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 $[Ti(NBu^t){(4-C_6H_4R)C(NSiMe_3)_2}Cl(py)_2]$ (R = H (1) or OMe (2)) are described. Thus, reaction of 1 or 2 with LiC_5H_5 gave the half-sandwich compounds $[Ti(NBu^{t}){(4-C_{6}H_{4}R)C(NSiMe_{3})_{2}}(\eta-C_{5}H_{5})]$ (R = H (**3**) or OMe (**4**)). Reaction of **1** with LiCH₂-SiMe₃ or LiCH(SiMe₃)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 SiMe₃ (6)). For comparative purposes, the 16-electron half-sandwich imido–alkyl complex [Ti(NBu^t)(η - $C_5Me_5)(CH_2SiMe_3)(py)$] (7) was prepared from LiCH₂SiMe₃ and [Ti(NBu^t)(η -C₅Me₅)Cl(py)]. Reaction of **1** with LiBH₄ gave the η^3 -borohydride derivative [Ti(NBu^t){PhC(NSiMe₃)₂}(η^3 - BH_4 (py)] (8), while treatment of 1 with LiN(SiMe_3)₂, LiO-2,6-C₆H₃R₂ (R = Me or Bu^t), or LiPhC(NSiMe₃)₂ gave the corresponding aryloxide, amide, or bis(benzamidinate) titanium imido complexes [Ti(NBu^t){PhC(NSiMe₃)₂}{N(SiMe₃)₂}(py)] (9), [Ti(NBu^t){PhC(NSiMe₃)₂}- $(O-2,6-C_6H_3R_2)(py)$] (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)5-15groups 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-C₆H₃Me₂ and 2,6-C₆H₃Prⁱ₂).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

^{*} 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. (1) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

⁽²⁾ Chisholm, M. H.; Rothwell, I. P. In Comprehensive Coordination *Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 2, p 162.

⁽³⁾ Nugent, W. A.; Mayer, J. M. Metal-Ligand Multiple Bonds; Wiley-Interscience: New York, 1988.

 ⁽⁴⁾ Wigley, D. E. Prog. Inorg. Chem. 1994, 42, 239.
 (5) Edelmann, F. T. Coord. Chem. Rev. 1994, 137, 403.

⁽⁶⁾ Barker, J.; Kilner, M. Coord. Chem. Rev. 1994, 133, 219.

⁽⁷⁾ Gómez, R.; Duchateau, R.; Chernega, A. N.; Meetsma, A.; Edelmann, F. T.; Teuben, J. H.; Green, M. L. H. *J. Chem. Soc., Dalton* Trans. 1995, 217.

⁽⁸⁾ Duchateau, R.; van Wee, C. T.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. Organometallics 1996, 15, 2279.
(9) Duchateau, R.; van Wee, C. T.; Teuben, J. H. Organometallics

^{1996, 15, 2291.}

⁽¹⁰⁾ Hagadorn, J. R.; Arnold, J. J. Chem. Soc., Dalton Trans. 1997, 3087.

⁽¹¹⁾ Hagadorn, J. R.; Arnold, J. Inorg. Chem. 1997, 36, 2928.

 ⁽¹²⁾ Hagadorn, J. R.; Arnold, J. J. Am. Chem. Soc. 1996, 118, 893.
 (13) Hao, S.; Feghali, K.; Gambarotta, S. Inorg. Chem. 1997, 36, 1745.

⁽¹⁴⁾ Cotton, F. A.; Matonic, J. H.; Murillo, C. A. J. Am. Chem. Soc. 1997, 119, 7889.

⁽¹⁵⁾ Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Wang, X. P. Inorg. Chem. 1997, 36, 896.

⁽¹⁶⁾ Mountford, P. Chem. Commun. 1997, 2127 (Review Feature Article). Wilson, P. J.; Blake, A. J.; Mountford, P.; Schröder, M. Chem. *Commun.* **1998**, 1007. Blake, A. J.; Dunn, S. C.; Green, J. C.; Jones, N. M.; Moody, A. G.; Mountford, P. *Chem. Commun.* **1998**, 1235.

⁽¹⁷⁾ Stewart, P. J.; Blake, A. J.; Mountford, P. Inorg. Chem. 1997, 36, 3616.

⁽¹⁸⁾ Ribeiro da Costa, M. H.; Avilez, M. T.; Teuben, J. H. Unpublished results cited in ref 5.

⁽¹⁹⁾ Stewart, P. J.; Blake, A. J.; Mountford, P. Inorg. Chem. 1997, 36. 1982.

⁽²⁰⁾ Dawson, D. Y.; Arnold, J. Organometallics **1997**, *16*, 1111. (21) Bochmann, M. In Comprehensive Organometallic Chemistry IF, Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: New York, 1995; Vol. 4, p 273.

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. CDCl₃ was dried over freshly ground calcium hydride at room temperature, C₆D₆ was dried over molten potassium, and C₆D₅CD₃ 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, ¹³C, and ¹¹B NMR spectra were recorded on a Bruker DPX 300 spectrometer. ¹H and ¹³C spectra were referenced internally to residual protio solvent (¹H) or solvent (¹³C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). The ¹¹B spectrum was referenced externally to BF₃ 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, oneand 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. $Li(4-C_6H_4R)C(NSiMe_3)_2$ (R = H or OMe),^{23,24} LiCH₂SiMe₃,²⁵ LiCH(SiMe₃)₂,²⁶ LiN(SiMe₃). OEt_2 ,²⁷ [Ti(NBu^t){PhC(NSiMe_3)₂}Cl(py)₂] (1),¹⁷ [Ti(NBu^t)-Cl₂(py)₃],²⁸ [Ti(NBu^t)(η^{5} -C₅Me₅)Cl(py)],²⁹ and LiO-2,6-C₆H₃R₂ $(R = Me \text{ or } Bu^{t})^{30}$ were prepared according to literature methods. LiC₅H₅ was prepared from *n*-butyllithium and freshly cracked C5H6 in cold hexanes.

[Ti(NBu^t){(4-C₆H₄OMe)C(NSiMe₃)₂}Cl(py)₂] (2). A solution of Li(4-C₆H₄OMe)C(NSiMe₃)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 \times 10 mL) and dried in vacuo. Yield: 0.74 g (54%).

