New Titanium Complexes Containing an Amidinate−Imide Supporting Ligand Set: Cyclopentadienyl, Alkyl, Borohydride, Aryloxide, and Amide Derivatives

Peter J. Stewart, Alexander J. Blake, and Philip Mountford*

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, U.K.

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A range of chloride metathesis reactions of the monomeric titanium *N*,*N*′-bis(trimethylsilyl)-benzamidinato−imido complexes $[Ti(NBu^t)\{(4\text{-}C_6H_4R)C(NSiMe_3)_2\}Cl(py)_2]$ (R = H (**1**) or OMe (**2**)) are described. Thus, reaction of **1** or **2** with LiC_5H_5 gave the half-sandwich compounds $[Ti(NBu^t)\{(4\text{-}C_6H_4R)C(NSiMe_3)_2\}(\eta\text{-}C_5H_5)]$ (R = H (**3**) or OMe (**4**)). Reaction of **1** with $LiCH_2SiMe_3$ or $LiCH(SiMe_3)_2$ gave the 14-electron, first fully characterized group 4 imido−alkyl derivatives $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}\{CH(R)SiMe_3\}(py)]$ (R = H (**5**) or $SiMe_3$ (**6**)). For comparative purposes, the 16-electron half-sandwich imido−alkyl complex $[Ti(NBu^t)(\eta\text{-}C_5Me_5)(CH_2SiMe_3)(py)]$ (**7**) was prepared from $LiCH_2SiMe_3$ and $[Ti(NBu^t)(\eta\text{-}C_5Me_5)Cl(py)]$. Reaction of **1** with $LiBH_4$ gave the η^3-borohydride derivative $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}(\eta^3\text{-}BH_4)(py)]$ (**8**), while treatment of **1** with $LiN(SiMe_3)_2$, $LiO\text{-}2,6\text{-}C_6H_3R_2$ (R = Me or Bu^t), or $LiPhC(NSiMe_3)_2$ gave the corresponding aryloxide, amide, or bis(benzamidinate) titanium imido complexes $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}\{N(SiMe_3)_2\}(py)]$ (**9**), $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}(O\text{-}2,6\text{-}C_6H_3R_2)(py)]$ (R = Me (**10**) or Bu^t (**11**)), or $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}_2(py)]$ (**13**). Activation parameters for the concerted, restricted rotation of the aryloxide and benzamidinate ligands in **11** are reported and point to a dissociatively activated mechanism. The X-ray structures of **5** and **7** have been determined.

Introduction

The organoimido (NR, where R is typically an alkyl or aryl)[1−4] and amidinate ($RC(NR')_2$ where R is usually H, alkyl or aryl and R′ is alkyl, aryl or trimethylsilyl)[5−15] groups are important supporting ligands in transition-metal chemistry. As part of an ongoing study of titanium imido chemistry,[16] we recently described the new *N*,*N*′-bis(trimethylsilyl)benzamidinate-supported complexes $[Ti(NR)\{PhC(NSiMe_3)_2\}Cl(py)_2]$ (R = Bu^t (**1**), $2,6\text{-}C_6H_3Me_2$ and $2,6\text{-}C_6H_3Pr^i_2$).[17] The overall trianionic, seven-electron donor amidinate−terminal imide ligand set in **1** and its homologues is a relatively unusual combination in transition-metal chemistry and has not been explored to any extent as a supporting ligand environment for preparing new compounds.[12,17−20] We were particularly interested to explore its potential for supporting new organometallic and related chemistry of titanium which has, to a considerable extent, been dominated by compounds with one or two cyclopentadienyl co-ligands.[21] Here, we report the synthesis, solution dynamics, and structures of new cyclopentadienyl, alkyl, borohydride, amide, and aryloxide titanium complexes containing the amidinate−imide ligand set and some related chemistry.[22]

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* To whom correspondence should be addressed. Philip Mountford is the Royal Society of Chemisty Sir Edward Frankland Fellow. E-mail: Philip.Mountford@Nottingham.ac.uk. WWW: http://www.nottingham.ac.uk/~pczwww/Inorganic/PMount.html.

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Experimental Section

General Methods and Instrumentation. All manipulations were carried out under an atmosphere of dinitrogen or argon using standard Schlenk-line or drybox techniques. All protio solvents and commercially available reagents were predried over activated molecular sieves, refluxed over an appropriate drying agent under an atmosphere of dinitrogen, and collected by distillation. $CDCl_3$ was dried over freshly ground calcium hydride at room temperature, C_6D_6 was dried over molten potassium, and $C_6D_5CD_3$ was dried over molten sodium. All NMR solvents were distilled under reduced pressure and stored under N_2 in a J. Young ampule. NMR samples were prepared in the drybox in 5 mm Wilmad tubes equipped with a Young's Teflon valve.

^1H, ^{13}C, and ^{11}B NMR spectra were recorded on a Bruker DPX 300 spectrometer. ^1H and ^{13}C spectra were referenced internally to residual protio solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). The ^{11}B spectrum was referenced externally to BF_3 in ethanol ($\delta = 0$ ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in hertz. Assignments were supported by DEPT-135 and DEPT-90, homo- and heteronuclear, one- and two-dimensional experiments as appropriate. IR spectra were recorded on a Nicolet 205 FTIR spectrometer in the range 4000−400 cm^{-1}. Samples were prepared in the drybox between KBr or CsBr plates as Nujol mulls or as thin films, and data are quoted in wavenumbers (ν, cm^{-1}). Elemental analyses were carried out by the analysis laboratory of this department.

Literature Preparations. $Li(4\text{-}C_6H_4R)C(NSiMe_3)_2$ (R = H or OMe),[23,24] $LiCH_2SiMe_3$,[25] $LiCH(SiMe_3)_2$,[26] $LiN(SiMe_3)\cdot OEt_2$,[27] $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}Cl(py)_2]$ (**1**),[17] $[Ti(NBu^t)Cl_2(py)_3]$,[28] $[Ti(NBu^t)(\eta^5\text{-}C_5Me_5)Cl(py)]$,[29] and $LiO\text{-}2,6\text{-}C_6H_3R_2$ (R = Me or Bu^t)[30] were prepared according to literature methods. LiC_5H_5 was prepared from *n*-butyllithium and freshly cracked C_5H_6 in cold hexanes.

$[Ti(NBu^t)\{(4\text{-}C_6H_4OMe)C(NSiMe_3)_2\}Cl(py)_2]$ (2). A solution of $Li(4\text{-}C_6H_4OMe)C(NSiMe_3)_2$ (0.760 g, 2.53 mmol) in THF (20 mL) was added over 10 min to a stirred solution of $[Ti(NBu^t)Cl_2(py)_3]$ (1.064 g, 2.53 mmol) in THF (20 mL) at −40 °C. The solution was allowed to warm to room temperature and then stirred for 17 h. Volatiles were removed under reduced pressure, and the resulting orange residue was dissolved in dichloromethane and filtered. Evaporation of the solvent and recrystallization from hexane yielded bright orange crystals of **2**, which were washed with pentane (2 × 10 mL) and dried in vacuo. Yield: 0.74 g (54%).

Characterization data for **3**. ^1H NMR ($CDCl_3$, 300.1 MHz, −15 °C): 9.37 (d, $J = 5.0$ Hz, 4 H, *ortho*-NC_5H_5), 7.89 (t, $J = 7.6$ Hz, 2 H, *para*-NC_5H_5), 7.48 (apparent t, apparent $J = 6.9$ Hz, 4 H, *meta*-NC_5H_5), 6.75 (s, 4 H, *ortho*- and *meta*-C_6H_4), 3.79 (s, 3 H, O*Me*), 0.94 (s, 9 H, NBu^t), −0.17 (s, 9 H, Si*Me*$_3$), −0.48 (s, 9 H, Si*Me*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz, −15 °C): 178.9 ($C_6H_4CN_2$), 158.5 (*ipso*-C_6H_4), 151.0 (*ortho*-NC_5H_5), 137.9 (*para*-NC_5H_5), 135.4 (*para*-C_6H_4), 126.6 (*ortho*-C_6H_4), 123.6 (*meta*-NC_5H_5), 112.5 (*meta*-C_6H_4), 67.7 (N*C*Me$_3$), 55.0 (O*Me*), 31.0 (NC*Me*$_3$), 2.6, 1.7 (2 × Si*Me*$_3$). IR (CsBr plates, Nujol): 1937 (w), 1886 (w), 1650 (w), 1606 (vs), 1574 (m), 1514 (s), a series of strong peaks from 1495 to 1350, 1291 (s), 1250 (vs), 1214 (s), 1205 (s), 1170 (s), 1154 (m), 1108 (m), 1070 (m), 1041 (s), 1013 (s), 980 (s), 843 (vs), 799 (m), 755 (s), 743 (s), 723 (s), 702 (s), 645 (s), 634 (s), 595 (w), 545 (m), 526 (m), 434 (w) cm^{-1}. Anal. Found (calcd for $C_{28}H_{44}ClN_5OSi_2Ti$): C, 55.4 (55.5); H, 7.4 (7.3); N, 11.5 (11.6)

^1H NMR data for **2′** ($CDCl_3$, 300.1 MHz, 0 °C): 8.95 (d, $J = 4.5$ Hz, 2 H, *ortho*-NC_5H_5), 7.94 (t, $J = 7.4$ Hz, 1 H, *para*-NC_5H_5), 7.57 (apparent t, apparent $J = 6.3$ Hz, 2 H, *meta*-NC_5H_5), 7.16 (d, $J = 8.2$ Hz, 2 H, C_6H_4), 6.89 (d, $J = 8.3$ Hz, 2 H, C_6H_4), 3.85 (s, 3 H, O*Me*), 1.14 (s, 9 H, NBu^t), −0.24 (s, 18 H, Si*Me*$_3$).

$[Ti(NBu^t)\{PhC(NSiMe_3)_2\}(\eta\text{-}C_5H_5)]$ (3). An orange solution of LiC_5H_5 (0.035 g, 0.48 mmol) and $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}Cl(py)_2]$ (0.274 g, 0.48 mmol) in toluene (25 mL) at room temperature became red upon stirring for 1 h and was then stirred for a further 15 h before being filtered. Volatiles were removed under reduced pressure to leave **3** as a red oil. Recrystallization from pentane at −80 °C yielded red crystals of **3**, which were washed with pentane (2 × 5 mL) and dried in vacuo. Yield: 0.145 g (68%).

^1H NMR ($CDCl_3$, 300.1 MHz, 25 °C): 7.38 (m, 3 H, *ortho*- and *para*-C_6H_5), 7.24 (m, 2 H, *meta*-C_6H_5), 6.39 (s, 5 H, C_5H_5), 0.99 (s, 9 H, NBu^t), −0.16 (s, 18 H, Si*Me*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz, 25 °C): 169.0 ($C_6H_5CN_2$), 139.5 (*ipso*-C_6H_5), 128.3, 127.9, 127.1 (*ortho*-, *meta*- and *para*-C_6H_5), 110.5 (C_5H_5), 67.0 (N*C*Me$_3$), 32.2 (NC*Me*$_3$), 1.7 (Si*Me*$_3$). IR (KBr plates, Nujol mull): 3098 (w), 3058 (w), 2919 (vs), 1951 (w), 1770 (w), 1662 (w), 1576 (w), 1540 (w), 1348 (m), 1246 (s), 1209 (w), 1176 (w), 1124 (w), 1073 (w), 1032 (w), 1006 (s), 996 (m), 921 (w), 843 (vs), 836 (vs), 806 (m), 793 (s), 777 (m), 763 (s), 712 (w), 700 (m), 688 (w), 618 (w), 603 (w), 592 (w), 546 (m), 523 (w), 507 (m), 478 (w) cm^{-1}. Anal. Found (calcd for $C_{22}H_{37}N_3Si_2Ti$): C, 58.4 (59.0); H, 8.3 (8.3); N, 9.2 (9.4).

