

Group 4 Imido Complexes Stabilized by a Tridentate Diamido-Donor Ligand

Alexander J. Blake,[†] Philip E. Collier,[‡] Lutz H. Gade,^{*,§} Philip Mountford,^{*,†} Julian Lloyd,[‡] Stephen M. Pugh,[‡] Martin Schubart,[§] Michael E. G. Skinner,[‡] and Dominique J. M. Trösch[§]

Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, U.K., Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, U.K., and Laboratoire de Chimie Organométallique et de Catalyse (CNRS UMR 7513), Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pascal, 67070 Strasbourg Cédex, France

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Reaction of the lithium amides [(2-C₅H₄N)C(CH₃){CH₂N(Li)SiMe₃}₂]₂ (**2a**) and [(2-C₅H₄N)C(CH₃){CH₂N(Li)-SiMe₂tBu}][2] (**2b**) with the imidotransition metal complexes [Ti(NtBu)Cl₂(py)₃], [Ti(N-2,6-C₆H₃iPr₂)Cl₂(py)₃], and [Zr(N-2,6-C₆H₃iPr₂)Cl₂(thf)₂] yielded the five-coordinate imido-titanium and -zirconium complexes [{κ³N-(2-C₅H₄N)C(CH₃)(CH₂NSiMe₂R)₂}Ti(NR')(py)] (R = Me, R' = tBu: **3a**, R = tBu, R' = tBu: **3b**, R = Me, R' = 2,6-C₆H₃iPr₂: **4a**, R = Me, R' = 2,6-C₆H₃Me₂: **4b**) and [{κ³N-(2-C₅H₄N)C(CH₃)(CH₂NSiMe₃)₂}Zr(N-2,6-C₆H₃iPr₂)(py)] (**5**). The tridentate diamido-pyridine ligand adopts a facial coordination mode in the distorted trigonal bipyramidal complexes with the imido ligand occupying an equatorial position, as was established by X-ray diffraction for **3a** and **5**. Sublimation of **3a** and **4a** yielded the pure four-coordinate imidotitanium complexes [{κ³N-(2-C₅H₄N)C(CH₃)(CH₂NSiMe₃)₂}Ti(NR')] (R' = tBu: **6**, 2,6-C₆H₃iPr₂: **7**) which were structurally characterized by X-ray crystallography. Reaction of **3a** with the Lewis acid B(C₆F₅)₃ also led to abstraction of the axially bound pyridine ligand and the formation of the adduct [py-B(C₆F₅)₃] and **6**. Reaction of **6** with thf, PMe₃, and pyridine led to the formation of pentacoordinate complexes [{κ³N-(2-C₅H₄N)C(CH₃)(CH₂NSiMe₃)₂}-Ti(NtBu)(thf)] (**8**), [{κ³N-(2-C₅H₄N)C(CH₃)(CH₂NSiMe₃)₂}Ti(NtBu)(PMe₃)] (**9**), and [{κ³N-(2-C₅H₄N)C(CH₃)(CH₂-NSiMe₃)₂}Ti(NtBu)(py)] (**3a**) in which the donor ligands occupy axial positions.

Introduction

First structurally authenticated just a decade ago,^{1,2} imido-titanium and -zirconium complexes have been the objects of intense study during the past few years.^{3–11} While the imido-metal unit is a well-studied and frequently encountered structural element in the coordination chemistry of group 5–7 metals,¹² the development of group 4 imido complex chemistry is still in

some senses lagging behind.¹³ An important reason for this apparent imbalance is the change in reactivity of the imido ligand on going from the center of the d-block to the left. Whereas the stability and relative chemical inertness of the imido ligands coordinated to molybdenum and tungsten permits their use as ancillary ligands in high oxidation state complexes of these metals,¹⁴ the increased polarity of the M = NR unit in the compounds of the titanium triad renders the imido ligand the preferential point of attack. In fact, it initially proved difficult to stabilize such complexes, and early work by Rothwell,^{1a} Roesky,^{1b} and others¹² led to species in which coordinative saturation and steric shielding almost completely suppressed the potential reactivity of the imido ligand. At the same time, it was well established through the work by Wolczanski and co-workers that transient, low coordinate group 4 imides display a remarkable reactivity toward hydrocarbons.¹⁵

A key objective of our work on group 4 imidotitanium complexes has been the combination of an efficient strategy to stabilize the imido unit while providing sufficient access to the coordination sphere of the metal to allow the systematic investigation of their reactivity.¹³ One possible approach has been the protection of the greater part of the coordination sphere of the metal by a polydentate ligand which not only meets the electronic demand of the highly Lewis acidic early transition metal center but ideally allows the generation of low-coordinate imido species under controlled conditions.¹⁶ These requirements

* To whom correspondence should be addressed. e-mail: Gade@chimie.u-strasbg.fr. e-mail: Philip.Mountford@chemistry.oxford.ac.uk.

[†] University of Nottingham.

[‡] University of Oxford.

[§] Université Louis Pasteur.

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are in principle met by a potentially tridentate dianionic ligand in which two amido functions are combined with a neutral pyridyl unit.^{17,18} In this work we report the synthesis and structural characterization of several imido-titanium and -zirconium complexes bearing such a multifunctional ligand system,¹⁹ and particular attention will be devoted to the possibility of generating stable low-coordinate derivatives.

Experimental Section

All manipulations were performed under an inert gas atmosphere of dried argon in standard (Schlenk) glassware which was flame dried prior to use or in an inert atmosphere drybox under N₂. Solvents were dried according to standard procedures and saturated with Ar. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and dried using standard techniques.

The ¹H, ¹³C, ³¹P, and ²⁹Si NMR spectra were recorded on Bruker AC 200, AM 300, or DRX 500 NMR spectrometers equipped with a B-VT-2000 variable temperature unit with tetramethylsilane and H₃PO₄ (85%, ext) as references. Infrared spectra were recorded on Perkin-Elmer 1420 and Bruker IRS 25 FT-spectrometers.

Elemental analyses were carried out in the microanalytical laboratories of the chemistry departments at Nottingham, Oxford and Würzburg. The ligand precursors (2-C₅H₄N)C(CH₃)(CH₂NHSiMe₃)₂ (**1a**)¹⁸ and (2-C₅H₄N)C(CH₃)(CH₂NHSiMe₃)₂ (**1b**),²⁰ and the corresponding lithium amides [(2-C₅H₄N)C(CH₃){CH₂N(Li)SiMe₃}₂]₂ (**2a**),²⁰ and [(2-C₅H₄N)C(CH₃){CH₂N(Li)SiMe₃}₂]₂ (**2b**)²⁰ as well as the imidotransition metal complexes [Ti(NtBu)Cl₂(py)₃]₂,^{7,8} [Ti(N-2,6-C₆H₃iPr₂)Cl₂(py)₃]₂⁸ and [Zr(N-2,6-C₆H₃iPr₂)Cl₂(thf)₂]₂²¹ were prepared according to published methods. All other chemicals used as starting materials were obtained commercially and used without further purification.

1) Preparation of the Compounds. [κ^3 N-(2-C₅H₄N)C(CH₃)-(CH₂NSiMe₃)₂}]Ti(NtBu)(py)] (**3a**). To a stirred solution of [Ti(NtBu)Cl₂(py)₃] (2.827 g, 6.72 mmol) in benzene (80 cm³) at 5 °C was added a cold solution of [(2-C₅H₄N)C(CH₃){CH₂N(Li)SiMe₃}₂]₂ (**2a**) (2.156 g, 6.72 mmol) in benzene (40 cm³). The resulting red solution was allowed to warm to room temperature, stirred for 18 h and filtered. The volatiles were removed under reduced pressure and the solid was extracted into pentane (25 cm³). Subsequent filtration and cooling to -26 °C afforded a yellow-brown solid which was washed with cold pentane (2 × 5 cm³) and dried in vacuo. Yield: 1.94 g (57%). Deep yellow crystals suitable for X-ray diffraction were grown from a saturated solution of pentane at -26 °C. Mp 48 °C (dec). ¹H NMR (200.1 MHz, C₆D₆, 295 K): δ = 0.19 (s, NSi(CH₃)₃), 1.06 (s, CH₃C), 1.52 (s, C(CH₃)₃), 3.27 (d, CHHNSi, ²J_{HH} = 12.5 Hz), 3.56 (d, CHHNSi), 6.60–6.72 (m, *m*-C₅H₄N and py-H⁵), 6.86 (d, py-H³, ³J_{HH} = 8.0 Hz), 6.92 (tt, *p*-C₅H₄N, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.8 Hz), 7.13 (ddd, py-H⁴, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.8 Hz), 9.23 (d, *o*-C₅H₄N, ³J_{HH} = 4.7 Hz), 9.60 (d, py-H⁶, ³J_{HH} = 5.3 Hz). {¹H}¹³C NMR (50.3 MHz, C₆D₆, 295 K): δ = 1.7 (NSi(CH₃)₂), 24.3 (CH₃C), 34.5 (C(CH₃)₃), 45.1 (CH₃C), 64.0 (CH₂NSi), 67.7 (C(CH₃)₃), 120.1 (C⁵), 120.2 (C³), 123.4 (*m*-C₅H₄N), 137.0 (*p*-C₅H₄N), 137.1 (C⁴), 150.2 (C⁶), 151.6 (*o*-C₅H₄N), 160.8 (C²). IR (CsBr plates, Nujol): ν = 1600 s, 1570 w, 1446 s, 1347 m, 1282 w, 1233 s, 1208 m, 1156 m, 1138 m, 1114 m, 1089 m, 1063 m, 1010 w, 1001 m, 952 w, 894 s, 868 s, 829 s, 792 m, 773 m, 752 m, 694 m, 682 w, 648 w, 628 w, 599 w, 571 w, 544 w, 521 w, 496 w, 436 w cm⁻¹. Anal. Calcd for C₂₄H₄₃N₅Si₂Ti: C 57.0; H 9.0; N 13.8. Found: C 56.4; H 9.0; N 13.8.