Characterization data for 3. ¹H NMR (CDCl₃, 300.1 MHz, -15 °C): 9.37 (d, J = 5.0 Hz, 4 H, ortho-NC₅H₅), 7.89 (t, J =7.6 Hz, 2 H, *para*-NC₅ H_5), 7.48 (apparent t, apparent J = 6.9Hz, 4 H, meta-NC₅ H_5), 6.75 (s, 4 H, ortho- and meta-C₆ H_4), 3.79 (s, 3 H, OMe), 0.94 (s, 9 H, NBu'), -0.17 (s, 9 H, SiMe₃), -0.48 (s, 9 H, SiMe₃). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz, -15 °C): 178.9 (C₆H₄*C*N₂), 158.5 (*ipso*-C₆H₄), 151.0 (*ortho*-NC₅H₅), 137.9 (para-N C_5 H₅), 135.4 (para- C_6 H₄), 126.6 (ortho- C_6 H₄),

(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

(27) Wannagat, U.; Niederprum, H. *Chem. Ber.* **1961**, *94*, 1540.
 (28) Blake, A. J.; Collier, P. E.; Dunn, S. C.; Li, W.-S.; Mountford, P.; Shishkin, O. V. *J. Chem. Soc., Dalton Trans.* **1997**, 1549.

(29) Dunn, S. C.; Mountford, P.; Robson, D. A. J. Chem. Soc., Dalton Trans. 1997, 293.

(30) Collier, P. E.; Blake, A. J.; Mountford, P. J. Chem. Soc., Dalton Trans. 1997, 2911.

123.6 (meta-N C_5H_5), 112.5 (meta- C_6H_4), 67.7 (N CMe_3), 55.0 (OMe), 31.0 $(NCMe_3)$, 2.6, 1.7 $(2 \times SiMe_3)$. 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 C₂₈H₄₄ClN₅OSi₂Ti): C, 55.4 (55.5); H, 7.4 (7.3); N, 11.5 (11.6)

¹H NMR data for **2**' (CDCl₃, 300.1 MHz, 0 °C): 8.95 (d, J =4.5 Hz, 2 H, ortho-NC₅H₅), 7.94 (t, J = 7.4 Hz, 1 H, para-NC₅ H_5), 7.57 (apparent t, apparent J = 6.3 Hz, 2 H, *meta*-NC₅H₃), 7.16 (d, J = 8.2 Hz, 2 H, C₆H₄), 6.89 (d, J = 8.3 Hz, 2 H, C₆H₄), 3.85 (s, 3 H, OMe), 1.14 (s, 9 H, NBu⁴), -0.24 (s, 18 H, Si*Me₃*).

 $[Ti(NBu^t){PhC(NSiMe_3)_2}(\eta - C_5H_5)] (3).$ An orange solution of LiC₅H₅ (0.035 g, 0.48 mmol) and [Ti(NBu^t){PhC-(NSiMe₃)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 $(2 \times 5 \text{ mL})$ and dried in vacuo. Yield: 0.145 g (68%).

¹H NMR (CDCl₃, 300.1 MHz, 25 °C): 7.38 (m, 3 H, orthoand para-C₆H₅), 7.24 (m, 2 H, meta-C₆H₅), 6.39 (s, 5 H, C₅H₅), 0.99 (s, 9 H, NBu^t), -0.16 (s, 18 H, SiMe₃). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz, 25 °C): 169.0 (C₆H₅CN₂), 139.5 (*ipso-C*₆H₅), 128.3, 127.9, 127.1 (*ortho-*, *meta-* and *para-C*₆H₅), 110.5 (C₅H₅), 67.0 (NCMe3), 32.2 (NCMe3), 1.7 (SiMe3). 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).

 $[Ti(NBu^{t}){(4-C_{6}H_{4}OMe)C(NSiMe_{3})_{2}}(\eta-C_{5}H_{5})]$ (4). A mixture of LiC₅H₅ (0.007 g, 0.97 mmol) and [Ti(NBu^t){(4-C₆H₄-OMe)C(NSiMe₃)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 (CDCl₃, 300.1 MHz, 298 K): 7.16 (d, J = 8.7 Hz, 2 H, C₆H₄), 6.90 (d, J = 8.7 Hz, 2 H, C₆H₄), 6.37 (s, 5 H, C₅H₅), 3.86 (s, 3 H, OMe), 0.98 (s, 9 H, NBul), -0.15 (s, 18 H, SiMe₃). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz, 298 K): 169.5 (C₆H₄*C*N₂), 159.7 (ipso-C₆H₄), 132.0 (para-C₆H₄), 128.4 (ortho-C₆H₄), 113.3 $(meta-C_6H_4)$, 110.5 (C_5H_5) , 66.9 $(NCMe_3)$, 55.3 (OMe), 32.2 (NCMe3), 1.8 (SiMe3). 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(NSiMe₃)₂}(CH₂SiMe₃)(py)] (5). Cold benzene (40 mL) was added to a mixture of $[Ti(NBu^t){PhC-}$ $(NSiMe_3)_2 \} Cl(py)_2] \ (1.117 \ g, \ 1.94 \ mmol) \ and \ LiCH_2 SiMe_3 \ (0.183 \ mmol) \ 0.183 \ mmol)$ 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 = 4.5Hz, 2 H, ortho-NC₅H₅), 7.20 (br s, 2 H, ortho-C₆H₅), 6.95 (m, 3 H, meta- and para-C₆H₅), 6.58 (t, ${}^{3}J = 7.7$ Hz, 1 H, para- NC_5H_5), 6.35 (apparent t, apparent J = 6.7 Hz, 2 H, meta-

⁽²³⁾ Wedler, M.; Knösel, F.; Noltemeyer, M.; Edelmann, F. T.; Behrens, U. J. Organomet. Chem. **1990**, 388, 21.

⁽²⁴⁾ Boeré, R. T.; Oakley, R. T.; Reed, R. W. J. Organomet. Chem. 1987, 331, 161.

 ⁽²⁵⁾ Tessier-Youngs, C.; Beachley, O. T. *Inorg. Synth.* 1986, 24, 95.
 (26) Davidson, P. J.; Harris, D. H.; Lappert, M. F. J. Chem. Soc., Dalton Trans. 1976, 2268.