$[Ti(NBu^t)\{(4\text{-}C_6H_4OMe)C(NSiMe_3)_2\}(\eta\text{-}C_5H_5)]$ (4). A mixture of LiC_5H_5 (0.007 g, 0.97 mmol) and $[Ti(NBu^t)\{(4\text{-}C_6H_4\text{-}OMe)C(NSiMe_3)_2\}Cl(py)_2]$ (0.059 g, 0.097 mmol) in toluene (15 mL) was heated at 90 °C under reduced pressure in a J. Young ampule for 64 h to give a red solution. The cooled solution was filtered, and volatiles were removed under reduced pressure to leave **4** as a red oil, which could not be crystallized. Yield: 0.043 g (95%).

^1H NMR ($CDCl_3$, 300.1 MHz, 298 K): 7.16 (d, $J = 8.7$ Hz, 2 H, C_6H_4), 6.90 (d, $J = 8.7$ Hz, 2 H, C_6H_4), 6.37 (s, 5 H, C_5H_5), 3.86 (s, 3 H, O*Me*), 0.98 (s, 9 H, NBu^t), −0.15 (s, 18 H, Si*Me*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz, 298 K): 169.5 ($C_6H_4CN_2$), 159.7 (*ipso*-C_6H_4), 132.0 (*para*-C_6H_4), 128.4 (*ortho*-C_6H_4), 113.3 (*meta*-C_6H_4), 110.5 (C_5H_5), 66.9 (N*C*Me$_3$), 55.3 (O*Me*), 32.2 (NC*Me*$_3$), 1.8 (Si*Me*$_3$). IR (KBr plates, thin film): 2958 (s), 2895 (m), 2837 (w), 1609 (s), 1577 (w), 1515 (m), 1425 (vs), 1403 (s), 1350 (w), 1293 (m), 1248 (vs), 1209 (w), 1172 (s), 1122 (w), 1107 (w), 1037 (w), 1018 (s), 1001 (s), 936 (w), 840 (vs), 792 (s), 779 (s), 758 (s), 686 (w), 648 (s), 602 (w), 544 (w), 504 (w) cm^{-1}. Satisfactory elemental analysis was not obtained for this compound, which was an oil.

$[Ti(NBu^t)\{PhC(NSiMe_3)_2\}(CH_2SiMe_3)(py)]$ (5). Cold benzene (40 mL) was added to a mixture of $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}Cl(py)_2]$ (1.117 g, 1.94 mmol) and $LiCH_2SiMe_3$ (0.183 g, 1.94 mmol) at 10 °C. The resulting orange solution was allowed to warm to room temperature and was then stirred for 19 h. After filtration, volatiles were removed under reduced pressure. The red-brown solid was dissolved in pentane and cooled to −25 °C for 2 days to give **5** as orange crystals. Yield: 0.268 g (25%).

^1H NMR ($C_6D_5CD_3$, 300.1 MHz, −50 °C): 8.58 (d, $J = 4.5$ Hz, 2 H, *ortho*-NC_5H_5), 7.20 (br s, 2 H, *ortho*-C_6H_5), 6.95 (m, 3 H, *meta*- and *para*-C_6H_5), 6.58 (t, $^3J = 7.7$ Hz, 1 H, *para*-NC_5H_5), 6.35 (apparent t, apparent $J = 6.7$ Hz, 2 H, *meta*-

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[22] Although for ease of representation all terminal titanium−imido bonds are drawn "Ti═NR", the formal metal−ligand multiple bond order in the complexes described herein is probably best thought of as three (pseudo-$\sigma^2\pi^4$; triple bonds) rather than as two.[4]

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NC$_5H_5$), 1.52 (s, 9 H, N*Bu*^{t}), 0.51 (d, ^2J = 11.4 Hz, 1 H, CH_aH$_b$SiMe$_3$), 0.30 (d, ^2J = 11.4 Hz, 1 H, CH$_a$$H_b$SiMe$_3$), 0.25 (s, 9 H, CH$_2$Si*Me*$_3$), 0.22 and −0.47 [2 × br s, 2 × 9 H, 2 × PhC(NSi*Me*$_3$)$_2$]. ^{13}C{^{1}H} NMR (C$_6$D$_5$CD$_3$, 75.5 MHz, −50 °C): 181.1 (C$_6$H$_5$*C*N$_2$), 151.9 (*ortho*-N*C*$_5$H$_5$), 141.3 (*ipso*-*C*$_6$H$_5$), 138.3 (*para*-N*C*$_5$H$_5$), 128.4, 128.1, 127.2 (*ortho*-, *meta*-, and *para*-*C*$_6$H$_5$), 124.3 (*meta*-N*C*$_5$H$_5$), 69.2 (N*C*Me$_3$), 49.5 (d of d, $^1J_{\mathrm{CH(a)}}$ = $^1J_{\mathrm{CH(b)}}$ = 104 Hz, *C*H$_2$SiMe$_3$), 33.5 (NC*Me*$_3$), 3.7 (CH$_2$Si*Me*$_3$), 2.7 [2 × PhC(NSi*Me*$_3$)$_2$]. Note: ^1J for the δ 49.5 *C*H$_2$SiMe$_3$ resonance was obtained from a gated-coupled ^{13}C NMR spectrum of **5** in the same solvent and at the same temperature. IR (CsBr plates, Nujol mull): 1602 (w), 1501 (m), 1246 (s), 1214 (w), 1176 (w), 1071 (w), 1040 (w), 1030 (w), 1003 (m), 992 (m), 978 (m), 917 (m), 842 (vs), 784 (m), 761 (s), 722 (m), 700 (s), 645 (w), 605 (w), 502 (m), 441 (w), 420 (w) cm^{-1}. Anal. Found (calcd for C$_{26}$H$_{48}$N$_4$Si$_3$Ti): C, 55.9 (56.9); H, 9.0 (8.8); N, 10.0 (10.2).

[Ti(NBu^t){PhC(NSiMe$_3$)$_2$}{CH(SiMe$_3$)$_2$}(py)] (6). Cold benzene (30 mL) was added to a mixture of [Ti(NBu^t){PhC(NSiMe$_3$)$_2$}Cl(py)$_2$] (0.255 g, 0.44 mmol) and LiCH(SiMe$_3$)$_2$ (0.074 g, 0.44 mmol) at 10 °C. The resulting brown solution was stirred for 3 h at 10 °C, and then volatiles were removed under reduced pressure. Extraction with pentane (2 × 10 mL) followed by filtration gave a brown solution. Cooling to −25 °C for 7 days gave **6** as brown crystals. Yield: 0.107 g (39%).

^{1}H NMR (C$_6$D$_5$CD$_3$, 300.1 MHz, −10 °C): 9.01 (br s, 2 H, *ortho*-NC$_5H_5$), 7.30 (m, 2 H, *ortho*-C$_6H_5$), 6.95 (m, 3 H, *meta*- and *para*-C$_6H_5$), 6.63 (t, J = 7.8 Hz, 1 H, *para*-NC$_5H_5$), 6.45 (apparent t, apparent J = 6.7 Hz, 2 H, *meta*-NC$_5H_5$), 1.46 (s, 9 H, N*Bu*^{t}), 0.34 [s, 18 H, CH(Si*Me*$_3$)$_2$], 0.25 [s, 9 H, PhC(NSi*Me*$_3$)(NSiMe$_3$)], −0.24 [s, 1 H, C*H*(SiMe$_3$)$_2$], −0.49 [s, 9 H, PhC(NSiMe$_3$)(NSi*Me*$_3$)]. ^{13}C{^{1}H} NMR (C$_6$D$_5$CD$_3$, 75.5 MHz, −10 °C): 181.2 (C$_6$H$_5$*C*N$_2$), 152.6 (*ortho*-N*C*$_5$H$_5$), 141.1 (*ipso*-*C*$_6$H$_5$), 138.8 (*para*-N*C*$_5$H$_5$), 124.2 (*meta*-N*C*$_5$H$_5$), 69.9 (N*C*Me$_3$), 52.9 [d, $^1J_{\mathrm{CH}}$ = 94 Hz, *C*H(SiMe$_3$)$_2$], 33.0 (NC*Me*$_3$), 5.2 [CH(Si*Me*$_3$)(SiMe$_3$)], 4.4 [CH(SiMe$_3$)(Si*Me*$_3$)], 3.4 [PhC(NSi*Me*$_3$)(NSiMe$_3$)], 2.3 [PhC(NSiMe$_3$)(NSi*Me*$_3$)]. Note: ^1J for the δ 52.9*C*H(SiMe$_3$)$_2$ resonance was obtained from a gated-coupled ^{13}C NMR spectrum of **6** in the same solvent and at the same temperature; the *ortho*-, *meta*- and *para*-*C*$_6$H$_5$ resonances were obscured by solvent. IR (CsBr plates, Nujol mull): 1650 (w), 1604 (w), 1578 (w), 1303 (w), 1246 (s), 1213 (w), 1169 (w), 1070 (w), 1042 (w), 1031 (w), 1003 (m), 993 (m), 918 (w), 843 (vs), 785 (m), 762 (m), 723 (m), 701 (m), 662 (w), 636 (w), 603 (w), 504 (m), 442 (w), 429 (w), 411 (w) cm^{-1}. Anal. Found (calcd for C$_{29}$H$_{56}$N$_4$Si$_4$Ti): C, 54.6 (56.1); H, 9.0 (9.1); N, 8.9 (9.0).

[Ti(NBu^t)(*η*-C$_5$Me$_5$)(CH$_2$SiMe$_3$)(py)] (7). Cold benzene (20 mL) was added to a mixture of [Ti(NBu^t)(*η*-C$_5$Me$_5$)Cl(py)] (0.399 g, 1.08 mmol) and LiCH$_2$SiMe$_3$ (0.103 g, 1.09 mmol) at 5 °C. The resulting brown solution was allowed to warm to room temperature and was then stirred for 17 h. After filtration, volatiles were removed under reduced pressure. The brown solid was dissolved in pentane and cooled to −80 °C for 2 days to give **7** as orange-brown crystals. Yield: 0.182 g (40%).