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[[κ^3 N-(2-C₅H₄N)C(CH₃)(CH₂NSiMe₃)₂}]Ti(NtBu)(py)] (**3b**). A solution of **2b** (929 mg 1.14 mmol) in 20 mL of benzene was added to a suspension of [(py)₃Ti(NtBu)Cl₂] (978 mg = 2.29 mmol) in benzene (20 mL) which was cooled at 6 °C. The reaction mixture was warmed to ambient temperature and then stirred for another 16 h. The solvent and liberated pyridine were then removed in vacuo, and the red-brown residue was extracted twice with 30 mL of toluene. Concentration of the extract in vacuo giving a volume of 5 mL and storage of the solution at -35 °C for 2 days yielded the reaction product **3b** as a red crystalline solid, which was isolated by filtration and washed with 5 mL of cold pentane and then dried in vacuo. Yield: 1.013 g (77%). ¹H NMR (300.1 MHz, C₆D₆, 295 K): δ = 0.20 (s, 6 H, SiCH₃CH₃), 0.34 (s, 6 H, SiCH₃CH₃), 0.86 (s, 18 H, *t*Bu), 1.06 (s, 3 H, CCH₃), 1.58 [s, 9 H, NC(CH₃)₃], 3.45 [d, ²J(HH) = 12.6 Hz, 2 H, CHHN], 3.65 (d, 2 H, CHHN), 6.61–6.72 (m, 3 H, H⁵ und *m*-C₅H₅N), 6.85 [d, ³J(H³H⁴) = 8.0 Hz, 1 H, H³], 6.92 (m, br, 1 H, *p*-C₅H₅N), 7.08 [td, ³J(H⁴H⁵) = 7.6 Hz, ⁴J(H⁴H⁶) = 1.8 Hz, 1 H, H⁴], 9.23 (s, br, 2 H, *o*-C₅H₅N), 9.55 [d, ³J(H⁶H⁵) = 4.3 Hz, 1 H, H⁶]. {¹H}¹³C NMR (75.5 MHz, C₆D₆, 295 K): δ = -2.8 (SiCH₃CH₃), -2.1 (SiCH₃CH₃), 20.8 (CH₂), 24.8 (CCH₃), 27.9 [C(CH₃)₃], 34.6 [NC(CH₃)₃], 45.4 (CCH₃), 64.8 [C(CH₃)₃], 68.3 [NC(CH₃)₃], 120.5, 120.6 (C³/C⁵), 123.3 (*m*-C₅H₅N), 136.7 (*p*-C₅H₅N), 138.0 (C⁴), 150.1 (C⁶), 151.4 (*o*-C₅H₅N), 160.8 (C²). IR (Nujol, CsBr): ν = 1638 w, 1598 s, 1443 s, 1406 w, 1364 m, 1348 m, 1282 w, 1245 s, 1228 s, 1208 m, 1201 m, 1158 m, 1148 m, 1137 m, 1111 m, 1088 m, 1065 s, 1038 m, 1008 w, 936 w, 897 s, 877 s, 824 s, 800 s, 776 s, 768 s, 755 s, 736 w, 698 s, 660 m, 628 w, 601 m, 544 w, 518 m, 508 m, 470 w, 447 w, 438 w cm⁻¹. Anal. Calcd for C₃₀H₅₅N₅Si₂Ti: C 61.1, H 9.4, N 11.9. Found: C 61.0, H 9.4, N 11.9.

[[κ^3 N-(2-C₅H₄N)C(CH₃)(CH₂NSiMe₃)₂}]Ti(N-2,6-C₆H₃iPr₂)(py)] (**4a**). To a mixture of solid [Ti(N-2,6-C₆H₃iPr₂)Cl₂(py)₃] (1.975 g, 3.72 mmol) and solid [(2-C₅H₄N)C(CH₃){CH₂N(Li)SiMe₃}₂]₂ (**2a**) (1.197 g, 3.72 mmol) was added cold (7 °C) benzene (50 mL). The resulting brown solution was stirred for 3 h at room temperature, and the volatiles were subsequently removed under reduced pressure. The brown solid residues were extracted into toluene (3 × 25 mL) and filtered. The solution was reduced in volume to 10 mL under reduced pressure and placed at 5 °C for 60 h. Complex **4a** formed during this time as a microcrystalline solid, which absorbed much of the solvent. The solid was washed at 5 °C with pentane (4 × 3 mL) and dried under reduced pressure at 5 °C. A second crop of **4a** was obtained from the washings. Yield: 1.675 g (74%). ¹H NMR (200.1 MHz, C₆D₆, 295 K): δ = 0.04 (s, 18 H, SiMe₃), 1.17 (s, 3 H, CH₃), 1.45 [d, ³J(HH) = 6.8 Hz, 12 H CH(CH₃)₂], 3.33 [d, ²J(HH) = 12.6 Hz, 2 H, CHHN], 3.82 (d, 2 H, CHHN), 4.73 [sep, 1 H, CH(CH₃)₂], 6.39 [tt, ³J(HH) = 7.33 Hz, ⁴J(HH) = 1.17 Hz, 1 H, H⁴ in C₅H₅N], 6.56 [d, ³J(H³H²) = 4.99 Hz, 2 H, H^{3,5} in C₅H₅N], 6.86 [dd, ³J(H³H⁴) = 7.9 Hz, 1 H, H³], 6.90 [ddd, ³J(H⁵H⁴) = 7.6 Hz, ³J(H⁵H⁶) = 5.3 Hz, J(H⁵H³) = 1.46 Hz, 1 H, H⁵], 6.98 [t, ³J(HH) = 7.63 Hz, 1 H, H⁴ in 2,6-*i*Pr₂C₆H₃], 7.03 [ddd, ³J(H⁴H⁶) = 1.76 Hz, 1 H, H⁴], 7.27 (d, 2 H, H^{3,5} in 2,6-*i*Pr₂C₆H₃), 8.96 (m, 2 H, H^{3,5} in C₅H₅N), 9.21 [ddd, ³J(H⁶H³) = 0.88 Hz, 1 H, H⁶]. {¹H}¹³C NMR (50.3 MHz, C₆D₆, 295 K): δ = 0.9 (SiMe₃), 24.5 (CCH₃), 25.5 [CH(CH₃)₂], 27.4 [CH(CH₃)₂], 47.0 (CCH₃), 64.2 (CH₂N), 119.3 (C⁶ in 2,6-*i*Pr₂C₆H₃), 119.5 (C³), 120.9 (C⁶ in C₅H₅N), 123.4 (C^{3,5} in 2,6-*i*Pr₂C₆H₃), 123.6 (C^{3,5} in C₅H₅N), 138.0 (C⁵), 138.6 (C⁴), 141.6 (C^{2,5} in 2,6-*i*Pr₂C₆H₃), 150.7 (C⁶), 152.7 (C^{2,5} in C₅H₅N), 156.2, 160.9 (C¹ in 2,6-*i*Pr₂C₆H₃, C²). {¹H}²⁹Si NMR (39.8 MHz, C₆D₆, 295 K): δ = -2.1. Anal. Calcd for C₃₂H₅₁N₅Si₂Ti: C 63.0, H 8.4, N 11.5. Found: C 62.9, H 8.4, N 11.4.

[[κ^3 N-(2-C₅H₄N)C(CH₃)(CH₂NSiMe₃)₂}]Ti(N-2,6-C₆H₃Me₂)(py)] (**4b**). To a stirred slurry of [Ti(N-2,6-C₆H₃Me₂)Cl₂(py)₃] (302 mg, 0.63 mmol) in pentane (30 cm³) at -30 °C was added a cold suspension of [(2-C₅H₄N)C(CH₃){CH₂N(Li)SiMe₃}₂]₂ (**2a**) (202 mg, 0.63 mmol) in pentane (20 cm³). The solution was allowed to warm to room temperature and was stirred for 18 h. The volatiles were removed under reduced pressure, and the red solid was re-extracted into pentane (30 cm³). After filtration the pentane solution was concentrated to 20 cm³. Recrystallization at -25 °C yielded the red crystalline product [[κ^3 N-(2-C₅H₄N)C(CH₃)(CH₂NSiMe₃)₂}]Ti(N-2,6-C₆H₃Me₂)(py)] (**4b**). Yield: 95 mg (27%). ¹H NMR (300.1 MHz, C₆D₆, 298 K): δ = 0.05 (18 H, s, SiMe₃), 1.20 (3 H, s, Me of N₂Npy), 2.81 (6 H, s, C₆H₃Me₂), 3.35 (2 H, d, ²J = 12.5 Hz, CHHN), 3.84 (2 H, d, ²J = 12.4 Hz, CHHN), 6.36