NC₅H₅), 1.52 (s, 9 H, NBu^t), 0.51 (d, ${}^{2}J = 11.4$ Hz, 1 H, $CH_aH_bSiMe_3$), 0.30 (d, $^2J = 11.4$ Hz, 1 H, $CH_aH_bSiMe_3$), 0.25 (s, 9 H, CH₂SiMe₃), 0.22 and -0.47 [2 \times br s, 2 \times 9 H, 2 \times PhC(NSiMe₃)₂]. ¹³C{¹H} NMR (C₆D₅CD₃, 75.5 MHz, -50 °C): 181.1 (C₆H₅CN₂), 151.9 (ortho-NC₅H₅), 141.3 (ipso-C₆H₅), 138.3 (para-NC5H5), 128.4, 128.1, 127.2 (ortho-, meta-, and para- C_6H_5), 124.3 (meta-N C_5H_5), 69.2 (NCMe₃), 49.5 (d of d, ¹ $J_{CH(a)}$ $= {}^{1}J_{CH(b)} = 104 \text{ Hz}, CH_{2}SiMe_{3}), 33.5 (NCMe_{3}), 3.7 (CH_{2}SiMe_{3}),$ 2.7 [2 × PhC(NSiMe₃)₂]. Note: ¹J for the δ 49.5 CH₂SiMe₃ resonance was obtained from a gated-coupled ¹³C 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 C₂₆H₄₈N₄Si₃Ti): C, 55.9 (56.9); H, 9.0 (8.8); N, 10.0 (10.2).

[Ti(NBu^t){PhC(NSiMe₃)₂}{CH(SiMe₃)₂}(py)] (6). Cold benzene (30 mL) was added to a mixture of [Ti(NBu^t){PhC-(NSiMe₃)₂}Cl(py)₂] (0.255 g, 0.44 mmol) and LiCH(SiMe₃)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%).

¹H NMR (C₆D₅CD₃, 300.1 MHz, -10 °C): 9.01 (br s, 2 H, ortho-NC5H5), 7.30 (m, 2 H, ortho-C6H5), 6.95 (m, 3 H, metaand para-C₆H₅), 6.63 (t, J = 7.8 Hz, 1 H, para-NC₅H₅), 6.45 (apparent t, apparent J = 6.7 Hz, 2 H, meta-NC₅H₅), 1.46 (s, 9 H, NBu⁴), 0.34 [s, 18 H, CH(SiMe₃)₂], 0.25 [s, 9 H, PhC-(NSiMe3)(NSiMe3)], -0.24 [s, 1 H, CH(SiMe3)2], -0.49 [s, 9 H, PhC(NSiMe₃)(NSiMe₃)]. ¹³C{¹H} NMR (C₆D₅CD₃, 75.5 MHz, -10 °C): 181.2 (C₆H₅CN₂), 152.6 (ortho-NC₅H₅), 141.1 (ipso-*C*₆H₅), 138.8 (*para*-N*C*₅H₅), 124.2 (*meta*-N*C*₅H₅), 69.9 (N*C*Me₃), 52.9 [d, ${}^{1}J_{CH} = 94$ Hz, $CH(SiMe_3)_2$], 33.0 (NCMe₃), 5.2 [CH(SiMe3)(SiMe3)], 4.4 [CH(SiMe3)(SiMe3)], 3.4 [PhC(NSiMe3)-(NSiMe₃)], 2.3 [PhC(NSiMe₃)(NSiMe₃)]. Note: ${}^{1}J$ for the δ 52.9CH(SiMe₃)₂ resonance was obtained from a gated-coupled ¹³C NMR spectrum of **6** in the same solvent and at the same temperature; the *ortho-*, *meta-* and *para-C* $_{\theta}$ H₅ 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 C₂₉H₅₆N₄Si₄Ti): C, 54.6 (56.1); H, 9.0 (9.1); N, 8.9 (9.0).

[Ti(NBu^t)(η -C₅Me₅)(CH₂SiMe₃)(py)**]** (7). Cold benzene (20 mL) was added to a mixture of [Ti(NBu^t)(η -C₅Me₅)Cl(py)] (0.399 g, 1.08 mmol) and LiCH₂SiMe₃ (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%).

¹H NMR (C₆D₆, 300.1 MHz, 25 °C): 8.14 (d, J = 4.8 Hz, 2 H, ortho-NC₅ H_5), 6.68 (t of t, ${}^{3}J = 7.7$ Hz, ${}^{4}J = 1.6$ Hz, 1 H, para-NC₅ H_5), 6.37 (apparent t, apparent J = 7.0 Hz, 2 H, meta-NC₅H₅), 1.94 (s, 15 H, C₅Me₅), 1.43 (s, 9 H, NBu^t), 0.54 (d, ²J = 10.9 Hz, 1 H, $CH_aH_bSiMe_3$), 0.37 (s, 9 H, $SiMe_3$), 0.14 (d, ²J = 10.9 Hz, 1 H, $CH_aH_bSiMe_3$). ¹³C{¹H} NMR (C₆D₆, 75.5 MHz, 25 °C): 150.5 (ortho-NC5H5), 137.9 (para-NC5H5), 123.8 (meta- NC_5H_5 , 117.1 (C_5Me_5), 66.9 ($NCMe_3$), 42.4 (d of d, ${}^1J_{CH(a)} =$ ${}^{1}J_{CH(b)} = 106$ Hz, CH_2SiMe_3), 33.6 (NCMe₃), 12.1 (C₅Me₅), 4.3 (SiMe₃). Note:¹J for the δ 42.4 CH₂SiMe₃ resonance was obtained from a gated-coupled ¹³C 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 $C_{23}H_{40}N_2SiTi$): C, 65.7 (65.7); H, 9.8 (9.6); N, 6.7 (6.7).

NMR-Scale Hydrogenolysis of [Ti(NBu'){PhC-(NSiMe_3)_2}{CH(SiMe_3)_2}(py)] (6). A solution of [Ti(NBu')-{PhC(NSiMe_3)_2}{CH(SiMe_3)_2}(py)] (10.7 mg, 0.017 mmol) in C_6D_6 (1.0 mL) was placed under 9.2 bar pressure of H₂ gas in a Fisher–Porter bottle at room temperature. After the orangebrown solution was stirred for 16 h, it became a very pale yellow. NMR analysis showed the formation of several products including Bu'NH₂, CH₂(SiMe₃)₂, and pyridine.

[Ti(NBu^t){PhC(NSiMe₃)₂}(\eta^3-BH₄)(py)**] (8).** An orange mixture of [Ti(NBu^t){PhC(NSiMe₃)₂}Cl(py)₂] (0.334 g, 0.58 mmol) and an excess of LiBH₄ (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%).