^{1}H NMR (C$_6$D$_6$, 300.1 MHz, 25 °C): 8.14 (d, J = 4.8 Hz, 2 H, *ortho*-NC$_5H_5$), 6.68 (t of t, ^3J = 7.7 Hz, ^4J = 1.6 Hz, 1 H, *para*-NC$_5H_5$), 6.37 (apparent t, apparent J = 7.0 Hz, 2 H, *meta*-NC$_5H_5$), 1.94 (s, 15 H, C$_5$*Me*$_5$), 1.43 (s, 9 H, N*Bu*^{t}), 0.54 (d, ^2J = 10.9 Hz, 1 H, CH_aH$_b$SiMe$_3$), 0.37 (s, 9 H, Si*Me*$_3$), 0.14 (d, ^2J = 10.9 Hz, 1 H, CH$_a$$H_b$SiMe$_3$). ^{13}C{^{1}H} NMR (C$_6D_6$, 75.5 MHz, 25 °C): 150.5 (*ortho*-N*C*$_5$H$_5$), 137.9 (*para*-N*C*$_5$H$_5$), 123.8 (*meta*-N*C*$_5$H$_5$), 117.1 (*C*$_5$Me$_5$), 66.9 (N*C*Me$_3$), 42.4 (d of d, $^1J_{\mathrm{CH(a)}}$ = $^1J_{\mathrm{CH(b)}}$ = 106 Hz, *C*H$_2$SiMe$_3$), 33.6 (NC*Me*$_3$), 12.1 (C$_5$*Me*$_5$), 4.3 (Si*Me*$_3$). Note:^1J for the δ 42.4 *C*H$_2$SiMe$_3$ resonance was obtained from a gated-coupled ^{13}C NMR spectrum of **7** in the same solvent and at the same temperature. IR (KBr plates, Nujol mull): 1928 (w), 1717 (w), 1653 (w), 1604 (m), 1483 (w), 1346 (m), 1234 (vs), 1204 (m), 1152 (w), 1111 (w), 1069 (w), 1043 (w), 1015 (w), 984 (w), 914 (m), 863 (s), 820 (m), 802 (w), 755 (m), 746 (w), 725 (m), 698 (s), 670 (w), 640 (w), 604 (w), 585 (w), 536 (m), 519 (m), 488 (w) cm^{-1}. Anal. Found (calcd for C$_{23}$H$_{40}$N$_2$SiTi): C, 65.7 (65.7); H, 9.8 (9.6); N, 6.7 (6.7).

NMR-Scale Hydrogenolysis of [Ti(NBu^t){PhC(NSiMe$_3$)$_2$}{CH(SiMe$_3$)$_2$}(py)] (6). A solution of [Ti(NBu^t){PhC(NSiMe$_3$)$_2$}{CH(SiMe$_3$)$_2$}(py)] (10.7 mg, 0.017 mmol) in C$_6$D$_6$ (1.0 mL) was placed under 9.2 bar pressure of H$_2$ gas in a Fisher−Porter bottle at room temperature. After the orange-brown solution was stirred for 16 h, it became a very pale yellow. NMR analysis showed the formation of several products including Bu^{t}NH$_2$, CH$_2$(SiMe$_3$)$_2$, and pyridine.

[Ti(NBu^t){PhC(NSiMe$_3$)$_2$}(*η*^{3}-BH$_4$)(py)] (8). An orange mixture of [Ti(NBu^t){PhC(NSiMe$_3$)$_2$}Cl(py)$_2$] (0.334 g, 0.58 mmol) and an excess of LiBH$_4$ (0.120 g, 5.51 mmol) in toluene (30 mL) was stirred for 72 h at room temperature and then filtered. Volatiles were removed under reduced pressure to leave an orange-brown oil. Extraction into hexane (20 mL) followed by cooling to −80 °C for 48 h afforded **8** as a yellow solid, which was washed with pentane (2 × 5 mL) and dried in vacuo. Yield: 0.170 g (62%).

^{1}H NMR (C$_6$D$_5$CD$_3$, 300.1 MHz, 25 °C): 8.60 (d, J = 4.5 Hz, 2 H, *ortho*-NC$_5H_5$), 7.20 (m, 2 H, *meta*-C$_6H_5$), 6.99 (m, 3 H, *ortho*- and *para*-C$_6H_5$), 6.69 (t, ^3J = 7.3 Hz, 1 H, *para*-NC$_5H_5$), 6.43 (apparent t, apparent J = 5.9 Hz, 2 H, *meta*-NC$_5H_5$), 1.53 (1:1:1:1 quart, $^1J_{\mathrm{BH}}$ = 86 Hz, 4 H, BH_4), 1.33 (s, 9 H, N*Bu*^{t}), −0.08 (s, 18 H, NSi*Me*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_5$CD$_3$, 75.5 MHz, −30 °C): 179.7 (C$_6$H$_5$*C*N$_2$), 151.0 (*ortho*-N*C*$_5$H$_5$), 141.8 (*ipso*-*C*$_6$H$_5$), 138.2 (*para*-N*C*$_5$H$_5$), 128.4 (*para*-*C*$_6$H$_5$), 128.0 (*ortho*-*C*$_6$H$_5$), 127.0 (*meta*-*C*$_6$H$_5$), 124.1 (*meta*-N*C*$_5$H$_5$), 69.7 (N*C*Me$_3$), 32.4 (NC*Me*$_3$), 2.5 (2 × PhC(NSi*Me*$_3$)$_2$). ^{11}B NMR (C$_6$H$_6$, 96.3 MHz, 25 °C): −10.7 (quint, ^1J = 86 Hz). IR (KBr plates, Nujol mull): 2464 (s) ν(B−H$_{\mathrm{terminal}}$), 2208 (m) and 2145 (m) ν(B−H$_{\mathrm{bridging}}$), 1605 (m), 1351 (m), 1247 (vs), 1214 (w), 1185 (m), 1156 (w), 1129 (w), 1090 (w), 1070 (w), 1042 (w), 1002 (s), 989 (vs), 922 (w), 841 (vs), 789 (m), 764 (s), 749 (s), 717 (m), 696 (s), 637 (w), 605 (w), 505 (m) cm^{-1}. IR (hexane solution, KBr cell, selected data): 2493 (m) ν(B−H$_{\mathrm{terminal}}$), 2205 (m) and 2151 (w) ν(B−H$_{\mathrm{bridging}}$) cm^{-1}. Anal. Found (calcd for C$_{22}$H$_{41}$BN$_4$Si$_2$Ti): C, 54.7 (55.5); H, 8.9 (8.7); N, 11.7 (11.8).

[Ti(NBu^t){PhC(NSiMe$_3$)$_2$}{N(SiMe$_3$)$_2$}(py)] (9). A solution of LiN(SiMe$_3$)$_2$·OEt$_2$ (0.419 g, 1.81 mmol) in toluene (15 mL) was added over 5 min to a stirred solution of [Ti(NBu^t){PhC(NSiMe$_3$)$_2$}Cl(py)$_2$] (1.041 g, 1.81 mmol) in toluene (15 mL) at room temperature. The solution was stirred for 40 h and then filtered. Volatiles were removed under reduced pressure to leave **9** as an orange oil, which could not be crystallized. Yield: 1.062 g (91%).

^{1}H NMR (CDCl$_3$, 300.1 MHz, −5 °C): 9.07 (br s, 2 H, *ortho*-NC$_5H_5$), 7.90 (t of t, ^3J = 7.7 Hz, ^4J = 1.6 Hz, 1 H, *para*-NC$_5H_5$), 7.59 (overlapping m, 2 H, *meta*-NC$_5H_5$), 7.36 (m, 4 H, *ortho*- and *meta*-C$_6H_5$), 7.15 (m, 1 H, *para*-C$_6H_5$), 1.18 (s, 9 H, N*Bu*^{t}), 0.12 and 0.06 [2 × s, 2 × 9 H, N(Si*Me*$_3$)$_2$], −0.05 and −0.67 [2 × s, 2 × 9 H, PhC(NSi*Me*$_3$)$_2$]. ^{13}C{^{1}H} NMR (CDCl$_3$, 75.5 MHz, −5 °C): 180.0 (C$_6$H$_5$*C*N$_2$), 152.7 (*ortho*-N*C*$_5$H$_5$), 141.5 (*ipso*-*C*$_6$H$_5$), 138.5 (*para*-N*C*$_5$H$_5$), 128.0, 127.7, 127.6, 127.0 (*ortho*- and *meta*-*C*$_6$H$_5$), 126.3 (*para*-*C*$_6$H$_5$), 124.0 (*meta*-N*C*$_5$H$_5$), 69.5 (N*C*Me$_3$), 32.5 (NC*Me*$_3$), 6.4 and 4.2 [N(Si*Me*$_3$)$_2$], 2.8 and 2.1 [PhC(NSi*Me*$_3$)$_2$]. Satisfactory elemental analysis was not obtained for this compound, which was an oil.

[Ti(NBu^t){PhC(NSiMe$_3$)$_2$}(O-2,6-C$_6$H$_3$Me$_2$)(py)] (10). A mixture of [Ti(NBu^t){PhC(NSiMe$_3$)$_2$}Cl(py)$_2$] (0.200 g, 0.35 mmol) and LiO-2,6-C$_6$H$_3$Me$_2$ (0.044 g, 0.35 mmol) in toluene (40 mL) was heated at 95 °C under reduced pressure in a J. Young ampule for 18 h. The solution was filtered, volatiles were removed under reduced pressure, and the orange residue was dissolved in pentane. Cooling to −80 °C for 2 days gave **10** as an orange-brown solid, which was washed with cold pentane (2 × 5 mL) and dried in vacuo. Yield: 0.112 g (55%).

^{1}H NMR (CDCl$_3$, 300.1 MHz, 25 °C): 8.88 (br m, 2 H, *ortho*-NC$_5H_5$), 7.84 (t, J = 7.6 Hz, 1 H, *para*-NC$_5H_5$), 7.43 (apparent t, apparent J = 7.3 Hz, 2 H, *meta*-NC$_5H_5$), 7.37 (m, 3 H, *ortho*- and *para*-C$_6H_5$), 7.29 (m, 2 H, *meta*-C$_6H_5$), 6.90 (d, J = 7.4 Hz,

Table 1. X-ray Data Collection and Processing Parameters for [Ti(NBu^t){PhC(NSiMe$_3$)$_2$}(CH$_2$SiMe$_3$)(py)] (5) and [Ti(NBu^t)(η-C$_5$Me$_5$)(CH$_2$SiMe$_3$)(py)] (7)

complex	**5**	**7**
mol formula	$C_{26}H_{48}N_4Si_3Ti$	$C_{23}H_{40}N_2SiTi$
fw	548.86	420.57
temp/°C	−123(2)	−123(2)
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
unit cell dimens		
a/Å	10.741(3)	9.287(4)
b/Å	10.919(2)	28.019(8) Å
c/Å	16.318(2)	9.819(2)
α/deg	73.676(12)	90
β/deg	80.68(2)	105.88(5)
γ/deg	63.357(15)	90
vol/Å^3	1640.2(4)	2457.7(13)
Z	2	4
density (calcd)/Mg m^{-3}	1.11	1.14
abs coeff/mm^{-1}	0.38	0.40
F(000)	592	912
cryst description	yellow block	orange cuboid
cryst size/mm	0.48 × 0.42 × 0.40	0.51 × 0.44 × 0.42
θ range for data collection/deg	2.54−25.01	2.60−25.05
scan type	$\omega-\theta$ with learnt profile	ω
index ranges	$-12 \le h \le 12, -12 \le k \le 12, -12 \le l \le 19$	$-11 \le h \le 11, -33 \le k \le 33, -11 \le l \le 11$
no. of reflns collected	5995	8276
no. of indep reflns	5517	4312
R(merge)	0.043	0.020
no. of obsd reflns [$I > 2\sigma(I)$]	4774	3530
abs corr	none	integration
max and min transmission		0.868 and 0.797
decay correction/%	14.0	random variation ±7.8
no. of data used in refinement	5505	4312
no. of restraints applied	0	0
no. of params refined	322	264
weighting scheme	Chebychev polynomial	Chebychev polynomial
ext coeff	43(7)	none
final R indices[a] [$I > 2\sigma(I)$]	$R_1 = 0.0576$, w$R_2 = 0.0628$	$R_1 = 0.0419$, w$R_2 = 0.0473$
R indices (all data)	$R_1 = 0.0659$, w$R_2 = 0.0797$	$R_1 = 0.0550$, w$R_2 = 0.0583$
goodness-of-fit	1.105 (on F^2)	1.115 (on F^2)
final $(\Delta/\sigma)_{max}$	0.03	0.04
largest residual peaks/e Å^{-3}	0.70 and −0.46	0.49 and −0.41

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; w$R_2 = \sqrt{\{\sum w(F_o^2 - F_c^2)^2/\sum(w(F_o^2)^2\}}$.