(1 H, m, H^5), 6.55 (2 H, m, $m\text{-NC}_5\text{H}_5$), 6.83 (1 H, t, ${}^3J = 7.6$ Hz, $p\text{-C}_6\text{H}_3\text{Me}_2$), 6.89–6.80 (3 H, m, overlapping $p\text{-NC}_5\text{H}_5$, $p\text{-C}_6\text{H}_3\text{Me}_2$ and H^3), 7.00 (1 H, td, ${}^3J(H^4H^5) = 7.5$ Hz, H^4 , ${}^3J(H^4H^3) = 7.5$ Hz, ${}^4J(H^4H^6) = 1.8$ Hz), 7.27 (2 H, d, ${}^3J = 7.4$ Hz, $m\text{-C}_6\text{H}_3\text{Me}_2$), 8.92 (2 H, d, ${}^3J(o\text{-H}m\text{-H}) = 4.6$ Hz, $o\text{-NC}_5\text{H}_5$, ${}^4J(o\text{-H}p\text{-H}) = 1.5$ Hz), 9.15 (1 H, dd, ${}^3J(H^6H^5) = 5.3$ Hz, H^{6J} (H^6H^4) = 1.8 Hz). $\{^1\text{H}\}^{13}\text{C}$ NMR (50.3 MHz, C_6D_6 , 295 K): $\delta = 1.1$ [Si(CH₃)₃], 21.3 [2,6-(CH₃)₂C₆H₃], 24.3 (CCH₃), 46.6 (CCH₃), 64.4 (CH₂N), 118.0 (C⁵), 119.6 (C³), 120.9 ($p\text{-2,6-C}_6\text{H}_3\text{Me}_2$), 123.7 ($m\text{-NC}_5\text{H}_5$), 128.4 ($m\text{-2,6-C}_6\text{H}_3\text{Me}_2$), 130.1 ($o\text{-2,6-C}_6\text{H}_3\text{Me}_2$), 137.5 (C⁴), 150.4 (C⁶), 152.1 ($o\text{-NC}_5\text{H}_5$), 160.0 ($ipso\text{-2,6-C}_6\text{H}_3\text{Me}_2$), 160.8 (C²). IR (benzene): $\nu = 3084$ w, 3033 w, 2993 w, 2953 s, 2895 w, 1600 s, 1582 s, 1473 m, 1446 s, 1435 vs, 1402 m, 1331 s, 1302 s, 1211 w, 1138 w, 1091 w, 1069, 1055 s, 1042, 1007 vs, 989 v, 949 vw, 909 s, 880 vs, 829 vs, 782 w, 760 w, 742 w, 702 vs, 629 vw cm^{-1} . Anal. Calcd for C₂₈H₄₅N₅Si₂Ti: C 60.7, H 7.8, N 12.7. Found: C 60.0, H 8.0, N 12.5.

[[$\kappa^3N\text{-(2-C}_5\text{H}_4\text{N)C(CH}_3\text{)(CH}_2\text{NSiMe}_3\text{)}_2$] $\text{Zr(N-2,6-C}_6\text{H}_3\text{iPr}_2\text{)-(py)}$]] (5**). To a solution of $\text{Zr(N-2,6-C}_6\text{H}_3\text{iPr}_2\text{)Cl}_2(\text{thf})_2$ (435 mg, 0.90 mmol) in benzene (20 mL) was added pyridine (0.15 mL, 147 mg, 1.85 mmol). The orange solution was stirred at room temperature for 2 h, after which time it was cooled to 10 °C and a solution of **2a** (290 mg, 0.90 mmol) in benzene (10 mL) was added. The resulting solution was stirred at room temperature for 18 h and filtered, and the volatiles were removed under reduced pressure to provide an orange solid residue. The residues were extracted with hexane (3 × 5 mL) and the extracts reduced to 3 mL and placed at –35 °C for 17 h. $[\{\kappa^3N\text{-(2-C}_5\text{H}_4\text{N)C(CH}_3\text{)(CH}_2\text{NSiMe}_3\text{)}_2\}\text{Zr(N-2,6-C}_6\text{H}_3\text{iPr}_2\text{)(py)}]$ (**5**) was obtained as red-orange microcrystals. Yield: 190 mg (32%). Orange crystals of **5** suitable for X-ray diffraction were obtained from a saturated solution of **5** in pentane at 5 °C over a period of 3 weeks. ^1H NMR (500.0 MHz, C_6D_6 , 295 K): $\delta = 0.03$ (s, 18 H, SiMe₃), 1.15 (s, 3 H, CH₃), 1.48 [d, ${}^3J(\text{HH}) = 7.0$ Hz, 12 H CH(CH₃)₂], 3.33 [d, ${}^2J(\text{HH}) = 12.5$ Hz, 2 H, CHHN] 3.93 (d, 2 H, CHHN), 4.74 [sep, 1 H, CH(CH₃)₂], 6.37 [apparent t, apparent $J(\text{HH}) = 5.5$, H^4 in C₅H₅N], 6.48 [broad, $H^{3,5}$ in C₅H₅N], 6.79 [broad, 1 H, H³], 6.81 [d, ${}^3J(H^3H^4) = 8.0$ Hz, H³], 6.98 [dd, ${}^3J(H^4H^5) = 8.0$, ${}^3J(H^4H^3) = 8.0$ Hz, 1 H, H⁴ in 2,6-*iPr*₂C₆H₃], 7.03 [t, ${}^3J(H^4H^6) = 7.5$ Hz, 1 H, H⁴], 7.39 (d, 2 H, H^{3,5} in 2,6-*iPr*₂C₆H₃), 9.01 (m, 2 H, H^{3,5} in C₅H₅N), 9.34 [d, ${}^3J(H^6H^5) = 5.0$ Hz, 1 H, H⁶]. $\{^1\text{H}\}^{13}\text{C}$ NMR (125.1 MHz, C_6D_6 , 295 K): $\delta = 0.5$ (SiMe₃), 25.4 [CH(CH₃)₂], 25.5 (CCH₃), 27.6 [CH(CH₃)₂], 47.7 (CCH₃), 63.1 (CH₂N), 116.3 (C⁴ in 2,6-*iPr*₂C₆H₃), 120.0 (C³), 121.1 (C⁶ in C₅H₅N), 123.0 (C^{3,5} in 2,6-*iPr*₂C₆H₃), 124.1 (*m* in C₅H₅N), 138.6 (C⁵), 139.0 (C⁴), 140.2 (C^{2,5} in 2,6-*iPr*₂C₆H₃), 151.1 (C⁶), 152.2 (C^{2,5} in C₅H₅N), 155.0 (C¹ in 2,6-*iPr*₂C₆H₃), 161.4 (C²). Anal. Calcd for C₃₂H₄₅N₅Si₂Zr: C 58.8, H 7.9, N 10.7. Found: C 58.7, H 8.2, N 10.5.**

NMR Tube Reaction of 3a with B(C₆F₅)₃. To a solution of **3a** (30 mg = 0.059 mmol) in C_6D_6 (0.5 mL) was added 31 mg of solid B(C₆F₅)₃ (0.0595 mmol). The resonances of the reaction product **6** (vide infra) could be observed after ca. 5 min along with the signals of $[\text{py-B(C}_6\text{F}_5\text{)}_3]$. The latter assignment was confirmed by direct synthesis of the adduct and spectroscopic characterization. ^1H NMR for $[\text{py-B(C}_6\text{F}_5\text{)}_3]$ (C_6D_6 , 300.1 MHz, 298 K): $\delta = 6.25$ (m, 2 H, H^{3,5}), 6.58 (m, 1 H, H⁴), 7.95 (m, 2 H, H^{2,6}). An isolation of pure compound **6** was not possible from this reaction.

[[$\kappa^3N\text{-(2-C}_5\text{H}_4\text{N)C(CH}_3\text{)(CH}_2\text{NSiMe}_3\text{)}_2$] Ti(NrBu)]] (6**). $[\{\kappa^3N\text{-(2-C}_5\text{H}_4\text{N)C(CH}_3\text{)(CH}_2\text{NSiMe}_3\text{)}_2\}\text{Ti(NrBu)(py)}]$ (**3a**) (0.50–1.00 g) was sublimed at 125 °C and 9×10^{-6} mbar over 2 h to provide analytically pure solid $[\{\kappa^3N\text{-(2-C}_5\text{H}_4\text{N)C(CH}_3\text{)(CH}_2\text{NSiMe}_3\text{)}_2\}\text{Ti(NrBu)}]$ (**6**) in quantitative yield. Yellow crystals suitable for X-ray diffraction were obtained by recrystallization of the compound from pentane solution at –25 °C over 2 weeks. ^1H NMR (300.1 MHz, C_6D_6 , 298 K): $\delta = 0.42$ [s, 18 H, Si(CH₃)₃], 0.98 (s, 3 H, CCH₃), 1.60 [s, 9 H, NC(CH₃)₃], 3.22 [d, ${}^2J(\text{HH}) = 12.8$ Hz, 2 H, CHHN], 3.72 (d, 2 H, CHHN), 6.27 (m, 1 H, H⁵), 6.65 (m, 1 H, H³), 6.86 (m, 1 H, H⁴), 8.71 (m, 1 H, H⁶). $\{^1\text{H}\}^{13}\text{C}$ NMR (75.5 MHz, C_6D_6 , 298 K): $\delta = 1.9$ [Si(CH₃)₃], 25.5 (CCH₃), 34.7 [C(CH₃)₃], 46.5 (CCH₃), 62.2 (CH₂N), 68.4 [C(CH₃)₃], 120.6 (C³), 121.5 (C⁵), 140.2 (C⁴), 149.0 (C⁶), 160.3 (C²). IR (Nujol, CsBr) 1600 (m), 1586 (m), 1523 (w), 1285 (m), 1244 (s), 1208 (m), 1158 (w), 1141 (w), 1088 (m), 1055 (s), 1026 (s), 836 (s), 778 (s), 721 (m), 684 (w), 630 (w), 584 (m), 504 (w). Anal. Calcd for C₁₉H₃₈N₄-Si₂Ti: C 53.5, H 9.0, N 13.1. Found: C 53.3, H 8.9, N 13.0.**

