$^t$-bpy]), 150.2 (6,6′-[Bu$^t$-bpy]), 143.9 (2-$C_4H_3N$), 135.9 (5,5′-[Bu$^t$-bpy]), 127.1 (2-(2,6-$MeC_6H_3$)), 125.5 (5-$C_4H_3N$), 121.1 (3-(2,6-$MeC_6H_3$)), 118.0 (3.3′-[Bu$^t$-bpy]), 117.1 (4-(2,6-$MeC_6H_3$)), 107.1 (4-$C_4H_3N$), 101.4 (3-$C_4H_3N$), 67.8 ($C_4H_3NCH_2N$), 62.1 ($C(CH_3)_3$-[Bu$^t$-bpy]), 34.5 ($C_4H_3NCH_2N$-($CH_3$)), 30.0 (C($CH_3$)$_3$-[Bu$^t$-bpy]), 18.2 (Me-(2,6-$MeC_6H_3$)). Anal. Found (calcd) for $C_{53}H_{64}N_5O_3Zr$: C, 68.93 (68.24); H, 6.75 (6.87); N, 7.11 (7.51).

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**Supporting Information Available:** Complete labeled ORTEP diagrams and tables giving data for the X-ray diffraction studies on **1**, **5**, **6**, **8**, and **11**; X-ray data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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