2 H, *meta*-O-2,6-C$_6$*H*$_3$Me$_2$), 6.52 (t, J = 7.4 Hz, 1 H, *para*-O-2,6-C$_6$*H*$_3$Me$_2$), 2.26 (s, 6 H, O-2,6-C$_6$H$_3$*Me*$_2$), 1.17 (s, 9 H, N*Bu^t*), −0.30 (s, 18 H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.5 MHz, 25 °C): 179.3 (C$_6$H$_5$*C*N$_2$), 161.6 (*ipso*-O-2,6-*C*$_6$H$_3$Me$_2$), 151.6 (*ortho*-N*C*$_5$H$_5$), 141.5 (*ipso*-*C*$_6$H$_5$), 138.7 (*para*-N*C*$_5$H$_5$), 128.2, 127.8, 127.5 (*ortho*-, *meta*-, and *para*-*C*$_6$H$_5$), 126.9 (*meta*-O-2,6-*C*$_6$H$_3$-Me$_2$), 126.5 (*ortho*-O-2,6-*C*$_6$H$_3$Me$_2$), 124.4 (*meta*-N*C*$_5$H$_5$), 116.5 (*para*-O-2,6-*C*$_6$H$_3$Me$_2$), 68.8 (N*C*Me$_3$), 32.7 (NC*Me*$_3$), 17.5 (O-2,6-C$_6$H$_3$*Me*$_2$), 1.9 (Si*Me*$_3$). IR (CsBr plates, Nujol mull): 1650 (w), 1603 (w), 1591 (w), 1504 (w), 1428 (s), 1401 (s), 1350 (w), 1303 (m), 1294 (m), 1261 (m), 1247 (s), 1235 (s), 1175 (w), 1128 (w), 1092 (m), 1070 (m), 1044 (m), 1030 (m), 1014 (m), 1003 (m), 993 (m), 916 (m), 892 (m), 840 (vs), 804 (m), 790 (m), 760 (s), 719 (m), 703 (m), 690 (m), 637 (w), 616 (w), 602 (w), 552 (w), 509 (s), 444 (w) cm^{-1}. Anal. Found (calcd for C$_{30}$H$_{46}$N$_4$OSi$_2$Ti): C, 60.2 (61.8); H, 8.1 (8.0); N, 9.2 (9.6).

[Ti(NBu^t){PhC(NSiMe$_3$)$_2$}(O-2,6-C$_6$H$_3$Bu^t$_2$)(py)] (11). A mixture of [Ti(NBu^t){PhC(NSiMe$_3$)$_2$}Cl(py)$_2$] (0.303 g, 0.53 mmol) and LiO-2,6-C$_6$H$_3$Bu^t$_2$ (0.112 g, 0.53 mmol) in benzene (40 mL) was heated at 80 °C under reduced pressure for 14 h. The solution was allowed to cool and then filtered. The volatiles were removed under reduced pressure to leave a yellow-orange oil, which was redissolved in pentane and filtered again. Cooling to −80 °C for 3 days gave yellow crystals of **11**. The mother liquor was decanted off, and the crystals were dried in vacuo. Yield: 0.296 g (84%).

^{1}H NMR (CDCl$_3$, 300.1 MHz, 25 °C): 8.87 (br m, 2 H, *ortho*-NC$_5$*H*$_5$), 7.79 (t, J = 7.6 Hz, 1 H, *para*-NC$_5$*H*$_5$), 7.44 (br m, 4 H, C$_6$*H*$_5$), 7.34 (apparent t, apparent J = 7.0 Hz, 2 H, *meta*-NC$_5$*H*$_5$), 7.23 (d, J = 7.8 Hz, 2 H, *meta*-O-2,6-C$_6$*H*$_3$Me$_2$), 7.21 (br s, 1 H, C$_6$*H*$_5$), 6.69 (t, J = 7.8 Hz, 1 H, *para*-O-2,6-C$_6$*H*$_3$-Me$_2$), 1.55 and 1.28 (2 × br s, 2 × 9 H, 2 × O-2,6-C$_6$H$_3$*Bu^t*), 1.13 (s, 9 H, N*Bu^t*), 0.05 and −0.63 (2 × br s, 2 × 9 H, 2 × Si*Me*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.5 MHz, 25 °C): 178.8 (C$_6$H$_5$*C*N$_2$), 164.3 (*ipso*-O-2,6-*C*$_6$H$_3$Bu^t$_2$), 152.1 (*ortho*-N*C*$_5$H$_5$), 141.4 (*ipso*-*C*$_6$H$_5$), 138.4 (*para*-N*C*$_5$H$_5$), 128.3, 127.8, 127.3 (*ortho*-, *meta*-, and *para*-*C*$_6$H$_5$), 125.0 (*meta*-O-2,6-*C*$_6$H$_3$Bu^t$_2$), 123.8 (*meta*-N*C*$_5$H$_5$), 116.7 (*para*-O-2,6-*C*$_6$H$_3$Bu^t$_2$), 70.1 (N*C*Me$_3$), 35.3 [O-2,6-C$_6$H$_3$(*C*Me$_3$)$_2$], 32.2 (NC*Me*$_3$), 31.8 [O-2,6-C$_6$H$_3$(C*Me*$_3$)$_2$], 2.3 (Si*Me*$_3$). Note: ortho resonances of the O-2,6-*C*$_6$H$_3$Bu^t$_2$ ligand were not observed. IR (CsBr plates, Nujol mull): 3064 (w), 1734 (w), 1602 (w), 1578 (w), 1544 (w), 1444 (vs), 1429 (vs), 1407 (vs), 1351 (w), 1311 (w), 1272 (s), 1260 (s), 1246 (s), 1233 (vs), 1207 (m), 1171 (w), 1152 (w), 1123 (w), 1105 (w), 1070 (w), 1042 (w), 1031 (w), 1003 (m), 994 (s), 917 (w), 874 (s), 842 (vs), 795 (w), 784 (m), 764 (m), 750 (s), 728 (w), 700 (s), 666 (w), 634 (w), 593 (w), 568 (w), 548 (w), 506 (m), 490 (w), 460 (w), 444 (w), 428 (w), 412 (w) cm^{-1}. Anal. Found (calcd for C$_{36}$H$_{58}$N$_4$OSi$_2$Ti): C, 62.9 (64.8); H, 8.9 (8.8); N, 7.3 (8.4).

[Ti(NBu^t){(4-C$_6$H$_4$OMe)C(NSiMe$_3$)$_2$}(O-2,6-C$_6$H$_3$Me$_2$)(py)] (12). A mixture of [Ti(NBu^t){(4-C$_6$H$_4$Me)C(NSiMe$_3$)$_2$}Cl(py)$_2$] (0.484 g, 0.80 mmol) and LiO-2,6-C$_6$H$_3$Me$_2$ (0.102 g, 0.80 mmol) in toluene (25 mL) was heated at 100 °C under reduced pressure in a J. Young ampule for 65 h. The solution was allowed to cool, and the volatiles were removed under reduced pressure. Extraction with CH$_2$Cl$_2$ and filtration gave a red solution. Volatiles were removed under reduced pressure to give **12** as a viscous red oil, which could not be crystallized. Yield: 0.455 g (93%).

^{1}H NMR (CDCl$_3$, 300.1 MHz, 25 °C): 8.87 (d, J = 4.2 Hz, 2 H, *ortho*-NC$_5$*H*$_5$), 7.83 (t, J = 7.3 Hz, 1 H, *para*-NC$_5$*H*$_5$), 7.41

(apparent t, apparent $J = 6.1$ Hz, 2 H, *meta*-$\mathrm{NC_5}\mathit{H_5}$), 7.21 (d, $J = 7.3$ Hz, 2 H, *meta*-O-2,6-$\mathrm{C_6}\mathit{H_3}\mathrm{Me_2}$), 6.89 (m, 4 H, $\mathrm{C_6}\mathit{H_4}$), 6.51 (t, $J = 7.3$ Hz, 1 H, *para*-O-2,6-$\mathrm{C_6}\mathit{H_3}\mathrm{Me_2}$), 3.85 (s, 3 H, O*Me*), 2.25 (s, 6 H, O-2,6-$\mathrm{C_6H_3}\mathit{Me_2}$), 1.16 (s, 9 H, N$\mathit{Bu^t}$), −0.28 (s, 18 H, Si$\mathit{Me_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, 75.5 MHz, 25 °C): 179.5 ($\mathrm{C_6H_4}\mathit{C}\mathrm{N_2}$), 159.6 (*ipso*-O-2,6-$\mathit{C_6}\mathrm{H_3Me_2}$ or *ipso*-$\mathit{C_6}\mathrm{H_4}$), 151.5 (*ortho*-N$\mathit{C_5}\mathrm{H_5}$), 138.6 (*para*-N$\mathit{C_5}\mathrm{H_5}$), 134.3 (*para*-$\mathit{C_6}\mathrm{H_4}$), 128.2 (*meta*-O-2,6-$\mathit{C_6}\mathrm{H_3Me_2}$), 127.4 (*ortho*-$\mathit{C_6}\mathrm{H_4}$), 126.5 (*ortho*-O-2,6-$\mathit{C_6}\mathrm{H_3Me_2}$), 124.4 (*meta*-N$\mathit{C_5}\mathrm{H_5}$), 116.4 (*para*-O-2,6-$\mathit{C_6}\mathrm{H_3Me_2}$), 113.1 (*meta*-$\mathit{C_6}\mathrm{H_4}$), 68.7 (N*C*$\mathrm{Me_3}$), 55.2 (O*Me*), 32.7 (NC$\mathit{Me_3}$), 17.5 ($\mathrm{C_6H_3}\mathit{Me_2}$), 1.9 (Si$\mathit{Me_3}$). Note: one of the two phenyl ring *ipso* carbons was not observed, or they are coincident with each other. IR (KBr plates, Nujol mull): 1609 (w), 1292 (w), 1249 (s), 1234 (w), 1171 (w), 1089 (w), 1016 (m), 997 (m), 842 (vs), 799 (m), 761 (w), 722 (w), 647 (w) $\mathrm{cm^{-1}}$. Anal. Found (calcd for $\mathrm{C_{31}H_{48}N_4O_2Si_2Ti}$): C, 57.8 (60.8); H, 7.7 (7.9); N, 7.9 (9.1).

[Ti(NBu^t){PhC(NSiMe$_3$)$_2$}$_2$(py)] (13). Toluene (30 mL) was added to a mixture of $[\mathrm{Ti(NBu^t)\{PhC(NSiMe_3)_2\}Cl(py)_2}]$ (0.120 g, 0.21 mmol) and $\mathrm{LiPhC(NSiMe_3)_2}$ (0.056 g, 0.21 mmol), and the resulting orange solution was heated at 90 °C under reduced pressure in a J. Young ampule for 16 h. After the solution was cooled, it was filtered and volatiles were removed to give **13** as an orange oil. Crude yield: 0.142 g (94%). Recrystallization from pentane failed to give a solid product. Attempts at sublimation led to decomposition.