¹H NMR (C₆D₅CD₃, 300.1 MHz, 25 °C): 8.60 (d, J = 4.5 Hz, 2 H, ortho-NC₅H₅), 7.20 (m, 2 H, meta-C₆H₅), 6.99 (m, 3 H, ortho- and para-C₆H₅), 6.69 (t, ${}^{3}J = 7.3$ Hz, 1 H, para-NC₅H₅), 6.43 (apparent t, apparent J = 5.9 Hz, 2 H, meta-NC₅H₅), 1.53 $(1:1:1:1 \text{ quart}, {}^{1}J_{BH} = 86 \text{ Hz}, 4 \text{ H}, BH_{4}), 1.33 \text{ (s, 9 H, NBu}),$ -0.08 (s, 18 H, NSiMe₃). ¹³C{¹H} NMR (C₆D₅CD₃, 75.5 MHz, -30 °C): 179.7 (C₆H₅CN₂), 151.0 (ortho-NC₅H₅), 141.8 (ipso-C₆H₅), 138.2 (para-NC₅H₅), 128.4 (para-C₆H₅), 128.0 (ortho- C_6H_5), 127.0 (meta- C_6H_5), 124.1 (meta-N C_5H_5), 69.7 (N CMe_3), 32.4 (NCMe₃), 2.5 (2 × PhC(NSiMe₃)₂). ¹¹B NMR (C₆H₆, 96.3 MHz, 25 °C): -10.7 (quint, ${}^{1}J = 86$ Hz). IR (KBr plates, Nujol mull): 2464 (s) ν (B–H_{terminal}), 2208 (m) and 2145 (m) ν (B– H_{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_{terminal}), 2205 (m) and 2151 (w) ν (B-H_{bridging}) cm⁻¹. Anal. Found (calcd for C₂₂H₄₁BN₄Si₂-Ti): C, 54.7 (55.5); H, 8.9 (8.7); N, 11.7 (11.8).

[Ti(NBu^t){PhC(NSiMe₃)₂}{N(SiMe₃)₂}(py)] (9). A solution of LiN(SiMe₃)₂·OEt₂ (0.419 g, 1.81 mmol) in toluene (15 mL) was added over 5 min to a stirred solution of [Ti(NBu^t)-{PhC(NSiMe₃)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%).

¹H NMR (CDCl₃, 300.1 MHz, -5 °C): 9.07 (br s, 2 H, *ortho* NC₅*H_s*), 7.90 (t of t, ³*J* = 7.7 Hz, ⁴*J* = 1.6 Hz, 1 H, *para*-NC₅*H_s*), 7.59 (overlapping m, 2 H, *meta*-NC₅*H_s*), 7.36 (m, 4 H, *ortho* and *meta*-C₆*H_s*), 7.15 (m, 1 H, *para*-C₆*H_s*), 1.18 (s, 9 H, N*Bu*⁴), 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]. ¹³C{¹H} NMR (CDCl₃, 75.5 MHz, -5 °C): 180.0 (C₆H₅CN₂), 152.7 (*ortho*-N*C*₅H₅), 141.5 (*ipso C*₆H₅), 138.5 (*para*-N*C*₃H₅), 128.0, 127.7, 127.6, 127.0 (*ortho* and *meta*-*C*₆H₅), 126.3 (*para*-*C*₆H₅), 124.0 (*meta*-N*C*₅H₅), 69.5 (N*C*Me₃), 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(NSiMe₃)₂}(O-2,6-C₆H₃Me₂)(py)] (10). A mixture of [Ti(NBu^t){PhC(NSiMe₃)₂}Cl(py)₂] (0.200 g, 0.35 mmol) and LiO-2,6-C₆H₃Me₂ (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%).

¹H NMR (CDCl₃, 300.1 MHz, 25 °C): 8.88 (br m, 2 H, *ortho*-NC₅*H₅*), 7.84 (t, J = 7.6 Hz, 1 H, *para*-NC₅*H₅*), 7.43 (apparent t, apparent J = 7.3 Hz, 2 H, *meta*-NC₅*H₅*), 7.37 (m, 3 H, *ortho*-and *para*-C₆*H₅*), 7.29 (m, 2 H, *meta*-C₆*H₅*), 6.90 (d, J = 7.4 Hz,

		U - · · ·
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	P1 (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)
Ζ	2	4
density (calcd)/Mg m ⁻³	1.11	1.14
abs coeff/mm ⁻¹	0.38	0.40
<i>F</i> (000)	592	912
cryst description	vellow block	orange cuboid
cryst size/mm	$0.48 \times 0.42 \times 0.40$	$0.51 \times 0.44 \times 0.42$
θ range for data collection/deg	2.54-25.01	2.60 - 25.05
scan type	$\omega - \theta$ with learnt profile	() ()
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 refins collected	5995	8276
no. of indep reflns	5517	4312
<i>R</i> (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	Chebychey polynomial	Chebychey 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)	$R_1 = 0.0659, wR_2 = 0.0797$	$R_1 = 0.0550$, w $R_2 = 0.0583$
goodness-of-fit	$1.105 \text{ (on } F^2)$	$1.115 (\text{on } F^2)$
final $(\Lambda/\sigma)_{max}$	0.03	0.04
largest residual peaks/e $Å^{-3}$	0.70 and -0.46	0.49 and -0.41
Sest residual peaks of r	00 414 0.10	orio data Vill

Table 1. X-ray Data Collection and Processing Parameters for $[Ti(NBu^{t}){PhC(NSiMe_3)_2}(CH_2SiMe_3)(py)]$ (5) and $[Ti(NBu^{t})(\eta - C_5Me_5)(CH_2SiMe_3)(py)]$ (7)

^a $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$; $wR_2 = \sqrt{\{\sum w(F_0^2 - F_c^2)^2 / \sum (w(F_0^2)^2)\}}$.

2 H, meta-O-2,6-C₆H₃Me₂), 6.52 (t, J = 7.4 Hz, 1 H, para-O-2,6-C₆H₃Me₂), 2.26 (s, 6 H, O-2,6-C₆H₃Me₂), 1.17 (s, 9 H, NBu^t), -0.30 (s, 18 H, SiMe₃). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz, 25 °C): 179.3 (C₆H₅CN₂), 161.6 (ipso-O-2,6-C₆H₃Me₂), 151.6 (ortho-NC5H5), 141.5 (ipso-C6H5), 138.7 (para-NC5H5), 128.2, 127.8, 127.5 (ortho-, meta-, and para-C₆H₅), 126.9 (meta-O-2,6-C₆H₃-Me₂), 126.5 (ortho-O-2,6-C₆H₃Me₂), 124.4 (meta-NC₅H₅), 116.5 (para-O-2,6-C₆H₃Me₂), 68.8 (NCMe₃), 32.7 (NCMe₃), 17.5 (O-2,6-C₆H₃Me₂), 1.9 (SiMe₃). 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 $C_{30}H_{46}N_{4}$ -OSi₂Ti): C, 60.2 (61.8); H, 8.1 (8.0); N, 9.2 (9.6).