[[$\kappa^3N\text{-(2-C}_5\text{H}_4\text{N)C(CH}_3\text{)(CH}_2\text{NSiMe}_3\text{)}_2$] $\text{Ti(N-2,6-C}_6\text{H}_3\text{iPr}_2)$]] (7**). $[\{\kappa^3N\text{-(2-C}_5\text{H}_4\text{N)C(CH}_3\text{)(CH}_2\text{NSiMe}_3\text{)}_2\}\text{Ti(N-2,6-C}_6\text{H}_3\text{iPr}_2\text{)(py)}]$ (**4b**) was sublimed at 155 °C and 1×10^{-6} mbar over 3 h to provide analytically pure $[\{\kappa^3N\text{-(2-C}_5\text{H}_4\text{N)C(CH}_3\text{)(CH}_2\text{NSiMe}_3\text{)}_2\}\text{Ti(N-2,6-C}_6\text{H}_3\text{iPr}_2)]$ (**7**) as a red solid in quantitative yield. Orange single crystals suitable for X-ray diffraction formed during sublimation. ^1H NMR (500.0 MHz, C_6D_6 , 295 K): $\delta = 0.28$ (s, 18 H, SiMe₃), 1.00 (s, 3 H, CH₃), 1.56 [d, ${}^3J(\text{HH}) = 7.0$ Hz, 12 H CH(CH₃)₂], 3.27 [d, ${}^2J(\text{HH}) = 13.0$ Hz, 2 H, CHHN] 3.80 (d, 2 H, CHHN), 4.25 [sep, 1 H, CH(CH₃)₂], 6.37 [apparent t, apparent $J(\text{HH}) = 6.0$ Hz, H^5 in C₅H₅N], 6.82 [d, ${}^3J(H^3H^4) = 8.0$ Hz, H³], 6.91 [dd, ${}^3J(H^4H^5) = 8.0$, ${}^3J(H^4H^3) = 8.0$ Hz, 1 H, H⁴ in 2,6-*iPr*₂C₆H₃], 6.963 [t, ${}^3J(H^4H^6) = 7.5$ Hz, 1 H, H⁴], 7.21 (d, 2 H, H^{3,5} in 2,6-*iPr*₂C₆H₃), 8.78 (m, 2 H, H^{3,5} in C₅H₅N). $\{^1\text{H}\}^{13}\text{C}$ NMR (125.5 MHz, C_6D_6 , 295 K): $\delta = 1.1$ (SiMe₃), 24.4 [CH(CH₃)₂], 25.4 (CCH₃), 28.8 [CH(CH₃)₂], 46.4 (CCH₃), 62.2 (CH₂N), 118.6 (C⁴ in 2,6-*iPr*₂C₆H₃), 121.1 (C³), 122.2 (C⁶ in C₅H₅N), 122.5 (C^{3,5} in 2,6-*iPr*₂C₆H₃), 138.7 (C⁴), 140.6 (C^{2,5} in 2,6-*iPr*₂C₆H₃), 146.9 (C⁶), 158.1 (C¹ in 2,6-*iPr*₂C₆H₃), 19.8 (C²). Anal. Calcd for C₂₇H₄₆N₄Si₂Ti: C 61.1, H 8.7, N 10.6. Found: C 60.3, H 8.9, N 10.4.**

NMR Tube Scale Synthesis of $[\{\kappa^3N\text{-(2-C}_5\text{H}_4\text{N)C(CH}_3\text{)(CH}_2\text{NSiMe}_3\text{)}_2\}\text{Ti(NrBu)(thf)}$]] (8**), $[\{\kappa^3N\text{-(2-C}_5\text{H}_4\text{N)C(CH}_3\text{)(CH}_2\text{NSiMe}_3\text{)}_2\}\text{Ti(NrBu)(PMe}_3\text{)}]$ (**9**), and $[\{\kappa^3N\text{-(2-C}_5\text{H}_4\text{N)C(CH}_3\text{)(CH}_2\text{NSiMe}_3\text{)}_2\}\text{Ti(NrBu)(py)}]$ (**3a**).** Tetrahydrofuran, PMe₃, or pyridine (0.06 mmol) were added via syringe to a solution of $[\{\kappa^3N\text{-(2-C}_5\text{H}_4\text{N)C(CH}_3\text{)(CH}_2\text{NSiMe}_3\text{)}_2\}\text{Ti(NrBu)}]$ (**6**) (26 mg, 0.06 mmol) in C_6D_6 (0.5 mL), providing solutions of $[\{\kappa^3N\text{-(2-C}_5\text{H}_4\text{N)C(CH}_3\text{)(CH}_2\text{NSiMe}_3\text{)}_2\}\text{Ti(NrBu)(thf)}$] (**8**), $[\{\kappa^3N\text{-(2-C}_5\text{H}_4\text{N)C(CH}_3\text{)(CH}_2\text{NSiMe}_3\text{)}_2\}\text{Ti(NrBu)(PMe}_3\text{)}]$ (**9**), and $[\{\kappa^3N\text{-(2-C}_5\text{H}_4\text{N)C(CH}_3\text{)(CH}_2\text{NSiMe}_3\text{)}_2\}\text{Ti(NrBu)(py)}]$ (**3a**) in quantitative yield by NMR.

8: ^1H NMR (300.1 MHz, C_6D_6 , 298 K): $\delta = 0.30$ [s, 18 H, Si(CH₃)₃], 1.02 (s, 3 H, CCH₃), 1.45 (m, 4 H, OCH₂CH₂), 1.55 [s, 9 H, C(CH₃)₃], 3.19 [d, ${}^2J(\text{HH}) = 12.6$ Hz, 2 H, CHHN], 3.62 (d, 2 H, CHHN), 3.76 (m, 4 H, OCH₂CH₂), 6.48 (m, 1 H, H⁵), 6.76 [d, ${}^3J(H^3H^4) = 8.1$ Hz, 1 H, H³], 7.01 [td, ${}^3J(H^4H^5) = 7.7$ Hz, ${}^3J(H^4H^6) = 2.0$ Hz, 1 H, H⁴], 9.22 [d, ${}^3J(H^6H^5) = 5.5$ Hz, 1 H, H⁶]. $^{13}\text{C}\{^1\text{H}\}$ -NMR (75.5 MHz, C_6D_6 , 298 K): $\delta = 1.6$ [s, Si(CH₃)₃], 24.6 (CCH₃), 25.6 (OCH₂CH₂), 34.6 [C(CH₃)₃], 45.8 (CCH₃), 62.9 CH₂N, 67.9 [C(CH₃)₃], 69.4 (OCH₂CH₂), 120.1 120.6 (C₃,C₅), 138.5 (C⁴), 149.6 (C⁶), 160.4 (C²).

9: ^1H NMR (C_6D_6 , 200.1 MHz, 298 K): $\delta = 0.19$ [s, 18 H, Si(CH₃)₃], 1.01 (s, 3 H, CCH₃), 1.14 [d, ${}^2J(\text{HP}) = 4.5$ Hz, 9 H, P(CH₃)₃], 1.52 [s, 9 H, C(CH₃)₃], 3.18 [d, ${}^2J(\text{HH}) = 12.7$ Hz, 2 H, CHHN], 3.59 (d, 2 H, CHHN), 6.55 (m, 1 H, H⁵), 6.79 (m, 1 H, H³), 7.04 (m, 1 H, H⁴), 9.27 (m, 1 H, H⁶). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6 , 50.3 MHz, 298 K): $\delta = 1.9$ [Si(CH₃)₃], 15.8 [d, ${}^1J(\text{PC}) = 11.2$ Hz, P(CH₃)₃], 24.6 (CCH₃), 35.1 [C(CH₃)₃], 45.5 (CCH₃), 63.7 (CH₂N), 67.8 [C(CH₃)₃], 120.5, 120.6 (C³, C⁵), 137.8 (C⁴), 149.4 (C⁶), 160.4 (C²). $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6 , 81.0 MHz, 298 K): $\delta = -31.4$. The formation of compound **3a** was confirmed by comparison of the spectroscopic data with those of an isolated sample.

Crystal Structure Determination of 3a, 5, 6, and 7. Crystal data collection and processing parameters are given in Table 1. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Stöck Stadi-4 four-circle (for **3a** and **6**) or Enraf-Nonius DIP2000 image plate diffractometer (for **5** and **7**), both equipped with an Oxford Cryosystems low-temperature device.^{22a} Data were collected at low temperature using Mo K α radiation. Equivalent reflections were merged and (for **5** and **7**) the images were processed with the DENZO and SCALEPACK programs.^{22b} Absorption and decay corrections were applied to the data as appropriate. The structures were solved by direct methods, and subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. Hydrogen atoms were placed geometrically and refined in a riding model. Structures were refined against F^2 (for **3a**) or F using appropriate weighting schemes. Examination of the refined secondary extinction parameter and of an agreement analysis suggested that no extinction correction was required for any of the structures.