^{1}H NMR ($\mathrm{CDCl_3}$, 300.1 MHz, 25 °C): 9.36 (br s, 2 H, *ortho*-$\mathrm{NC_5}\mathit{H_5}$), 7.01 (t, $J = 7.6$ Hz, 1 H, *para*-$\mathrm{NC_5}\mathit{H_5}$), 7.46 (apparent t, apparent $J = 6.2$ Hz, 2 H, *meta*-$\mathrm{NC_5}\mathit{H_5}$), 7.29 (br s, 5 H, $\mathrm{C_6}\mathit{H_5}$), 1.20 (s, 9 H, N$\mathit{Bu^t}$), −0.14 (br s, 36 H, Si$\mathit{Me_3}$). Satisfactory elemental analysis was not obtained for this compound, which was an oil.

Crystal Structure Determinations for [Ti(NBu^t){PhC(NSiMe$_3$)$_2$}(CH$_2$SiMe$_3$)(py)] (5) and [Ti(NBu^t)(η-C$_5$Me$_5$)(CH$_2$SiMe$_3$)(py)] (7). General Procedure. Crystal data collection and processing parameters are given in Table 1. Crystals were mounted in a film of RS3000 perfluoropolyether oil (Hoechst) on a glass fiber and transferred to a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.[31] Data were collected using Mo Kα radiation ($\lambda = 0.710\,73$ Å). For **7**, an absorption correction was applied to the data. Equivalent reflections were merged, and the structures were solved by direct methods using SIR92.[32] Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms: these were refined anisotropically against F^2. Data for **5** were corrected for extinction via an overall secondary extinction parameter;[33] for **7**, examination of the refined extinction parameter and an agreement analysis suggested that no extinction correction was required. All crystallographic calculations were performed using SIR92 and CRYSTALS-PC.[34] A full listing of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1 of this Journal.

Additional Details for [Ti(NBu^t){PhC(NSiMe$_3$)$_2$}(CH$_2$SiMe$_3$)(py)] (5). H atoms for the phenyl and pyridine groups and for the $\mathrm{CH_2}$ of the (trimethylsilyl)methyl group were located from difference maps. H atoms for the $\mathrm{SiMe_3}$ and $\mathrm{Bu^t}$ groups were placed geometrically. The positions and the isotropic displacement parameters of the H atoms of the trimethylsilylmethyl $\mathrm{CH_2}$ group were freely refined, and other H atoms were refined in a riding model with common isotropic temperature factors for the phenyl, pyridine, *tert*-butyl, and three trimethylsilyl groups of H atoms.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Ti(NBu^t){PhC(NSiMe$_3$)$_2$}(CH$_2$SiMe$_3$)(py)] (5)

Ti(1)−N(1)	1.690(2)	N(1)−C(5)	1.460(3)
Ti(1)−N(2)	2.194(2)	Ti(1)−N(3)	2.122(2)
Ti(1)−N(4)	2.217(2)	Ti(1)−C(1)	2.187(3)
Ti(1)···H(11)	2.54(3)	C(1)−H(11)	0.97(3)
Ti(1)···H(12)	2.38(4)	C(1)−H(12)	0.88(4)

N(1)−Ti(1)−N(2)	110.89(9)	Ti(1)−N(1)−C(5)	168.0(2)
N(1)−Ti(1)−N(3)	106.18(9)	N(1)−Ti(1)−C(1)	111.7(1)
N(2)−Ti(1)−N(3)	63.74(8)	N(4)−Ti(1)−C(1)	89.8(1)
N(1)−Ti(1)−N(4)	101.5(1)	N(2)−Ti(1)−N(4)	89.20(8)
N(3)−Ti(1)−N(4)	146.60(8)	N(2)−Ti(1)−C(1)	136.7(1)
N(3)−Ti(1)−C(1)	96.9(1)	Ti(1)−C(1)−Si(1)	126.9(2)
Ti(1)−C(1)−H(11)	100(2)	Ti(1)−C(1)−H(12)	91(3)
H(11)−C(1)−H(12)	107(3)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [Ti(NBu^t)(η-C$_5$Me$_5$)(CH$_2$SiMe$_3$)(py)] (7)[a]

Ti(1)−N(1)	1.727(2)	Ti(1)···H(11)	2.62(3)
Ti(1)−N(2)	2.202(2)	Ti(1)···H(12)	2.63(3)
Ti(1)−C(1)	2.167(2)	N(1)−C(5)	1.447(3)
C(1)−H(11)	0.86(3)	C(1)−H(12)	0.99(3)
Ti(1)−$\mathrm{Cp_{cent}}$	2.204		

N(1)−Ti(1)−C(1)	106.33(9)	Ti(1)−C(1)−Si(1)	123.8(1)
N(2)−Ti(1)−C(1)	98.25(8)	Ti(1)−C(1)−H(11)	113(2)
$\mathrm{Cp_{cent}}$−Ti(1)−N(1)	125.9	Ti(1)−C(1)−H(12)	107(2)
$\mathrm{Cp_{cent}}$−Ti(1)−N(2)	110.4	$\mathrm{Cp_{cent}}$−Ti(1)−C(1)	114.5

[a] $\mathrm{Cp_{cent}}$ is the computed centroid for the ring containing atoms C(9)−C(13).

Additional Details for [Ti(NBu^t)(η-C$_5$Me$_5$)(CH$_2$SiMe$_3$)(py)] (7). All H atoms were located from Fourier difference syntheses. The positions and the isotropic displacement parameters of the H atoms of the $\mathrm{CH_2}$ linkage of the (trimethylsilyl)methyl group were freely refined. Other H atoms were refined in a riding model with equivalent isotropic displacement parameters for each $\mathrm{CH_3}$ group and for the pyridine H atoms.

NMR Kinetic Analysis for [Ti(NBu^t){PhC(NSiMe$_3$)$_2$}(O-2,6-C$_6$H$_3$Bu$^t_2$)(py)] (11).[35,36] ^{1}H NMR spectra of a solution of **11** in $\mathrm{CDCl_3}$ were recorded between 268 and 283 K. Lorentzian curve fitting of the *tert*-butyl and trimethylsilyl group resonances afforded $\nu_{1/2(\mathrm{obs})}$ (observed line widths at half-height) values. Subtraction of the estimated natural line width (obtained at the low-temperature limit) from $\nu_{1/2(\mathrm{obs})}$ gave the corrected excess line widths at half-height $\nu_{1/2(\mathrm{corr})}$. At each temperature, the NMR first-order rate constant k_{obs} was calculated according to $k_{\mathrm{obs}} = \pi\nu_{1/2(\mathrm{corr})}$. Chemical *exchange* rate constants (k_{exch}) were calculated as $2k_{\mathrm{obs}}$.[35] The $\nu_{1/2(\mathrm{corr})}$ values, exchange rate constants, and activation parameters derived from standard Eyring plots (provided as Supporting Information) are listed in Table 4.

Results and Discussion

Starting Complexes. The previously reported[17] titanium *tert*-butyl imido compound $[\mathrm{Ti(NBu^t)\{PhC(NSiMe_3)_2\}Cl(py)_2}]$ (**1** at center in Scheme 1) is readily available in good yields by treatment of $[\mathrm{Ti(NBu^t)Cl_2(py)_3}]$[28] with $\mathrm{LiPhC(NSiMe_3)_2}$.[23,24] Since introduction of a *para*-substituent into the benzene ring of the *N*,*N′*-bis(trimethylsilyl)benzamidinate ligand can sometimes aid crystallization of the complexes, we report here the homologous complex $[\mathrm{Ti(NBu^t)\{(4\text{-}C_6H_4OMe)C(NSiMe_3)_2\}Cl(py)_2}]$ (**2**). Thus, addition of $\mathrm{Li(4\text{-}C_6H_4OMe)C(NSiMe_3)_2}$ to a THF solution of $[\mathrm{Ti(NBu^t)Cl_2(py)_3}]$ gave the air- and

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Table 4. Excess Line Widths, Exchange Rate[a] Constants, and Activation Parameters for $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}(O\text{-}2,6\text{-}C_6H_3Bu^t{}_2)(py)]$ (11)[a]

Excess Line Widths and Rate Constants[b]

	tert-butyl resonances		trimethylsilyl resonances	
temp (K)	$\nu_{1/2(corr)}$ (s^{-1})	k_{exch} (s^{-1})	$\nu_{1/2(corr)}$ (s^{-1})	k_{exch} (s^{-1})
268	0.185	1.16	0.157	0.989
273	0.466	2.93	0.306	1.93
278	1.167	7.33	0.965	6.06
283	2.422	15.2	1.948	12.25

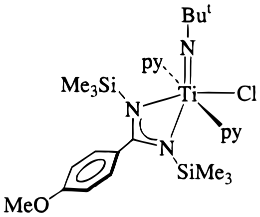
Activation Parameters

	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J $mol^{-1}\cdot K^{-1}$)	$\Delta G^\ddagger{}_{278}$ (kJ mol^{-1})
Bu^t group exchange	106 ± 12	155 ± 31	62.9 ± 2.4
$SiMe_3$ group exchange	107 ± 17	155 ± 58	62.9 ± 3.6

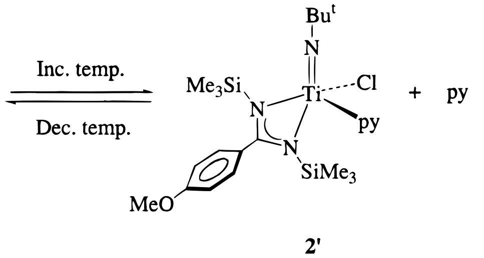
[a] See the text and Experimental Section for further details. [b] These are average (for the two different Bu^t or $SiMe_3$ groups) values for $\nu_{1/2}$(corr) and k_{exch}, where $\nu_{1/2}$(corr) is the excess line width and k_{exch} is the associated chemical exchange rate constant (see Experimental Section for further details).

moisture-sensitive, red complex **2** in 54% yield after recrystallization from hexane. Full characterization data for **2** and all the new complexes described herein are given in the Experimental Section and will not be discussed if interpretation is straightforward.

The solution NMR behavior of **2** is analogous to that reported previously for the complexes $[Ti(NR)\{PhC(NSiMe_3)_2\}Cl(py)_2]$ (R = Bu^t, 2,6-$C_6H_3Me_2$, or 2,6-$C_6H_3Pr^i{}_2$) in that it exists in a temperature-dependent equilibrium with the corresponding mono(pyridine) adduct $[Ti(NBu^t)\{(4\text{-}C_6H_4OMe)C(NSiMe_3)_2\}Cl(py)]$ (**2′**) as illustrated in eq1. The structures of **2** and **2′** are proposed by analogy with those reported before for the non-*para*-substituted homologues. The complexes **1** and **2** are useful precursors to new organometallic and coordination complexes of titanium as described below and illustrated in Scheme 1.