[Ti(NBu^t){PhC(NSiMe₃)₂}(O-2,6-C₆H₃Bu^t₂)(py)] (11). A mixture of [Ti(NBu^t){PhC(NSiMe₃)₂}Cl(py)₂] (0.303 g, 0.53 mmol) and LiO-2,6-C₆H₃Bu^t₂ (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%).

¹H NMR (CDCl₃, 300.1 MHz, 25 °C): 8.87 (br m, 2 H, *ortho*-NC₅*H*₅), 7.79 (t, J = 7.6 Hz, 1 H, *para*-NC₅*H*₅), 7.44 (br m, 4 H, C₆*H*₅), 7.34 (apparent t, apparent J = 7.0 Hz, 2 H, *meta*-NC₅*H*₅), 7.23 (d, J = 7.8 Hz, 2 H, *meta*-O-2,6-C₆*H*₃Me₂), 7.21 (br s, 1 H, C₆*H*₅), 6.69 (t, J = 7.8 Hz, 1 H, *para*-O-2,6-C₆*H*₃-

Me₂), 1.55 and 1.28 (2 \times br s, 2 \times 9 H, 2 \times O-2,6-C₆H₃Bu⁴), 1.13 (s, 9 H, NBu^t), 0.05 and -0.63 (2 \times br s, 2 \times 9 H, 2 \times SiMe3). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz, 25 °C): 178.8 (C₆H₅CN₂), 164.3 (*ipso*-O-2,6-C₆H₃Bu^t₂), 152.1 (*ortho*-NC₅H₅), 141.4 (ipso-C₆H₅), 138.4 (para-NC₅H₅), 128.3, 127.8, 127.3 (*ortho-*, *meta-*, and *para-C*₆H₅), 125.0 (*meta-*O-2,6-C₆H₃Bu^t₂), 123.8 (meta-NC₅H₅), 116.7 (para-O-2,6-C₆H₃Bu^t₂), 70.1 (NC-Me₃), 35.3 [O-2,6-C₆H₃(CMe₃)₂], 32.2 (NCMe₃), 31.8 [O-2,6-C₆H₃(CMe₃)₂], 2.3 (SiMe₃). Note: ortho resonances of the O-2,6- C_{θ} H₃Bu^t₂ 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 C₃₆H₅₈N₄OSi₂Ti): C, 62.9 (64.8); H, 8.9 (8.8); N, 7.3 (8.4)

[Ti(NBu^t){(4-C₆H₄OMe)C(NSiMe₃)₂}(O-2,6-C₆H₃Me₂)-(py)] (12). A mixture of [Ti(NBu^t){(4-C₆H₄Me)C(NSiMe₃)₂}-Cl(py)₂] (0.484 g, 0.80 mmol) and LiO-2,6-C₆H₃Me₂ (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 CH₂Cl₂ 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%).

¹H NMR (CDCl₃, 300.1 MHz, 25 °C): 8.87 (d, J = 4.2 Hz, 2 H, ortho-NC₅H₅), 7.83 (t, J = 7.3 Hz, 1 H, para-NC₅H₅), 7.41

(apparent t, apparent J = 6.1 Hz, 2 H, meta-NC₅H₅), 7.21 (d, J = 7.3 Hz, 2 H, meta-O-2,6-C₆H₃Me₂), 6.89 (m, 4 H, C₆H₄), 6.51 (t, J = 7.3 Hz, 1 H, para-O-2,6-C₆H₃Me₂), 3.85 (s, 3 H, OMe), 2.25 (s, 6 H, O-2, 6-C₆H₃Me₂), 1.16 (s, 9 H, NBu⁴), -0.28(s, 18 H, SiMe₃). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz, 25 °C): 179.5 (C₆H₄*C*N₂), 159.6 (*ipso*-O-2,6-*C*₆H₃Me₂ or *ipso*-*C*₆H₄), 151.5 (ortho-NC₅H₅), 138.6 (para-NC₅H₅), 134.3 (para-C₆H₄), 128.2 (meta-O-2,6-C6H3Me2), 127.4 (ortho-C6H4), 126.5 (ortho-O-2,6-C₆H₃Me₂), 124.4 (meta-NC₅H₅), 116.4 (para-O-2,6-C₆H₃-Me₂), 113.1 (meta-C₆H₄), 68.7 (NCMe₃), 55.2 (OMe), 32.7 (NCMe₃), 17.5 (C₆H₃Me₂), 1.9 (SiMe₃). 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) cm⁻¹. Anal. Found (calcd for C₃₁H₄₈N₄O₂Si₂Ti): C, 57.8 (60.8); H, 7.7 (7.9); N, 7.9 (9.1).

[Ti(NBu^t){PhC(NSiMe₃)₂}₂(py)] (13). Toluene (30 mL) was added to a mixture of [Ti(NBu^t){PhC(NSiMe₃)₂}Cl(py)₂] (0.120 g, 0.21 mmol) and LiPhC(NSiMe₃)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.

¹H NMR (CDCl₃, 300.1 MHz, 25 °C): 9.36 (br s, 2 H, ortho- NC_5H_5), 7.01 (t, J = 7.6 Hz, 1 H, para- NC_5H_5), 7.46 (apparent t, apparent J = 6.2 Hz, 2 H, *meta*-NC₅H₅), 7.29 (br s, 5 H, C₆H₅), 1.20 (s, 9 H, NBu^t), -0.14 (br s, 36 H, SiMe₃). Satisfactory elemental analysis was not obtained for this compound, which was an oil.