(22) (a) Cosier, J.; Glazer, A. M. *J. Appl. Crystallogr.* **1986**, *19*, 105. (b) Gewirth, D. *The HKL Manual*; written with the cooperation of the program authors, Otwinowski, Z., Minor, W., Eds.; Yale University: New Haven, CT, 1995.

Table 1. X-ray Data Collection and Processing Parameters for **3a**, **5**, **6**, and **7**.

	3a	5	6	7
empirical formula	C ₂₄ H ₄₃ N ₅ Si ₂ Ti	C ₃₂ H ₅₁ Cl ₂ N ₅ Si ₂ Zr	C ₁₉ H ₃₈ N ₄ Si ₃ Ti	C ₂₇ H ₄₆ N ₄ Si ₂ Ti
fw	505.71	653.19	426.61	530.76
temp/°C	-123(1)	-123(1)	-53(1)	-123(1)
wavelength/Å	0.71069	0.71069	0.71069	0.71069
space group	<i>P</i> -1	<i>P</i> 2 ₁ /c	<i>P</i> 2 ₁ /n	<i>P</i> 2 ₁ /n
<i>a</i> /Å	9.535(3)	16.6470(8)	11.934(9)	10.7730(4)
<i>b</i> /Å	10.125(3)	11.5510(3)	14.011(11)	15.9220(6)
<i>c</i> /Å	15.948(3)	19.335(1)	15.255(11)	18.7080(4)
α/deg	90.63(3)			
β/deg	106.61(3)	106.248(2)	90.39(6)	103.294(2)
γ/deg	105.40(2)			
<i>V</i> /Å ³	1416.1	3569.4	2551	3122.9
<i>Z</i>	2	4	4	4
<i>d</i> (calcd)/mg·m ⁻³	1.19	1.22	1.11	1.13
abs coeff/mm ⁻¹	0.41	0.39	0.44	0.36
<i>R</i> indices ^a	<i>R</i> ₁ = 0.022 [<i>I</i> > 2σ(<i>I</i>)], <i>wR</i> ₂ = 0.101 [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.050 [<i>I</i> > 3σ(<i>I</i>)], <i>R</i> _w = 0.046 [<i>I</i> > 3σ(<i>I</i>)]	<i>R</i> ₁ = 0.107 [<i>I</i> > 2σ(<i>I</i>)], <i>R</i> _w = 0.085 [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.037 [<i>I</i> > 3σ(<i>I</i>)], <i>R</i> _w = 0.040 [<i>I</i> > 3σ(<i>I</i>)]
<i>R</i> indices (all data -for refinement on <i>F</i> ² only)	<i>wR</i> ₂ = 0.049, <i>wR</i> ₂ = 0.108			

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = \sqrt{\{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}}; R_w = \sqrt{\{\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2\}}.$$

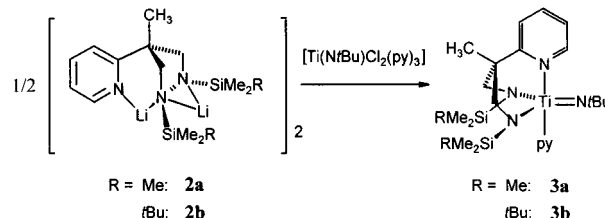
For compound **5** the carbons of the two SiMe₃ groups were disordered and were refined in an isotropic model with similarity restraints applied to the Si–C distances. For compound **6** the best available crystal from a selection of alternatives examined was a weak diffractor with average *I*/σ(*I*) = 4.15. Data were collected to θ = only 22.5° since a preliminary examination showed that there were no measurable data at higher θ values. The satisfactory displacement parameters, and bond lengths and angles, merit publication of this structure. Without doubt the data are of sufficient quality to establish unambiguously the overall geometry and connectivity. The relatively high *R*₁ of 0.107 for data with *I* > 2σ(*I*) is almost certainly only a consequence of weak diffraction. For comparison, *R*₁ and *R*_w for data with *I* > 3σ(*I*) are 0.082 and 0.076, respectively.

Crystallographic calculations were performed using SHELXS-96, SIR92, SHELXL-96, or CRYSTALS-PC.²³ A full listing of atomic coordinates, bond lengths and angles and displacement parameters for **3a**, **5**, **6**, and **7** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Results and Discussion

Synthesis of [$\{\kappa^3N-(2-C_5H_4N)C(CH_3)(CH_2NSiMe_2R)_2\}Ti(NR')(py)$] (**3a,b** and **4a,b**). The previously reported *tert*-butylimido complex [Ti(*Nt*Bu)Cl₂(py)₃]^{7,8} was reacted with 1 equiv of the lithiated ligand [(2-C₅H₄N)C(CH₃){CH₂N(Li)-SiMe₂R}]₂ (R = Me: **2a**, *t*Bu: **2b**)^{18,20} in benzene at 5 °C. After workup the red-brown complexes [$\{\kappa^3N-(2-C_5H_4N)C(CH_3)(CH_2NSiMe_2)_2\}Ti(NtBu)(py)$] (**3a**) and [$\{\kappa^3N-(2-C_5H_4N)C(CH_3)(CH_2NSiMe_2tBu)_2\}Ti(NtBu)(py)$] (**3b**) were isolated in 57% and 77% yield, respectively (Scheme 1).

The analytical and NMR spectroscopic data of both compounds are consistent with their formulation as five-coordinate, pseudo-trigonal bipyramidal pyridine adducts containing the diamido-pyridine ligand bound facially to the metal center. In particular, the ¹H NMR resonance of the *ortho*-hydrogen H⁶ of the pyridyl ring at 9.60 ppm is indicative of the pyridyl nitrogen bound tightly to the titanium center. A similar chemical shift of the corresponding signal (δ 9.31) was observed in the structurally characterized alkyl complex [$\{\kappa^3N-(2-C_5H_4N)C-$

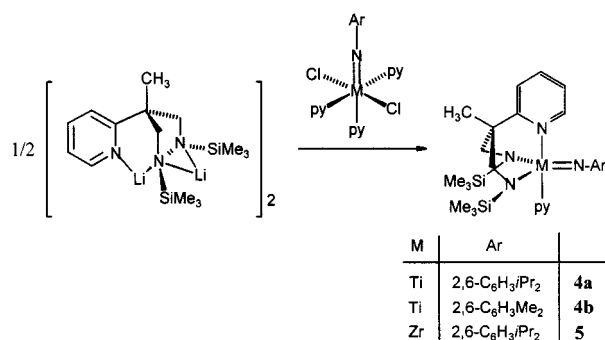
Scheme 1. Synthesis of the Five-Coordinate Imidotitanium Complexes **3a** and **3b**

(CH₃)(CH₂NSiMe₂)₂}Ti(CH₂SiMe₃)Cl].¹⁸ In contrast the resonance assigned to the H⁶ proton in the “free” ligand **1a** and in the complex [$\{\kappa^2N-(2-C_5H_4N)C(CH_3)(CH_2NSiMe_2)_2\}Ti(CH_2SiMe_2)_2$], where the bulky dialkyl ligands preclude coordination of the pyridyl function, are found significantly further upfield at δ 8.55 and 8.47, respectively.¹⁸ The trans disposition of the pyridine ligand and pyridyl fragment was established using NOE NMR difference experiments. The {¹H}¹³C NMR spectrum of **3a** confirmed the proposed structure given in Scheme 1. The spectrum shows the three resonances attributable to the *ortho* (δ 151.6), *para* (δ 137.0), and *meta* (δ 123.4) pyridine carbon atoms. The methyl group carbon resonance of the *tert*-butylimido occurs at δ 34.5 with the quaternary carbon signal at δ 67.7. The chemical shift of the SiMe₃ methyl group carbon atoms is upfield at δ 1.7 with the other methyl group of the diamido-pyridine ligand appearing at 24.3 ppm. The two quaternary carbon environments corresponding to the atoms C¹ (δ 45.1) and C² (δ 160.8) are also observed. The remaining signals (δ 120.2, 137.1, 120.1, and 150.2) are from the methine carbon atoms of the ligand pyridyl fragment C³, C⁴, C⁵, and C⁶ respectively.

The NMR spectra of complex **3b** are very similar to those of compound **3a**. The only differences are the ¹H NMR signals associated with the diastereotopic *tert*-butyldimethylsilyl group; namely those for the *tert*-butyl group (δ 0.86) and two inequivalent methyl groups (δ 0.20 and 0.34). The *tert*-butyl imido methyl resonance occurs at 1.58 ppm and the H⁶ resonance of the pyridyl unit shows the pyridyl function also to be coordinated (9.55 ppm).

To further vary the coordination environment in the imidotitanium complexes, the arylimido compounds the arylimido complexes [Ti(N-2,6-C₆H₃R₂)Cl₂(py)₃] (R = Me, *i*Pr)⁸ were reacted with 1 equiv of the lithium amide **2a** yielding the

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Scheme 2. Synthesis of the Arylimido Complexes **4a**, **4b**, and **5**

corresponding imido complexes [$\{\kappa^3N-(2-C_5H_4N)C(CH_3)(CH_2NSiMe_3)_2\}Ti(N-2,6-C_6H_3R_2)(py)$] ($R = iPr$: **4a**, Me : **4b**) (Scheme 2). The coordination number of five, and thus the coordination number of five, can again be inferred from the chemical shifts of the H⁶ protons in the ¹H NMR spectra of both complexes (**4a**: $\delta(H^6) = 9.21$, **4b** 9.15).