2



(1)

2′

Cyclopentadienyl Derivatives. The half-sandwich complex $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}(\eta\text{-}C_5H_5)]$ (**3**) was prepared by a straightforward metathesis reaction between $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}Cl(py)_2]$ (**1**) and LiC_5H_5 in toluene (Scheme 1). Recrystallization from pentane gave **3** in 68% yield. The *para*-methoxy-substituted benzamidinate derivative $[Ti(NBu^t)\{(4\text{-}C_6H_4OMe)C(NSiMe_3)_2\}(\eta\text{-}C_5H_5)]$ (**4**) was synthesized from **2** and LiC_5H_5 in toluene. Compound **4** is an oil, however, and could not be crystallized.

The half-sandwich compounds **3** and **4** are proposed to possess the 16-electron, monomeric structures illustrated in Scheme 1. Although we have been unable to obtain diffraction-quality crystals, we found that the solution molecular weight of **3** in CH_2Cl_2 (using the Signer vapor diffusion method[37]) was 395; this is 12% lower than that expected for a monomer (447.6) but consistent with this complex (and presumably therefore **4**) adopting mononuclear, nonbridged structures in solution.

The pyridine-free 16-electron compounds $[Ti(NBu^t)\{RC(NR')_2\}(\eta\text{-}C_5H_5)]$ (**3** and **4**) may be compared with the formally 20-electron bis(cyclopentadienyl) complexes $[Ti(\eta\text{-}C_5H_5)(\eta\text{-}C_5R_5)(NBu^t)(L)]$ (R = H or Me, L = py or py-Bu^t)[38] and the 18-electron cyclopentadienyl−indenyl complex $[Ti(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)(NBu^t)(py)]$, all of which exist as pyridine adducts.[29] On the other hand, the bis(pentamethylcyclopentadienyl) complexes $[Ti(\eta\text{-}C_5Me_5)_2(NAr)]$ do not contain coordinated pyridine.[39] On the basis of Brintzinger's "coordination aperture" approach,[40] Teuben has recently suggested that the steric requirements of the *N*,*N′*-bis(trimethylsilyl)benzamidinate ligand are similar to those of C_5Me_5 and greater than those of C_5H_5.[8] In the two systems that we have studied (i.e., **3** and **4**), the amidinate−cyclopentadienyl set behaves as though it is sterically comparable to bis(pentamethylcyclopentadienyl).

Alkyl Derivatives. Syntheses. Reaction of $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}Cl(py)_2]$ (**1**) with 1 equiv of the lithiated bulky alkyls $LiCH(R)SiMe_3$ (R = H or $SiMe_3$) in cold benzene followed by recrystallization from pentane afforded the orange-brown, highly air-sensitive 14-electron alkyl derivatives $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}\{CH(R)SiMe_3\}(py)]$ (R = H **5** or $SiMe_3$ **6**) in ca. 30% yield (Scheme 1). The crystals of **5** were suitable for X-diffraction analysis (vide infra). Reaction of **1** with $Mg(CH_2Ph)_2$, MeLi, or $ZnMe_2$ in hexane or benzene gave inseparable mixtures of products.

For the purposes of comparison we also prepared the new 16-electron, half-sandwich alkyl complex [Ti(N-

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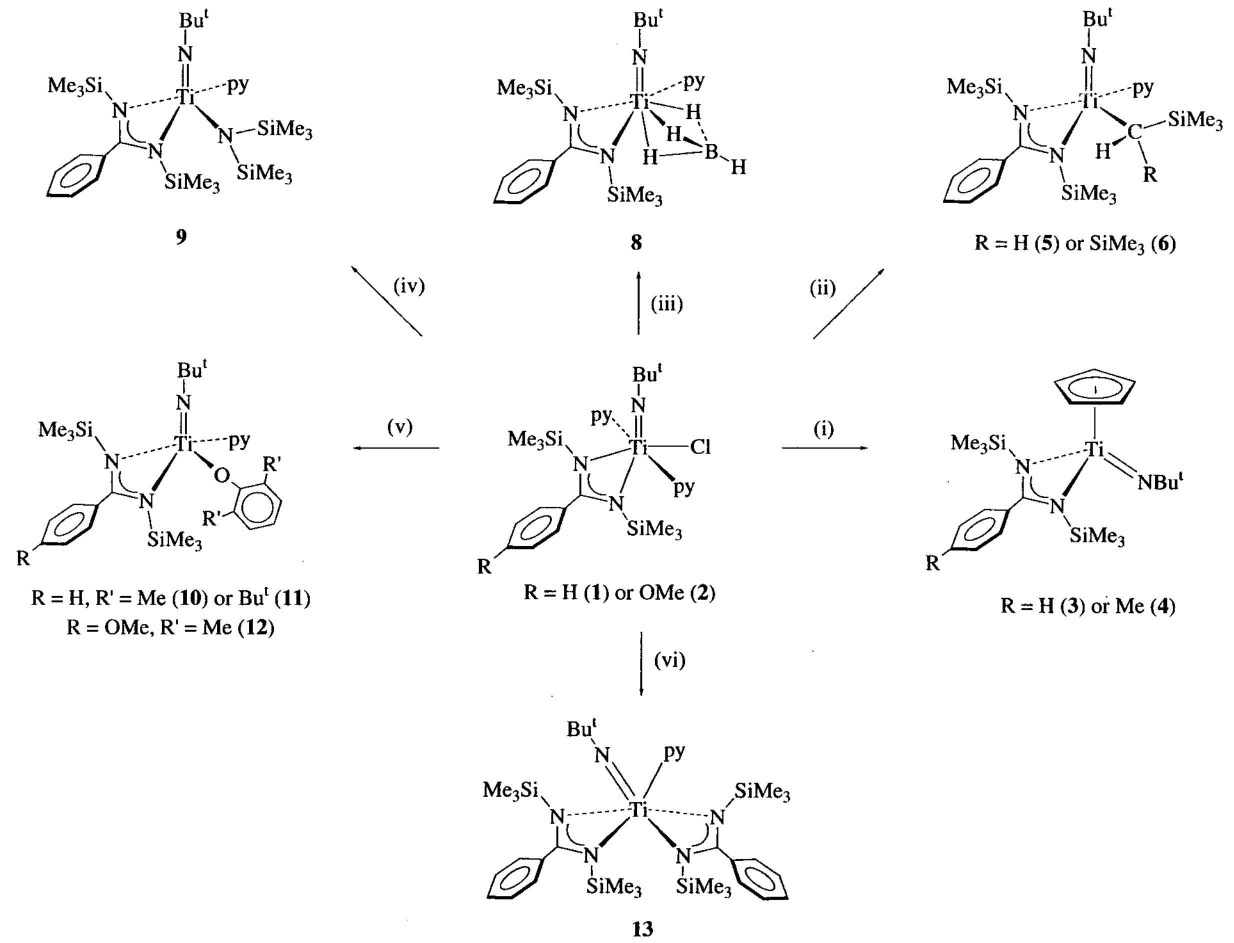
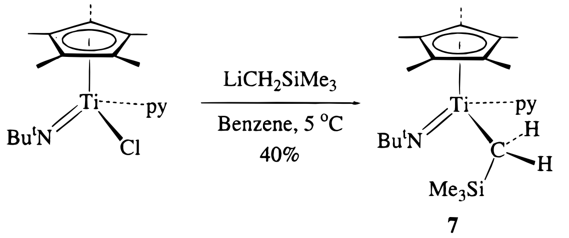
Scheme 1[a]



[a] Reagents and conditions: (i) LiC_5H_5, toluene, room temperature (for **3**) or 90 °C, 15−64 h, 68−95%; (ii) $LiCH_2SiMe_3$ or $LiCH(SiMe_3)_2$, benzene, 10 °C then room temperature, 3−19 h, 25−29%; (iii) $LiBH_4$ (9.5 equivs), toluene, room temperature, 72 h, 62%; (iv) $LiN(SiMe_3)_2{\cdot}OEt_2$, toluene, room temperature, 40 h, 91%; (v) LiO-2,6-$C_6H_3Me_2$ or LiO-2,6-$C_6H_3Bu^t{}_2$, benzene or toluene, 80−100 °C, 14−65 h, 55−93%; (vi) $LiPhC(NSiMe_3)_2$, toluene, 90 °C, 16 h, 94%.

Bu^t)(η-C_5Me_5)(CH_2SiMe_3)(py)] (**7**, see eq 2) from $LiCH_2SiMe_3$ and [Ti(NBu^t)(η-C_5Me_5)Cl(py)][29,41] in cold benzene. Cooling a saturated pentane solution of **7** to −80 °C for 48 h gave orange-brown, diffraction-quality crystals in 40% yield. The modest crystallized yields of **5**−**7** reflect the high solubility of these complexes in hydrocarbon solvents. When crude reaction mixtures were examined, or the reactions were carried out in C_6D_6 in NMR tubes, the yields were effectively quantitative and no other organometallic products were observed.



(2)

7

Complexes **5**−**7** are rare examples of group 4 terminal imido alkyl derivatives and the first to be structurally characterized.[4] Wolczanski was the first to report monomeric titanium imido alkyl complexes, namely [Ti($NSiBu^t{}_3$)($NHSiBu^t{}_3$)(R)(THF)] (R = Me or Bu^t (quite thermally unstable)).[42] σ-Bond hydrogenolysis of these complexes afforded the transient hydride [Ti($NSiBu^t{}_3$)($NHSiBu^t{}_3$)(H)(THF)] and ultimately [Ti_2(μ-$NSiBu^t{}_3$)$_2$($NHSiBu^t{}_3$)$_2$]. We were, therefore, interested in exploring the reactions of our alkyl complexes toward H_2. However, an NMR-scale hydrogenolysis of [Ti(NBu^t){$PhC(NSiMe_3)_2$}{$CH(SiMe_3)_2$}(py)] (**6**) in C_6D_6 gave extensive reduction and several products including Bu^tNH_2, $CH_2(SiMe_3)_2$, and pyridine. These reactions were therefore not pursued.

X-ray Structures of 5 and 7. Details of data collection, processing, and structure solution are given in Table 1 and the Experimental Section. To facilitate H-atom location,[43] X-ray data were collected at −123(2) °C.

A view of the molecular structure of [Ti(NBu^t){$PhC(NSiMe_3)_2$}(CH_2SiMe_3)(py)] (**5**) is shown in Figure 1, and important bond lengths and angles are listed in Table 2. Compound **5** has a five-coordinate

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(43) The location and refinement of H atoms in X-ray work is often difficult because the peaks due to H atoms in Fourier difference maps are typically of similar magnitude to the noise level.[53] Low-temperature data collection reduces thermal motion and can aid H atom treatment.