Crystal Structure Determinations for [Ti(NBu^t){PhC- $(NSiMe_3)_2$ (CH₂SiMe₃)(py)] (5) and $[Ti(NBu^t)(\eta - C_5Me_5) -$ (CH₂SiMe₃)(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 K α 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(NSiMe₃)₂}-(CH₂SiMe₃)(py)] (5). H atoms for the phenyl and pyridine groups and for the CH₂ of the (trimethylsilyl)methyl group were located from difference maps. H atoms for the SiMe3 and Bu^t groups were placed geometrically. The positions and the isotropic displacement parameters of the H atoms of the trimethylsilylmethyl CH2 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(NSiMe₃)₂}(CH₂SiMe₃)(py)]

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) N(1)-Ti(1)-N(3)	110.89(9) 106.18(9)	Ti(1)-N(1)-C(5) N(1)-Ti(1)-C(1)	168.0(2) 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 $[Ti(NBu^t)(\eta - C_5Me_5)(CH_2SiMe_3)(py)]$ (7)^a

	(8) [(-			571 (*)
	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)-Cp _{cent}	2.204		
ľ	N(1) - Ti(1) - C(1)	106.33(9)	Ti(1)-C(1)-Si(1)	123.8(1)
ľ	N(2) - Ti(1) - C(1)	98.25(8)	Ti(1)-C(1)-H(11)	113(2)
($Cp_{cent}-Ti(1)-N(1)$	125.9	Ti(1) - C(1) - H(12)	107(2)
($\hat{Cp}_{cent} - Ti(1) - N(2)$	110.4	Cpcent-Ti(1)-C(1)	114.5

^a Cp_{cent} is the computed centroid for the ring containing atoms C(9) - C(13).

Additional Details for [Ti(NBu^t)(η-C₅Me₅)(CH₂SiMe₃)-(py)] (7). All H atoms were located from Fourier difference syntheses. The positions and the isotropic displacement parameters of the H atoms of the CH₂ 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 $\ensuremath{CH_3}$ group and for the pyridine H atoms.

NMR Kinetic Analysis for [Ti(NBu^t){PhC(NSiMe₃)₂}-(**O-2,6-C₆H₃Bu^t**₂)(**py**)] (11).^{35,36} ¹H NMR spectra of a solution of 11 in CDCl₃ were recorded between 268 and 283 K. Lorentzian curve fitting of the *tert*-butyl and trimethylsilyl group resonances afforded $\nu_{1/2(obs)}$ (observed line widths at halfheight) values. Subtraction of the estimated natural line width (obtained at the low-temperature limit) from $v_{1/2(obs)}$ gave the corrected excess line widths at half-height $v_{1/2(corr)}$. At each temperature, the NMR first-order rate constant k_{obs} was calculated according to $k_{obs} = \pi v_{1/2(corr)}$. Chemical *exchange* rate constants (k_{exch}) were calculated as $2k_{obs}$.³⁵ The $\nu_{1/2(corr)}$ 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 reported¹⁷ titanium *tert*-butyl imido compound [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 [Ti(NBu^t)Cl₂- $(py)_3]^{28}$ with LiPhC(NSiMe_3)₂.^{23,24} Since introduction of a para-substituent into the benzene ring of the N,Nbis(trimethylsilyl)benzamidinate ligand can sometimes aid crystallization of the complexes, we report here the homologous complex [Ti(NBu^t){(4-C₆H₄OMe)C(NSiMe₃)₂}- $Cl(py)_2$ (2). Thus, addition of $Li(4-C_6H_4OMe)C(NSiMe_3)_2$ to a THF solution of $[Ti(NBu^t)Cl_2(py)_3]$ gave the air- and

⁽³¹⁾ Cosier, J.; Glazer, A. M. *J. Appl. Crystallogr.* **1986**, *19*, 105. (32) Altomare, A.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. J. Appl. Crystallogr. 1994, 27, 435.

^{. (33)} Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664. (34) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. CRYSTALS Issue 10; Chemical Crystallography Laboratory, University of Oxford, 1996.

⁽³⁵⁾ Green, M. L. H.; Wong, L.-L.; Sella, A. Organometallics 1992, 11. 2660.

Table 4.	Excess 1	Line Widths,	Exchange 1	Rate ^a	Constants,	and	Activation	Paramete	ers for
		[Ti(NBu ^t){F	PhC(NSiMe	3) ₂ }(O-	2,6-C ₆ H ₃ Bu	1 ^t 2)(p	y)] (11) ^a		

	Exces	s Line Widths and Ra	ate Constants ^b			
	tert-butyl resonances		trimethyls	trimethylsilyl resonances		
temp (K)	$\nu_{1/2(\text{corr})} (\text{s}^{-1})$	k_{exch} (s ⁻¹)	$v_{1/2(\text{corr})}$ (s ⁻¹)	$k_{\rm exch}$ (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 Param	eters			
	ΔH^{\ddagger} (k.	J mol ⁻¹)	ΔS^{\ddagger} (J mol ⁻¹ ·K ⁻¹)	$\Delta G^{\ddagger}_{278}$ (kJ mol ⁻¹)		
Bu ^t group exchange	106	\pm 12 155 \pm 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 Butor SiMe₃ groups) values for $v_{1/2}$ (corr) and k_{exch} , where $v_{1/2}$ (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- $(NSiMe_3)_2$ $Cl(py)_2$ $(R = Bu^t, 2, 6 - C_6H_3Me_2, or 2, 6 - C_6H_3 - C_6H_3Me_2)$ Pr_{2}^{i} in that it exists in a temperature-dependent equilibrium with the corresponding mono(pyridine) adduct $[Ti(NBu^t){(4-C_6H_4OMe)C(NSiMe_3)_2}Cl(py)]$ (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.

Cyclopentadienyl Derivatives. The half-sandwich complex $[Ti(NBu^t){PhC(NSiMe_3)_2}(\eta - C_5H_5)]$ (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-C₆H₄OMe)C- $(NSiMe_3)_2$ $\{(\eta - C_5H_5)\}$ (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 method³⁷) 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)- $\{RC(NR')_2\}(\eta$ -C₅H₅)] (**3** and **4**) may be compared with the formally 20-electron bis(cyclopentadienyl) complexes $[Ti(\eta-C_5H_5)(\eta-C_5R_5)(NBu^t)(L)]$ (R = H or Me, L = py or py-Bu^t)³⁸ and the 18-electron cyclopentadienyl-indenyl complex $[Ti(\eta-C_5H_5)(\eta-C_9H_7)(NBu^t)(py)]$, all of which exist as pyridine adducts.²⁹ On the other hand, the bis(pentamethylcyclopentadienyl) complexes [Ti(η -C₅-Me₅)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 C₅Me₅ and greater than those of C₅H₅.⁸ 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 SiMe₃) in cold benzene followed by recrystallization from pentane afforded the orange-brown, highly air-sensitive 14electron alkyl derivatives [Ti(NBu^t){PhC(NSiMe₃)₂}- $\{CH(R)SiMe_3\}(py)\}$ (R = H 5 or SiMe₃ 6) in ca. 30% yield (Scheme 1). The crystals of 5 were suitable for Xdiffraction analysis (vide infra). Reaction of **1** with $Mg(CH_2Ph)_2$, MeLi, or ZnMe₂ 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-

⁽³⁶⁾ Sandström, J. Dynamic NMR Spectroscopy, Academic Press: London, 1992.