In view of the previously established successful synthetic methodology to prepare the aryylimido complexes via *tert*-butylimido–arylamine exchange reactions,⁸ the complex **3a** was reacted with 1 equiv of 2,6-dimethylaniline in an NMR tube. After 30 min the ¹H NMR spectrum showed that **3a** had undergone 20% conversion to the 2,6-dimethylphenylimido complex **4b**. A scale-up reaction was not successful in isolating a sample of **4b** by this method. An analogous NMR tube reaction of **3a** using the non *ortho*-disubstituted 4-methylaniline resulted in degradation of the complex.

Synthesis of [$\{\kappa^3N-(2-C_5H_4N)C(CH_3)(CH_2NSiMe_3)_2\}Zr(N-2,6-C_6H_3iPr_2)(py)$] (5**).** In view of the results for titanium discussed above, it was reasoned that a similar method might also be used to obtain such derivatives of the heavier, second row transition element zirconium. The properties of zirconium differ somewhat from those of titanium, and unlike that of its lighter counterpart the preparation of a zirconium imido dichloride complex analogous to the titanium complexes referred to above is not straightforward. Zirconium is not, for example, known to undergo facile imide-amine metathesis reactions such as are known for titanium.⁸ The preparation of one particularly useful precursor has, however, been published by Wigley and co-workers.²¹ Here, the reaction of $[ZrCl_4(thf)_2]$ with $LiHN-2,6-C_6H_3iPr_2$ in *thf* yields the imido-diamido complex $[Zr(N-2,6-C_6H_3iPr_2)(HN-2,6-C_6H_3iPr_2)(thf)_2]$, which may be converted to the dichloride $[Zr(N-2,6-C_6H_3iPr_2)Cl_2(thf)_2]$ by reaction with Me_3SiCl . However, reaction of this starting material with **2a** did not lead to a pure isolable complex, and it was only in the presence of pyridine that a zirconium analogue of **3a**, [$\{\kappa^3N-(2-C_5H_4N)C(CH_3)(CH_2NSiMe_3)_2\}Zr(N-2,6-C_6H_3iPr_2)(py)$] (**5**) was isolated (Scheme 2). Its identity was confirmed by NMR and IR spectroscopy and by satisfactory elemental analysis.

Given the success of the tridentate diamido-pyridine ligand in forming Group 4 imido complexes, it was interesting to attempt to prepare complexes containing the related bidentate/monodentate diamide/pyridine ligand set which contains no tether between the diamide fragment and pyridyl group. The dilithium diamide $Li_2[CH_2(CH_2NSiMe_3)_2]$, employed previously by us in the chemistry of early-late heterodimetallic complexes,^{24–27} was chosen because the amido ligand emulates closely the diamide section of the diamido-pyridine ligand in

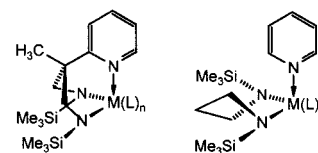


Figure 1. Tridentate diamido-pyridine and bidentate/monodentate diamide/pyridine ligand sets.

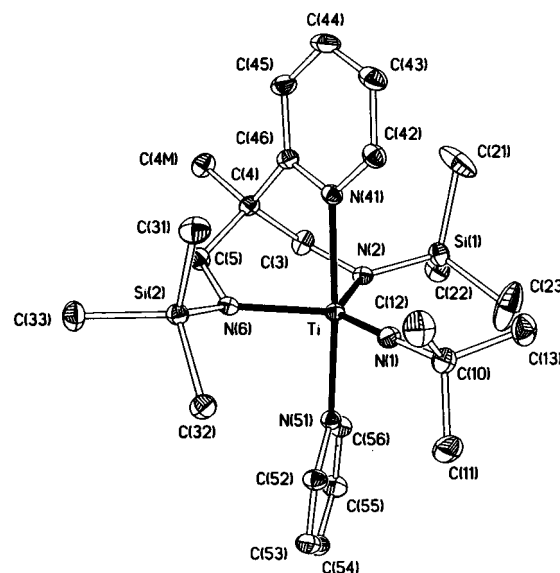


Figure 2. Displacement ellipsoid plot of **3a**. Hydrogen atoms are omitted, and displacement ellipsoids are drawn at the 35% probability level.

3–5: both have bulky trimethylsilyl amide substituents, a three-carbon alkane backbone between the amide groups, and should form six-membered chelate rings (Figure 1)

Reactions of $Li_2[CH_2(CH_2NSiMe_3)_2]$ with $[Ti(NtBu)Cl_2(py)_3]$ or $[Zr(N-2,6-C_6H_3iPr_2)Cl_2(thf)_2]$ on an NMR tube scale in C_6D_6 , or with $[Ti(NtBu)Cl_2(py)_3]$ on a larger scale in benzene, resulted in rapid decomposition and an unidentifiable mixture of products, as evidenced by ¹H NMR spectroscopy. It would therefore seem that the tethered pyridyl arm of the diamido-pyridine ligand does indeed play an important role in providing stability to its complexes. In complexes containing the diamide/pyridine ligand set, dissociation of the pyridine donor is unhindered and may result in total loss of the pyridine into the bulk solution. The resulting metal complex, now containing an unprotected face on the metal center, is consequently exposed to attack and is therefore far more likely to undergo side reactions leading to decomposition.

X-ray Structure Analyses of 3a and 5. To firmly establish the structures of the new five-coordinate imido complexes an X-ray crystallographic study of compounds **3a** and **5** was carried out. The molecular structure of **3a** is shown in Figure 2 and selected bond distances and angles are presented in Table 2.

The geometry around the five-coordinate titanium(IV) atom of **3a** is best described as approximately trigonal bipyramidal with the pyridyl fragment of the polydentate ligand and the pyridine molecule in the axial positions. The equatorial sites are occupied by the two amide functionalities and the *tert*-

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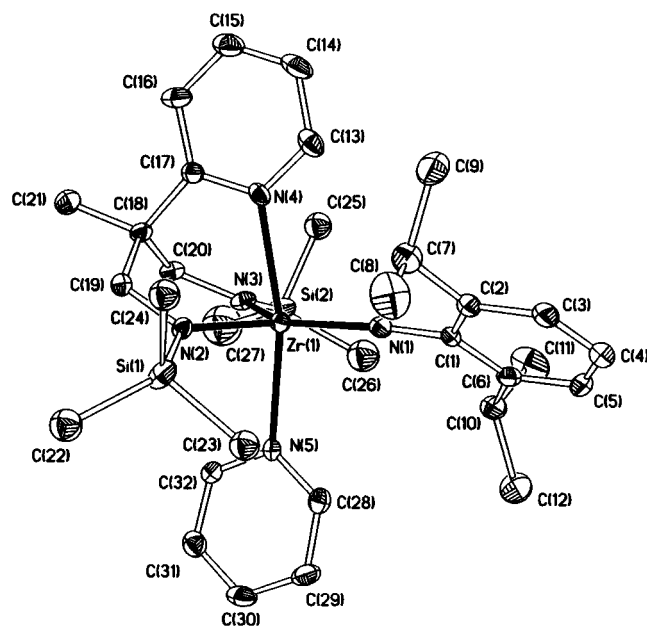


Figure 3. Displacement ellipsoid plot of **5**. Hydrogen atoms are omitted, and displacement ellipsoids are drawn at the 25% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3a**

Ti(1)–N(1)	1.724(2)	Ti(1)–N(51)	2.278(2)
Ti(1)–N(2)	2.025(2)	N(1)–C(10)	1.457(3)
Ti(1)–N(6)	1.983(2)	N(2)–Si(1)	1.709(2)
Ti(1)–N(41)	2.203(2)	N(6)–Si(2)	1.722(2)
N(1)–Ti–N(2)	130.09(9)	N(2)–Ti–N(51)	87.19(7)
N(1)–Ti–N(6)	115.84(9)	N(6)–Ti–N(41)	83.79(8)
N(1)–Ti–N(41)	96.73(8)	N(6)–Ti–N(51)	95.12(8)
N(1)–Ti–N(51)	96.45(8)	N(41)–Ti–N(51)	165.83(7)
N(2)–Ti–N(6)	113.33(8)	Ti–N(1)–C(10)	175.10(17)
N(2)–Ti–N(41)	80.34(7)		

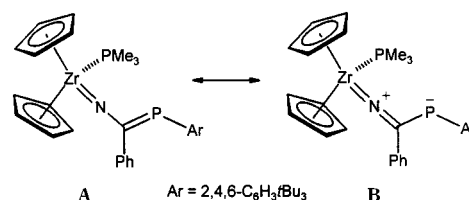
Table 3. Selected Bond Lengths (Å) and Angles (deg) for **5**

Zr(1)–N(1)	1.916(4)	Zr(1)–N(5)	2.390(4)
Zr(1)–N(2)	2.073(3)	N(1)–C(1)	1.377(6)
Zr(1)–N(3)	2.106(4)	N(2)–Si(1)	1.717(4)
Zr(1)–N(4)	2.348(4)	N(3)–Si(2)	1.719(4)
N(1)–Zr(1)–N(2)	123.4(1)	N(3)–Zr(1)–N(4)	81.3(1)
N(1)–Zr(1)–N(3)	131.7(2)	N(2)–Zr(1)–N(5)	89.7(1)
N(1)–Zr(1)–N(4)	98.8(2)	N(3)–Zr(1)–N(5)	90.2(1)
N(1)–Zr(1)–N(5)	94.8(1)	N(4)–Zr(1)–N(5)	166.4(2)
N(2)–Zr(1)–N(3)	104.6(2)	Zr(1)–N(1)–C(1)	172.3(3)
N(2)–Zr(1)–N(4)	82.3(1)		

butylimido group. The Ti=N_{imido} bond length [at 1.724(2) Å] is somewhat longer than in the starting material [Ti(N*t*Bu)Cl₂(py)₃] [1.705(3) Å]⁸ but is still within the range of known titanium *tert*-butylimido bond lengths.¹³ The near linear Ti–N_{imido}–C bond angle [175.10(17)°] implies the *tert*-butylimido group is acting as a four-electron donor to the metal center (vide infra). Interestingly, the pyridine nitrogen atom is substantially less tightly bound to the metal center than the nitrogen atom of the pyridyl fragment, as reflected in the longer bond length [Ti–N(41) 2.203(2) Å compared to Ti–N(51) 2.278(2) Å].