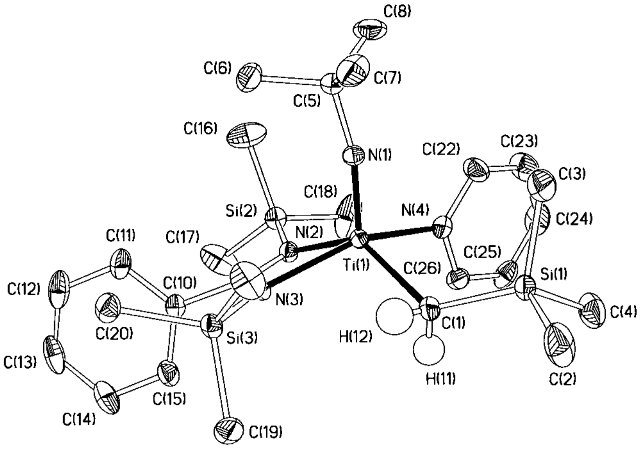

Figure 1. Displacement ellipsoid plot (30% probability) of [Ti(NBu^t){PhC(NSiMe$_3$)$_2$}(CH$_2$SiMe$_3$)(py)] (**5**). Hydrogen atoms except those of the methylene linkage of the CH$_2$-SiMe$_3$ ligand are omitted.

titanium (4+) center which possesses a distorted square-based pyramidal geometry, with the *tert*-butylimido ligand in the apical position. The titanium−imido nitrogen bond distance in **5** [Ti(1)−N(1) = 1.690(2) Å] lies in the middle of the range of values (ca. 1.67−1.73 Å) usually found for this linkage.[44,45] The angle subtended at the imido nitrogen atom [Ti(1)−N(1)−C(5)] is 168.0(2)°, and so the NBu^t ligand is capable of being a four-electron donor. The small benzamidinate ligand bite angle [N(2)−Ti(1)−N(3) = 63.74(8)°] is typical of this ligand,[5,6] although the Ti−N(amidinate) bond lengths are similar [Ti(1)−N(2) = 2.194(2) Å and Ti(1)−N(3) = 2.122(2) Å], the longer is trans to the (trimethylsilyl)methyl group, reflecting the stronger trans influence of this ligand. The Ti(1)−C(1) distance of 2.187(3) Å is just beyond the upper end of the range of Ti−C single bonds using this silylated alkyl ligand [range from 2.051(4) to 2.179(2) Å for six previous examples].[46−51] The α-hydrogen atoms of the methylene carbon were readily located from Fourier difference maps and positionally refined with individual isotropic displacement parameters. One of these hydrogen atoms has a significantly shorter distance to titanium [Ti(1)···H(12) = 2.38(4) Å] than the other [Ti(1)···H(11) = 2.54(3) Å]; the difference [0.09(5) Å] between the C(1)−H$_\alpha$ distances, however, is not significant.

Displacement ellipsoid plots of [Ti(NBu^t)(η-C$_5$Me$_5$)(CH$_2$SiMe$_3$)(py)] (**7**) are shown in Figure 2, and important bond lengths and angles are listed in Table 3. Compound **7** contains a titanium (4+) center which, if the pentamethylcyclopentadienyl ligand is thought of as occupying a single coordination site, can be considered to be four-coordinate. The Ti−alkyl carbon bond length [Ti(1)−C(1) = 2.167(2) Å] is slightly shorter than the corresponding distance of 2.187(3) Å in **5**. As for **5**, the methylene hydrogen atoms of the CH$_2$SiMe$_3$ ligand were located from Fourier difference syntheses and were positionally refined in an isotropic model; the Ti(1)···H(11) and Ti(1)···H(12) distances of 2.62(3) and 2.63(3) Å, respectively, are equivalent within estimated experimental error.

Spectroscopic Characterization of 5−7. The ^{1}H and ^{13}C NMR data for **5**−**7** (see Experimental Section) are broadly consistent with the structures proposed in Scheme 1 and eq 2 and the X-ray structure determinations. Assignments were confirmed by homo- and heteronuclear correlation and nOe experiments. We shall mention only those NMR data pertinent to the fluxional behavior and to probing any possible α-agostic interactions in these electron-deficient alkyl complexes (see also Discussion section below). In the IR spectra of complexes **5**−**7** there were no low-frequency ν(C−H) bands that could be indicative of agostic interactions.[52]

At room temperature, the SiMe$_3$ groups of the benzamidinate ligand in [Ti(NBu^t){PhC(NSiMe$_3$)$_2$}(CH$_2$-SiMe$_3$)(py)] (**5**) appeared as a broad resonance in toluene-d_8 solution. At −50 °C, these appear as two singlets and the chemically inequivalent methylene hydrogen atoms of the (trimethylsilyl)methyl group give rise to two mutually coupled, well-resolved doublets at 0.30 and 0.51 ppm with a geminal ^2J coupling constant of 11.4 Hz. The gated-decoupled ^{13}C NMR spectrum at this temperature shows an apparent triplet (formally a doublet of doublets) at δ 49.5 ppm for the methylene carbon with a $^1J_{CH}$ coupling constant of 104 Hz.

The alkyl methine carbon in **6** gave rise to a doublet (δ 52.9 ppm) with a $^1J_{CH}$ coupling constant of 93 Hz at −10 °C. For [Ti(NBu^t)(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)(py)] (**7**), the methylene hydrogens of the (trimethylsilyl)methyl ligand appeared as two mutually coupled doublets at 0.14 and 0.54 ppm with a geminal coupling constant of 10.9 Hz; the methylene carbon appeared as an apparent triplet at δ 42.4 ppm with a $^1J_{CH}$ coupling constant of 106 Hz.

Discussion of 5−7. Compounds **5**−**7** are rare examples of group 4 terminal imido-supported alkyl complexes and the first in this class to be structurally characterized. Transition-metal imido complexes with alkyl ligands are well-established for the subsequent triads.[4] The compounds have formal 14- (**5** or **6**) or 16- (**7**) valence electron counts for titanium, and this raises the possibility of Ti−H−C$_\alpha$ agostic[52] interactions. Well-established examples of α- and β-agostic alkyltitanium compounds, namely [TiCl$_3$Me(dmpe)] and [TiCl$_3$Et-(dmpe)] [dmpe = 1,2-bis(dimethylphosphino)ethane], respectively, were first reported by Green and coworkers.[53]

For **5**, the 14-valence electron count for titanium and the location of H(12) and Ti(1)···H(12) distance of 2.38(4) Å raises a priori the possibility of an α-agostic interac-

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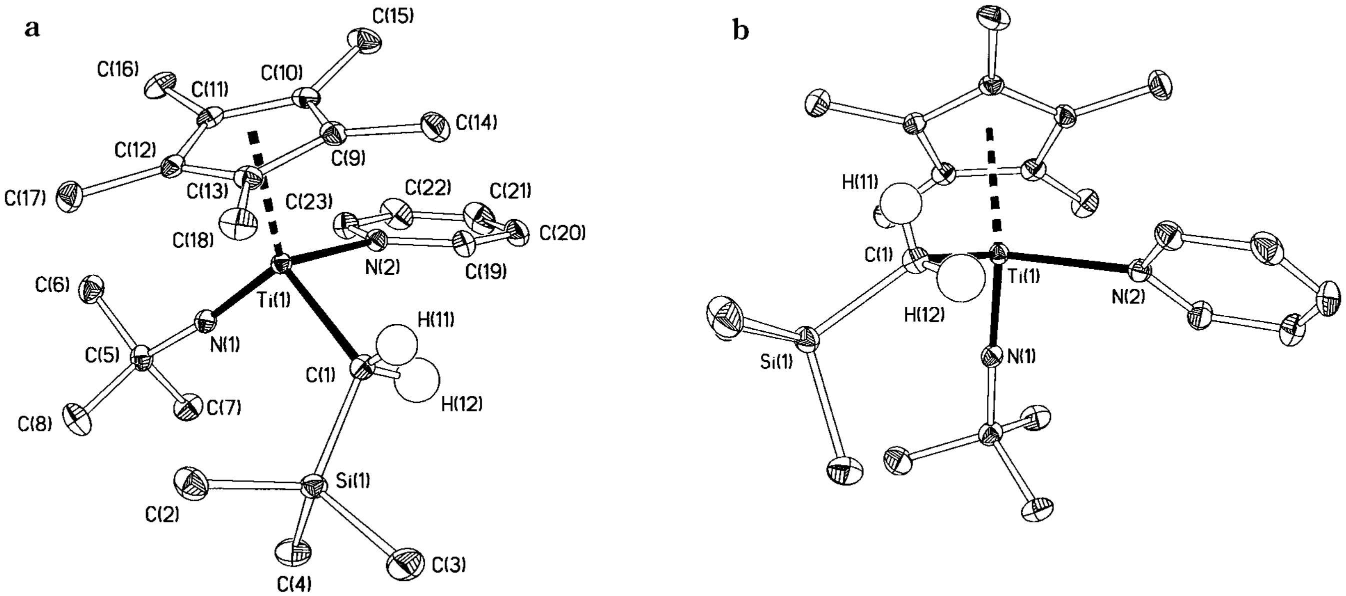

Figure 2. Two displacement ellipsoid plots (30% probability) of [Ti(NBu^t)(η-C$_5$Me$_5$)(CH$_2$SiMe$_3$)(py)] (**7**): (a) general view, (b) view showing the location of the methylene hydrogen atoms with respect to the Ti(NBu^t)(η-C$_5$Me$_5$) equatorial plane. Hydrogen atoms except those of the methylene linkage of the CH$_2$SiMe$_3$ ligand are omitted.

tion, since the Ti···H distance in the α-agostic complex [TiCl$_3$Me(dmpe] was 2.447(3) Å as determined by neutron diffraction at 20 K.[53] The other two Ti···H$_\alpha$ distances were 2.803(3) and 2.737(3) Å. Before consideration of the NMR data, it will be helpful to discuss the structure of [Ti(NBu^t)(η-C$_5$Me$_5$)(CH$_2$SiMe$_3$)(py)] (**7**, Figure 2).

Like **5**, compound **7** contains a CH$_2$SiMe$_3$ alkyl ligand bound to an apparently electron-deficient titanium center but in this case the X-ray structure does not reveal a sufficiently close Ti···H contact [Ti(1)···H(11) = 2.62(3), Ti(1)···H(12) = 2.63(3) Å] to suggest a significant α-agostic interaction. Furthermore, the C(1)−Ti(1)−N(2) angle of 98.25(8)° in **7** is very similar to that in the 16-electron chloride precursor [Ti(NBu^t)(η-C$_5$Me$_5$)Cl(py)] where the Cl−Ti−N(pyridine) angle is 97.3(1)°.[41] This implies, therefore, that the C(1)−Ti(1)−N(2) angle in **7** shows no tendency to open up to accommodate an α-agostic interaction. We conclude that there is no structural evidence for an α-agostic interaction in **7**.

The $^1J_{\mathrm{CH}}$ coupling contants for the alkyl α-carbons in **5** (104 Hz), **6** (93 Hz), and **7** (106 Hz) are significantly lower than those expected for normal C(sp^3)−H bonds (120−130 Hz) but do not necessarily imply α-agostic interactions. These low $^1J_{\mathrm{CH}}$ values are in fact most likely due to the bulky, electropositive SiMe$_3$ groups. In the authentic α-agostic complex [Y(η-C$_5$Me$_5$)$_2${CH(SiMe$_3$)$_2$}], for example, the methine α-carbon $^1J_{\mathrm{CH}}$ is 84.2 Hz, which is considerably lower than that of **6**.[54] The appearance of the methylene resonances as apparent triplets in the ^{13}C spectra of **5** and **7** (for which the methylene hydrogens are chemically inequivalent) suggests that the two $^1J_{\mathrm{CH}}$ coupling constants are identical. This in turn is consistent with neither α-hydrogen of the methylene group being strongly agostic. Although there could be a fast, dynamic "rocking" of the methylene (in-place or dissociative[55,56]) such that each α-hydrogen spends half of its time in an agostic interaction, this appears to be unlikely given the normal value for the observed $^1J_{\mathrm{CH}}$ in **5** and **7**.