⁽³⁷⁾ Clark, E. P. *Ind. Eng. Chem., Anal. Ed.* **1941**, *13*, 820.
(38) For a discussion of the metal–ligand interactions and electron counting problems in [Ti(η-C₅H₅)(η-C₅R₅)(NBu¹)(py)], see ref 29.
(39) Andersen, R. A.; Bergman, R. G. Personal communication.

⁽⁴⁰⁾ Hortmann, K.; Brintzinger, H. H. New J. Chem. 1992, 16, 51.



^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) $LiN(SiMe_3)_2$ ·OEt₂, toluene, room temperature, 40 h, 91%; (v) $LiO-2,6-C_6H_3Me_2$ or $LiO-2,6-C_6H_3Bu_2^t$, 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 -C₅Me₅)(CH₂SiMe₃)(py)] (7, see eq 2) from LiCH₂-SiMe₃ and [Ti(NBu^t)(η -C₅Me₅)Cl(py)]^{29,41} in cold benzene. Cooling a saturated pentane solution of 7 to



 $-80\ ^\circ\text{C}$ 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.

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^t₃)(NHSiBu^t₃)(R)(THF)] (R = Me or Bu^t (quite thermally unstable)).⁴² σ -Bond hydrogenolysis of these complexes afforded the transient hydride [Ti(NSiBu^t₃)-(NHSiBu^t₃)(H)(THF)] and ultimately [Ti₂(μ -NSiBu^t₃)₂-(NHSiBu^t₃)₂]. We were, therefore, interested in exploring the reactions of our alkyl complexes toward H₂. However, an NMR-scale hydrogenolysis of [Ti(NBu^t)-{PhC(NSiMe₃)₂}{CH(SiMe₃)₂}(py)] (**6**) in C₆D₆ gave extensive reduction and several products including Bu^tNH₂, CH₂(SiMe₃)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

⁽⁴¹⁾ Bai, Y.; Noltemeyer, M.; Roesky, H. W. Z. Naturforsch. 1991, 46b, 1357.

⁽⁴²⁾ Cummins, C. C.; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffmann, R. J. Am. Chem. Soc. **1991**, *113*, 2985.

⁽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(NSiMe₃)₂}(CH₂SiMe₃)(py)] (5). Hydrogen atoms except those of the methylene linkage of the CH₂-SiMe₃ ligand are omitted.

titanium (4+) center which possesses a distorted squarebased 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 - 1.73Å) 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 $[N(2)-Ti(1)-N(3) = 63.74(8)^{\circ}]$ 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 silvlated 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 $[Ti(1)\cdots H(12) = 2.38(4) \text{ Å}]$ than the other $[Ti(1)\cdots H(11) = 2.54(3) \text{ Å}]$; the difference [0.09(5) Å] between the C(1)–H_a distances, however, is not significant.

Displacement ellipsoid plots of [Ti(NBu^t)(η -C₅Me₅)(CH₂-SiMe₃)(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 CH₂SiMe₃ 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 ¹H and ¹³C 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 SiMe₃ groups of the benzamidinate ligand in [Ti(NBu¹){PhC(NSiMe₃)₂}(CH₂-SiMe₃)(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 ¹³C 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 ${}^{1}J_{CH}$ coupling constant of 93 Hz at -10 °C. For [Ti(NBu^t)(η^{5} -C₅Me₅)(CH₂SiMe₃)(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 ${}^{1}J_{CH}$ 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_{α} agostic⁵² interactions. Well-established examples of α - and β -agostic alkyltitanium compounds, namely [TiCl₃Me(dmpe)] and [TiCl₃Et(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) \cdots H(12) distance of 2.38(4) Å raises a priori the possibility of an α -agostic interac-

⁽⁴⁴⁾ Allen, F. H.; Kennard, O. *Chem. Des. Automation News* **1993**, *8*, 1, 31.

⁽⁴⁵⁾ Fletcher, D. A.; McMeeking, R. F.; Parkin, D. J. Chem. Inf. Comput. Sci. 1996, 36, 746.

⁽⁴⁶⁾ Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffmann, J. C. J. Am. Chem. Soc. **1985**, 107, 5931.

⁽⁴⁷⁾ Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffmann, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987**, *109*, 200

⁽⁴⁸⁾ Chesnut, R. W.; Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffmann, J. C. *Polyhedron* **1987**, *6*, 2019.

⁽⁴⁹⁾ Eisch, J. J.; Caldwell, K. R.; Werner, S.; Kruger, C. Organometallics **1991**, 10, 3417.

⁽⁵⁰⁾ Gomez-Sal, P.; Mena, M.; Palacios, F.; Royo, P.; Serrano, R.; Carreras, S. M. *J. Organomet. Chem.* **1989**, *375*, 59.

⁽⁵¹⁾ Gomez, R.; Cuenca, T.; Royo, P.; Herrmann, W. A.; Herdtweck, E. J. Organomet. Chem. **1990**, 382, 103.

⁽⁵²⁾ Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

⁽⁵³⁾ Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K.; Schultz, A. J.; Williams, J. M.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1629 and references therein.



Figure 2. Two displacement ellipsoid plots (30% probability) of $[Ti(NBu^t)(\eta-C_5Me_5)(CH_2SiMe_3)(py)]$ (7): (a) general view, (b) view showing the location of the methylene hydrogen atoms with respect to the $Ti(NBu^t)(\eta-C_5Me_5)$ equatorial plane. Hydrogen atoms except those of the methylene linkage of the CH_2SiMe_3 ligand are omitted.

tion, since the Ti···H distance in the α -agostic complex [TiCl₃Me(dmpe] was 2.447(3) Å as determined by neutron diffraction at 20 K.⁵³ The other two Ti···H_{α} 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 -C₅Me₅)(CH₂SiMe₃)(py)] (7, Figure 2).