The molecular geometry of the zirconium complex **5** closely resembles that of the titanium *tert*-butylimido analogue **3a** discussed above and is displayed in Figure 3. The principal bond lengths and angles are listed in Table 3. The complex possesses the expected distorted trigonal bipyramidal geometry, with the pyridyl and pyridine donors occupying the axial sites. The Zr=N_{imido} bond length of 1.916(4) Å is longer than in most other structurally characterized terminal zirconium aryl or alkyl

Chart 1



imides; the majority lie in the range 1.84–1.88 Å.²⁸ The only reported zirconium aryl- or alkylimido bond length longer than this belongs to the complex [Zr(NC(Ph)PAr)(η^5 -C₅H₅)₂(PMe₃)] (**A**) (Zr=N_{imido}) = 1.93(2) Å, reported by Breen and Stephan.²⁹ This is perhaps not surprising as not only does the imide compete with the cyclopentadienyl groups for π -donation to the metal d-orbitals, but it may be viewed as existing in two resonance forms as proposed by the authors (Chart 1).²⁹

This requires lone-pair donation from the imido nitrogen atom to form an N=C double bond and will substantially weaken the ability of the nitrogen to π -donate to the metal, reducing the M=N bond order and lengthening the bond. Nonetheless, the fact that the bond length in **5** resembles that of **A** more than it does the typically reported values of Zr=N_{imido} may suggest that the bond order in **5** may be lower than in other systems, and that nitrogen π -donation to the metal is proportionally weaker. No consequence of this can apparently be inferred from the Zr–N_{imido}–C bond angle, however, which at 172.3(3)° is within the range of a linear imido linkage (155° < M=N–R < 180°). As in the structure of **3a**, the pyridine ligand in **5** is somewhat less tightly bound to the metal center than the pyridyl fragment {Zr–N(5) = 2.390(4) Å; Zr–N(4) = 2.348(4) Å}.

The sum of the bond angles subtended at the amido nitrogen atoms are, in both complexes **3a** and **5** close to 360°. The trigonal planar nature of these nitrogen atoms implies that they are capable of acting as three-electron donors to the metal center via 2p _{π} –d _{π} π -bonding interactions and therefore that the valence electron count in this complex could conceivably be 18. When orbital symmetry is considered, however, the situation is somewhat less straightforward (Figure 4).

Assuming an orientation of Cartesian axes as in Figure 3, the (n + 1)s, three (n + 1)p, and nd_{z²} orbitals are involved in the σ -bonding framework, and the nd_{xy} orbital is of the correct symmetry to overlap only with the imido in-plane 2p_x orbital forming one of the imido π -bonds (Figure 3, **II**). Although this leaves three metal d-orbitals and three nitrogen 2p _{π} donor orbitals, the nd_{x²–y²} orbital (**I**) does not have the appropriate orientation to overlap with any of these. This leaves only nd_{xz} and nd_{yz} acceptor orbitals, which, although they may interact with the imide and/or amide 2p_z π -donor orbitals, are capable of accepting only four bonding electrons in total. Of these two remaining nd orbitals, the nd_{xz} interacts fully with the out of phase combination of amide 2p_z orbitals (**III**) while the in-phase combination of amide 2p_z orbitals competes with the imide for the nd_{yz} (**IV**). Due to the comparatively long bond lengths of the metal-amides relative to the metal-imide bond {M=N_{imido} = 1.724(2) Å for titanium and 1.916(4) Å for zirconium; M–N_{amide} average = 2.004(2) Å for titanium and 2.090(5) Å for zirconium}, this situation is likely to result in a greater contribution to the metal–ligand π -bonding from the imide than from the amides. The remaining pair of ligand-based

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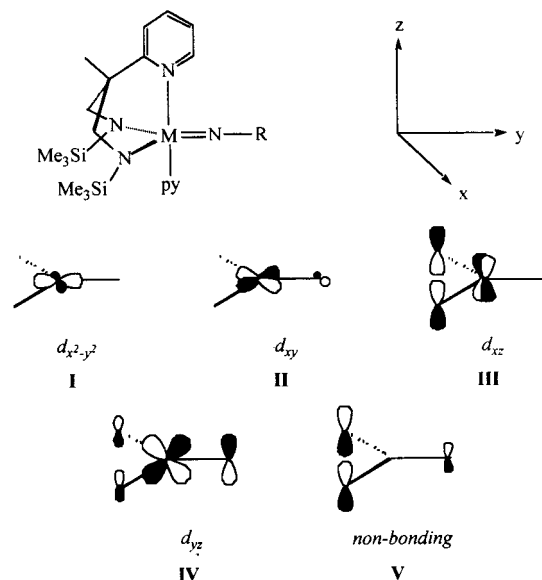


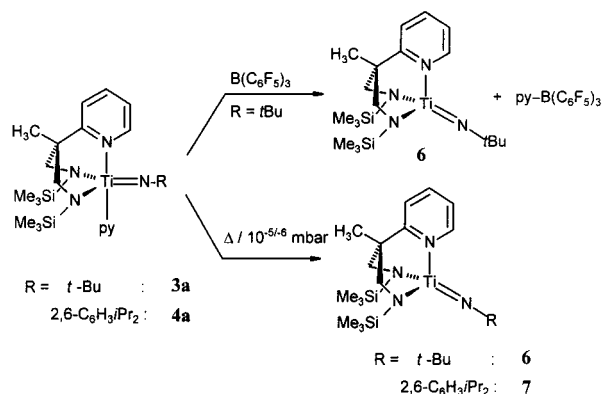
Figure 4. Metal d -orbital orientation, showing nd_x-2p_x ($n = 3, 4$) bonding interactions and nonbonding orbitals.

electrons is therefore thought to reside in a nonbonding orbital combination based mainly on the amide groups (V). All three lone pairs cannot, therefore, be donated simultaneously, and thus the electron count is symmetry restricted to 16. Similar conclusions were drawn by Rothwell and co-workers concerning their related structurally characterized bis(pyridine) bis(amide) zirconium imide [$Zr(N-2,6-C_6H_3iPr_2)(NH-2,6-C_6H_3iPr_2)(py)_2$] [$py' = 4-C_5H_4N(NC_4H_4)$],³⁰ and are not uncommon in other systems; for example, in the apparently 20-electron osmium imido complex [$Os(N-2,6-C_6H_3iPr_2)_3$]³¹ symmetry considerations restrict the valence electron count to 18.

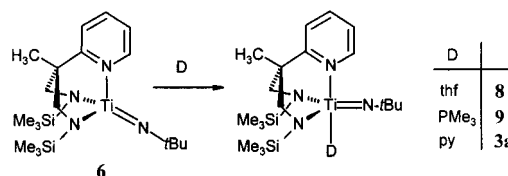
Synthesis and Structural Characterization of the Four-coordinate Imidotitanium Complexes [$\{\kappa^3N-(2-C_5H_4N)C(CH_3)(CH_2NSiMe_3)_2\}Ti(NR)$] ($R = tBu$: **6, $2,6-C_6H_3iPr_2$: **7**).** As stated above, the main objective for the use of the tripodal diamido-pyridine ligands in the synthesis of imido complexes of the group 4 metal is the possibility of generating low-coordinate complexes under controlled conditions. The systems were originally conceived as four-coordinate compounds which might undergo thermal decoordination of the pyridyl unit of the tripodal ligand, thus generating the desired three-coordinate analogues of Wolczanski's highly reactive imides.¹⁵ As described above, all the complexes obtained by reaction of the precursor materials with the polyfunctional amides were found to possess 5-fold coordination with one of the pyridine ligands present in the starting materials bound in an axial position. It was therefore of interest to investigate whether this additional pyridine ligand was essential for the stability of the compounds and if they might be converted to the targeted four-coordinate species on a preparative scale.

Initially, it was attempted to abstract the axial pyridine ligand in **3a** by reaction with a Lewis acid which should serve as an acceptor to the pyridine. Reaction of **3a** with $B(C_6F_5)_3$ resulted in the immediate and selective conversion of the complex giving the adduct $[(py)-B(C_6F_5)_3]$ and a new imido species **6** (Scheme 3). While the NMR spectroscopic data for **6** in this mixture were consistent with its formulation of the pyridine-free

Scheme 3. Synthesis of the Four-coordinate Imidotitanium Complexes **6** and **7**



Scheme 4. Reaction of **6** with Donor Ligands



complex (vide infra), the separation of both products and thus the complete characterization of **6** was not possible.