In summary, the structural and NMR data for **7** militate against an agostic interaction. For complexes **5** and **6**, we suggest that neither has a strong agostic interaction. This may mean that the apparently close Ti···H contact in the solid state for **5** is simply a consequence of the inherent difficulty in accurately locating H atoms with X-ray data or alternatively that the agostic interaction is not sufficient to perturb the $^1J_{\mathrm{CH}}$ coupling constant. In this context we note that the authentic α-agostic interaction in [TiCl$_3$Me(dmpe)] did not lead to any detectable lowering of the averaged $^1J_{\mathrm{CH}}$ coupling constant.[53]

η^3-Borohydride Derivative. Reaction of [Ti(NBu^t){PhC(NSiMe$_3$)$_2$}Cl(py)$_2$] (**1**) with an excess of LiBH$_4$ in toluene for 72 h gave, after standard workup, the yellow, hexane-soluble borohydride complex [Ti(NBu^t){PhC(NSiMe$_3$)$_2$}(η^3-BH$_4$)(py)] (**8**) in 62% recrystallized yield.

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(62) Pyridine exchange via an equilibrium between **11** and **11**·py would be analogous to the well-characterized equilibrium between [Ti(NR){PhC(NSiMe$_3$)$_2$}Cl(py)$_2$] and [Ti(NR){PhC(NSiMe$_3$)$_2$}Cl(py)] + py as described in ref 17.

(63) The temperature at which the two benzamidinate SiMe$_3$ group resonances decoalesce (and hence any implications for the associated $\Delta G^\ddagger$ for exchange) will depend on their frequency separation ($\delta\nu$) in the slow-exchange limit.[36] For **9** and **11,** the slow-exchange ^{1}H NMR $\delta\nu$ is 186 and 204 Hz, respectively. It was not possible to measure $\delta\nu$ for **10** or **12**, but we feel that it is reasonable to assume that the values will be comparable to those of **9** and **11**.

To our knowledge, this is the first borohydride derivative of a group 4 imido complex.

The ^{1}H NMR spectrum of **8** at room temperature revealed resonances for fluxional benzamidinate (i.e., the $SiMe_3$ groups appear as a single sharp singlet), *tert*-butylimido, and pyridine groups, along with a broad 1:1:1:1 quartet ($^{1}J_{BH} = 86$ Hz) at 1.53 ppm which integrated as four ^{1}H atoms; this was assigned as a highly fluxional BH_4 ligand. These data do not distinguish between possible borohydride (i.e., η^1-, η^2-, or η^3-) ground-state coordination modes. Cooling the sample to −70 °C did not affect the borohydride or benzamidinate $SiMe_3$ resonances. The ^{11}B NMR spectrum at room temperature is a binomial quintet at −10.73 ppm with a $^{1}J_{BH}$ coupling of 86 Hz. This is consistent with the fast exchange of bridging and terminal BH_4 hydrogen atoms proposed to account for the ^{1}H NMR spectrum. The rapid exchange of bridging and terminal hydrogen atoms in such complexes is normal due to the small energy differences between bonding modes for the BH_4 ligand.[57] Although we were unable to obtain diffraction-quality crystals of **8**, the coordination mode of the BH_4 ligand could be elucidated from IR data.

Infrared spectroscopy can be useful in inferring the coordination mode of the BH_4 ligand.[58] In the solid state (Nujol mull), **8** gave rise to three IR bands in the B−H stretching region, namely a strong absorption at 2464 cm^{-1} assigned to $\nu(B-H_{terminal})$ and two weaker bands at 2208 and 2145 cm^{-1} assigned to $\nu(B-H_{bridging})$. The other ligands present in **8** do not give strong absorptions in this region. The solution infrared spectrum in hexane showed a $\nu(B-H_{terminal})$ absorption at 2493 cm^{-1} and two $\nu(B-H_{bridging})$ absorptions at 2205 and 2151 cm^{-1}, confirming that the coordination mode. The shift in the position of the $\nu(B-H_{terminal})$ absorption in solution is presumably due to matrix effects. This pattern of absorptions indicates a tridentate coordination mode;[58] the three bands may be designated as A_1 (terminal) and A_1 and E (bridging), respectively, if local C_{3v} symmetry for the $Ti(\mu\text{-}H)_3BH$ moiety is assumed. A bidentate tetrahydroborate ligand should give rise to two strong $\nu(B-H_{terminal})$ absorptions, as in the bis(*N,N'*-bis(trimethylsilyl)benzamidinato) titanium (+3) tetrahydroborate complex, $[Ti\{PhC(NSiMe_3)_2\}_2(\eta^2\text{-}BH_4)]$.[59]

Amide, Aryloxide, and Bis(*N,N'*-bis(trimethylsilyl)benzamidinate) Derivatives. Reaction of 1 equiv of $LiN(SiMe_3)_2{\cdot}Et_2O$ with $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}Cl(py)_2]$ (**1**) in toluene at room temperature afforded the amido complex $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}\{N(SiMe_3)_2\}(py)]$ (**9**) as an orange oil (Scheme 1), which could not be crystallized. The use of the less bulky $LiNMe_2$ led to a mixture of products. Reaction of 1 equiv of LiO-2,6-$C_6H_3Me_2$ with **1** in toluene at 90 °C followed by recrystallization from pentane at −80 °C afforded the aryloxide complex $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}(O\text{-}2,6\text{-}C_6H_3Me_2)(py)]$ (**10**) as an orange-brown solid in 55% yield. Analogous procedures gave $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}(O\text{-}2,6\text{-}C_6H_3Bu^t_2)(py)]$ (**11**) as a yellow solid in 84% yield. The *para*-methoxy-substituted benzamidinate derivative $[Ti(NBu^t)\{(4\text{-}C_6H_4OMe)C(NSiMe_3)_2\}(O\text{-}2,6\text{-}C_6H_3Me_2)(py)]$ (**12**) was also synthesized.

Reaction of 1 equiv of $LiPhC(NSiMe_3)_2$ with $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}Cl(py)_2]$ (**1**) in toluene at 90 °C followed by filtration and removal of volatiles afforded the pyridine adduct $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}_2(py)]$ (**13**) as an orange oil. The pyridine-free compound $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}_2]$ has been previously reported[60] and is not available via our route, which gives the pyridine adduct only. The new compound **13** is extremely soluble in hydrocarbon solvents and could not be crystallized; attempts to sublime **13** under high vacuum led to decomposition.

Complexes **9**−**13** are fluxional in solution on the NMR time scale. The NMR spectra for all four compounds show the expected resonances for pyridine, Bu^t, and benzamidinate phenyl groups. The ^{1}H NMR spectrum of **9** at room temperature contains additional broad resonances in the $SiMe_3$ region, indicating fluxionality of the amide and benzamidinate ligands. Cooling a $CDCl_3$ sample of **9** to −5 °C froze out these processes, and the spectra showed four separate resonances assignable to the two inequivalent $SiMe_3$ groups of the benzamidinate ligand and to the two inequivalent $SiMe_3$ groups of the bis(trimethylsilyl)amide ligand.

The *ortho*-substituted aryloxide derivatives **9**−**12** are also fluxional. At room temperature, the NMR spectra of **10** and **12** showed one resonance for the chemically inequivalent benzamidinate $SiMe_3$ groups and one resonance for the *ortho*-methyl groups, consistent with fluxional behavior of the two types of ligand on the NMR time scale. Cooling a $CDCl_3$ sample of **10** caused the signal for $SiMe_3$ to broaden substantially but not to decoalesce; likewise, only one relatively sharp *ortho*-methyl group singlet was observed at low temperature. For the considerably more sterically crowded complex **11**, the room-temperature NMR spectra show four broad resonances for the two benzamidinate $SiMe_3$ and two phenoxide *ortho*-*tert*-butyl groups and the exchange processes are completely frozen out at ca. −10 °C. We have studied the dynamic behavior of **11** by variable-temperature ^{1}H NMR line shape analysis for the exchanging $SiMe_3$ and *ortho*-Bu^t resonances. Further details are provided in the Experimental Section; excess line widths, rate constants, and activation parameters (derived from standard Eyring plots provided in the Supporting Information) for $SiMe_3$ and *ortho*-Bu^t exchange are listed in Table 4.

The striking similarity of the two sets of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G_{278}{}^{\ddagger}$ activation parameters in Table 4 suggest that $SiMe_3$ group exchange and Bu^t group exchange are concerted processes and share a common transition state. The $\Delta G_{278}{}^{\ddagger}$ values of ca. 63 kJ mol^{-1} are within the range found previously for $SiMe_3$ exchange in fluxional benzamidinate complexes.[8,61] The line widths of the $SiMe_3$ and Bu^t resonances were unaffected by addition of ca. 1.5 equiv of free pyridine to a $CDCl_3$ sample of **11** at room temperature (although a slight broadening of the coordinated pyridine resonances was observed, possibly due a separate *associative* exchange process for the pyridine molecules[62]). It is, therefore, likely that the $SiMe_3$ and Bu^t exchange process does not involve loss of pyridine in the rate-determining step.

Simple aryl ring rotation about the $O-C_{ipso}$ bond axis provides an adequate mechanism for the *tert*-butyl group exchange in **15**. For the $SiMe_3$ group exchange, at least two mechanisms are possible. These include either a process involving in-place rotation of the benzamidinate ligand about the $Ti{\cdots}C(N_2)$ axis[8] or one in which a nitrogen atom of the benzamidinate ligand dissociates (partially or entirely) to facilitate exchange, as proposed previously by Edelmann.[61] The latter (dissociatively activated) possibility is better supported by the large positive values of $\Delta S^{\ddagger}$ and would also be consistent with the large value for $\Delta H^{\ddagger}$, as such a process would involve bond-breaking in the transition state.

In conclusion, it appears that the correlated $SiMe_3$ and Bu^t group exchange processes in **11** involve some degree of Ti−N(benzamidinate) bond cleavage to give a four-coordinate intermediate or transition state by which exchange occurs. In the absence of activation parameter data, it is not possible to identify the type of process involved in exchanging the benzamidinate ligand $SiMe_3$ groups in **9**, **10**, or **12**. However, it is likely that the readily frozen out exchange in the bis(trimethylsilyl)amido complex **9** also involves some degree of Ti−N(benzamidinate) bond cleavage.[63] In **10** and **12**, the $SiMe_3$ group exchange activation energy appears to be much lower[63] so a mechanism involving in-place benzamidinate ligand rotation about the Ti···$C(N_2)$ axis may be the more probable and the $SiMe_3$ and aryloxide *ortho*-Me group exchange processes may or may not be correlated.

Summary and Conclusions

We have shown that the unusual amidinate−imide ligand set can support a range of titanium substitution chemistry leading to new complexes, including cyclopentadienyl, alkyl, borohydride, amide, and aryloxide derivatives. There was no evidence for competing redox chemistry or amidinate or imide ligand-centered reactions (such as have been found in certain Schiff-base-supported titanium alkyl complexes[64]). Neither the 14-electron $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}\{CH(R)SiMe_3\}(py)]$ (R = H or $SiMe_3$) nor the 16-electron $[Ti(NBu^t)(\eta\text{-}C_5Me_5)\{CH_2SiMe_3\}(py)]$ show conclusive evidence for an α-agostic C−H−Ti interaction. The fluxional processes in the amide and aryloxide have been examined and suggest that two types of mechanism (dissociative and nondissociative) may be possible depending on the steric constraints.

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Supporting Information Available: Eyring plots for **11** (2 pages). X-ray crystallographic files, in CIF format, for **5** and **7** are available on the Internet only. Ordering and access information is given on any current masthead page.

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