The isolation of the pure complex [$\{\kappa^3N-(2-C_5H_4N)C(CH_3)(CH_2NSiMe_3)_2\}Ti(NtBu)$] (**6**) was achieved upon high vacuum sublimation of **3a** at 125 °C and 10^{-5} mbar giving the pyridine-free compound as an orange crystalline solid. Similar heating of **4a** to 155 °C under a dynamic vacuum of 10^{-6} mbar provided [$\{\kappa^3N-(2-C_5H_4N)C(CH_3)(CH_2NSiMe_3)_2\}Ti(N-2,6-C_6H_3iPr_2)$] (**7**). The formulation of both compounds **6** and **7** (Scheme 4) as the pyridine-free complexes was established by elemental analysis and NMR spectroscopy. The most notable difference in the spectra with respect to the starting materials **3a** and **4a**, apart from the absence of the resonances of the pyridine ligand, is the shift of the 1H NMR resonances of the H^6 -hydrogen nuclei to higher field (δ 8.71 and 8.78 in **6** and **7**, respectively, in comparison to δ 9.60 and 9.21 in **3a** and **4a**). This clearly shows that coordination or noncoordination of a donor function can only be inferred from the H^6 chemical shift in complexes of equal coordination number and geometry.

To establish the detailed molecular structures of **6** and **7** and to establish their 4-fold coordination single-crystal X-ray structure analyses of both compounds were carried out. Their molecular structures are shown in Figures 5 and 6 while the principal bond lengths and interbond angles are given in Tables 4 and 5.

The result of the X-ray diffraction study confirmed the monomeric four-coordinate molecular structure of **6**. Its most remarkable feature is the fact that, rather than adopting a tetrahedral geometry, compound **3** possesses what is nearer to a trigonal monopyramidal geometry, the remaining ligands having shifted very little to protect the face of the metal from which the pyridine was lost. A similar structure has been reported recently by Cloke and co-workers in the diamido-amine Ti(III) complex [$\{\text{Me}_3\text{SiN}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_2\}\text{Ti}\{\text{CH}(\text{SiMe}_3)_2\}$].³² At 350.6°, the sum of the bond angles $\{N(1)-Ti-N(2), N(1)-Ti-N(3), \text{ and } N(2)-Ti-N(3)\}$ about titanium are consistent with this atom being located only around 0.6(1) Å out of the

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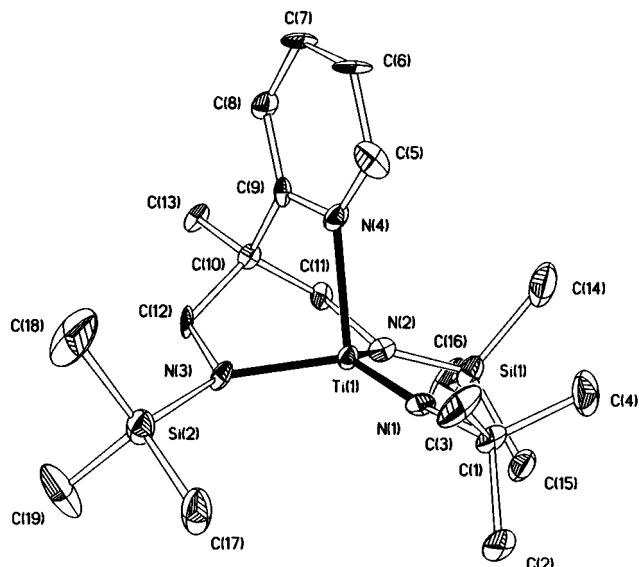


Figure 5. Displacement ellipsoid plot of **6**. Hydrogen atoms are omitted, and displacement ellipsoids are drawn at the 25% probability level.

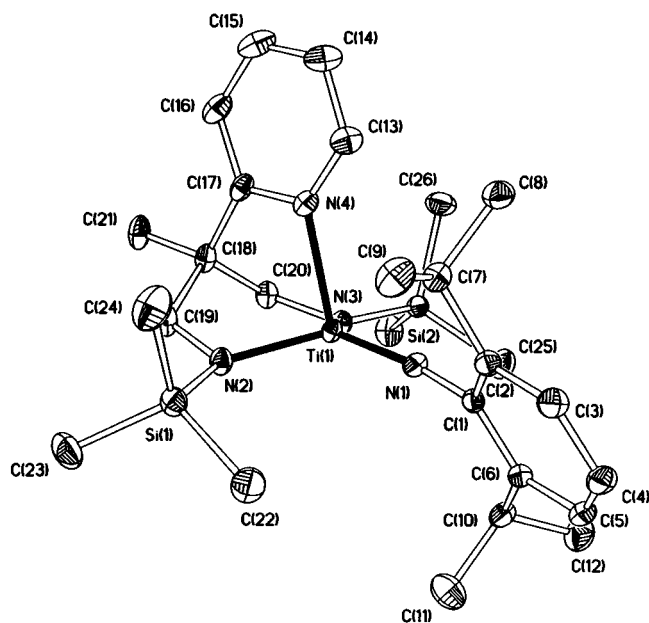


Figure 6. Displacement ellipsoid plot of **7**. Hydrogen atoms are omitted, and displacement ellipsoids are drawn at the 25% probability level.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **6**

Ti(1)–N(1)	1.701(9)	N(1)–C(1)	1.49(1)
Ti(1)–N(2)	1.936(8)	N(2)–Si(1)	1.719(9)
Ti(1)–N(3)	1.934(9)	N(3)–Si(2)	1.730(9)
Ti(1)–N(4)	2.14(1)		
N(1)–Ti(1)–N(2)	119.7(4)	N(2)–Ti(1)–N(4)	94.9(4)
N(1)–Ti(1)–N(3)	121.7(4)	N(3)–Ti(1)–N(4)	93.2(4)
N(2)–Ti(1)–N(3)	109.2(4)	Ti(1)–N(1)–C(1)	174.3(8)
N(1)–Ti(1)–N(4)	111.1(4)		

N(1), N(2), and N(3) plane. For comparison, the sum of the expected angles in a tetrahedral complex is 328.5°. As a consequence of the lower coordination number in comparison to **3a** all the metal–ligand bonds in **6** are significantly shorter than in the five coordinate pyridine adduct [Ti=N_{imide} **3a**: 1.724–(2), **6**: 1.701(9); Ti–N_{amide(av)} **3a**: 2.004(2), **6**: 1.935(9); Ti–N_{py} **3a**: 2.203(2), **6**: 2.14(1) Å].

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **7**

Ti(1)–N(1)	1.750(1)	N(1)–C(1)	1.374(2)
Ti(1)–N(2)	1.915(1)	N(2)–Si(1)	1.728(2)
Ti(1)–N(3)	1.927(1)	N(3)–Si(2)	1.734(1)
Ti(1)–N(4)	2.126(1)		
N(1)–Ti(1)–N(2)	117.82(7)	N(2)–Ti(1)–N(4)	92.94(6)
N(1)–Ti(1)–N(3)	122.40(6)	N(3)–Ti(1)–N(4)	90.44(6)
N(2)–Ti(1)–N(3)	111.17(6)	Ti(1)–N(1)–C(1)	169.5(1)
N(1)–Ti(1)–N(4)	114.46(6)		

The structure of **7** closely resembles that of the *tert*-butylimido analogue **6**. Again, the titanium environment is best described as distorted trigonal monopyramidal, with the pyridyl donor occupying the apical position. The titanium atom is displaced from the N(1)/N(2)/N(3) plane by just 0.317 Å, the sum of angles {N(1)–Ti–N(2), N(1)–Ti–N(3), and N(2)–Ti–N(3)} in this case being 352.0°. The Ti=N_(imide) bond length is 0.049–(9) Å longer than that in **6**, consistent with observations made of other alkyl- and arylimides and attributed to a partial delocalization of nitrogen π -electron density onto the aryl ring.³³ The Ti–N_(imide)–C bond angle of 169.5(1)° is well within the range of a linear imido group. Both **6** and **7** have an electron count of 14 at titanium.

Upon reaction of **6** with donor ligands such as thf, PMe₃, and pyridine the five-coordinate complexes [{ κ^3 N-(2-C₅H₄N)-C(CH₃)(CH₂NSiMe₃)₂}Ti(N t Bu)(thf)] (**8**), [{ κ^3 N-(2-C₅H₄N)-C(CH₃)(CH₂NSiMe₃)₂}Ti(N t Bu)(PMe₃)] (**9**), and [{ κ^3 N-(2-C₅H₄N)-C(CH₃)(CH₂NSiMe₃)₂}Ti(N t Bu)(py)] (**3a**) were obtained (Scheme 4). Of these **8** and **9** were only characterized spectroscopically since they slowly decomposed upon attempts to isolate them. In the case of **9**, coordination of the phosphine ligand to the tetravalent titanium center is inferred from the coordination shift of ca. 30 ppm observed in the ³¹P NMR spectrum [$\delta(^{31}\text{P}) = -31.4$ in comparison to -62.0 for the free phosphine].

Conclusions

The diamido-pyridine ligands employed in this study provided the key to the preparation and structural characterization of a new class of imido complexes of the group 4 metals. In these, the metal center is protected by the tripodal ligand while leaving significant space around the potentially reactive imido unit. This provides promising opportunities for their use as chemical reagents. Preliminary studies have already in part supported this view, including C–H bond activation in reactions with methylacetylenes³⁴ and C–N coupling reactions with allenes and various polar unsaturated substrates.^{19,35} Further systematic studies into their reactivity are underway in our laboratories.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **3a**, **5**, **6**, and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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