Like 5, compound 7 contains a CH₂SiMe₃ 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 -C₅Me₅)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 ${}^{1}J_{CH}$ 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(sp³)-H bonds (120–130 Hz) but do not necessarily imply α -agostic interactions. These low ${}^{1}J_{CH}$ values are in fact most likely due to the bulky, electropositive SiMe₃ groups. In the authentic α -agostic complex $[Y(\eta-C_5Me_5)_2\{CH-$ (SiMe₃)₂], for example, the methine α -carbon ¹ J_{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 ¹³C spectra of 5 and 7 (for which the methylene hydrogens are chemically inequivalent) suggests that the two ${}^{1}J_{CH}$ 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 ${}^{1}J_{CH}$ 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_{CH} coupling constant. In this context we note that the authentic α -agostic interaction in [TiCl₃Me(dmpe)] did not lead to any detectable lowering of the averaged ¹J_{CH} coupling constant.⁵³

 η^3 -Borohydride Derivative. Reaction of [Ti(NBu^t)-{PhC(NSiMe₃)₂}Cl(py)₂] (1) with an excess of LiBH₄ in toluene for 72 h gave, after standard workup, the yellow, hexane-soluble borohydride complex [Ti(NBu^t){PhC-(NSiMe₃)₂}(η^3 -BH₄)(py)] (8) in 62% recrystallized yield.

(57) Jarid, A.; Lledos, A.; Jean, Y.; Volatron, F. *Chem. Eur. J.* **1995**, *I*, 436.

(58) Marks, T. J.; Kolb, J. R. Chem. Rev. 1977, 77, 263.
(59) Dick, D. G.; Duchateau, R.; Edema, J. J. H.; Gambarotta, S. Inorg. Chem. 1993, 32, 1959.

(60) Unpublished results cited in ref 12.

(61) Wedler, M.; Knösel, F.; Edelmann, F. T.; Behrens, U. Chem. Ber. 1992, 125, 1313.

(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 SiMe₃ group resonances decoalesce (and hence any implications for the associated ΔG^{\ddagger} for exchange) will depend on their frequency separation $(\delta \nu)$ in the slow-exchange limit.³⁶ For **9** and **11**, the slow-exchange ¹H 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**.

⁽⁵⁴⁾ Bruno, J. W.; Smith, J. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, M. *J. Am. Chem. Soc.* **1986**, *108*, 40.

⁽⁵⁵⁾ Green, M. L. H.; Sella, A.; Wong, L.-L. Organometallics **1992**, *11*, 2650.

⁽⁵⁶⁾ Green, M. L. H.; Wong, L.-L. *J. Chem. Soc., Dalton Trans.* **1989**, 2133.

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

The ¹H NMR spectrum of **8** at room temperature revealed resonances for fluxional benzamidinate (i.e., the SiMe₃ groups appear as a single sharp singlet), tertbutylimido, 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 ¹H atoms; this was assigned as a highly fluxional BH4 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 SiMe₃ resonances. The ¹¹B 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 BH₄ hydrogen atoms proposed to account for the ¹H 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 BH₄ ligand.⁵⁷ Although we were unable to obtain diffractionquality crystals of 8, the coordination mode of the BH4 ligand could be elucidated from IR data.

Infrared spectroscopy can be useful in inferring the coordination mode of the BH₄ 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 ν (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 ν (B–H_{terminal}) absorption at 2493 cm⁻¹ and two ν (B-H_{bridging}) absorptions at 2205 and 2151 cm⁻¹, confirming that the coordination mode. The shift in the position of the ν (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 $C_{3\nu}$ symmetry for the $Ti(\mu-H)_3BH$ moiety is assumed. A bidentate tetrahydroborate ligand should give rise to two strong ν (B–H_{terminal}) absorptions, as in the bis(*N*,*N*-bis(trimethylsilyl)benzamidinato) titanium (+3) tetrahydroborate complex, $[Ti{PhC(NSiMe_3)_2}_2(\eta^2-BH_4)]$.⁵⁹

Amide, Arvloxide, and Bis(N.N-bis(trimethylsilyl)benzamidinate) Derivatives. Reaction of 1 equiv of LiN(SiMe₃)₂·Et₂O with [Ti(NBu^t){PhC(NSiMe₃)₂}Cl- $(py)_2$ (1) in toluene at room temperature afforded the amido complex [Ti(NBu^t){PhC(NSiMe₃)₂}{N(SiMe₃)₂}-(py)] (9) as an orange oil (Scheme 1), which could not be crystallized. The use of the less bulky LiNMe₂ led to a mixture of products. Reaction of 1 equiv of LiO-2,6-C₆H₃Me₂ with 1 in toluene at 90 °C followed by recrystallization from pentane at -80 °C afforded the aryloxide complex [Ti(NBu^t){PhC(NSiMe₃)₂}(O-2,6-C₆H₃-Me₂)(py)] (10) as an orange-brown solid in 55% yield. Analogous procedures gave [Ti(NBu^t){PhC(NSiMe₃)₂}(O- $2,6-C_6H_3Bu_2^{t}(py)$] (11) as a yellow solid in 84% yield. The para-methoxy-substituted benzamidinate derivative $[Ti(NBu^{t}){(4-C_{6}H_{4}OMe)C(NSiMe_{3})_{2}}(O-2,6-C_{6}H_{3}-C_{6}$ $Me_2(py)$ (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 reported⁶⁰ 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 ¹H NMR spectrum of **9** at room temperature contains additional broad resonances in the SiMe₃ region, indicating fluxionality of the amide and benzamidinate ligands. Cooling a CDCl₃ sample of **9** to -5 °C froze out these processes, and the spectra showed four separate resonances assignable to the two inequivalent SiMe₃ groups of the benzamidinate ligand and to the two inequivalent SiMe₃ 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 SiMe₃ 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 CDCl₃ sample of **10** caused the signal for SiMe₃ to broaden substantially but not to decoalesce; likewise, only one relatively sharp orthomethyl 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 SiMe3 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 variabletemperature ¹H NMR line shape analysis for the exchanging SiMe₃ 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 SiMe₃ and ortho-Bu^t exchange are listed in Table 4.

The striking similarity of the two sets of ΔH^{\ddagger} , ΔS^{\ddagger} , and $\Delta G_{278}^{\ddagger}$ activation parameters in Table 4 suggest that SiMe₃ 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 SiMe₃ exchange in fluxional benzamidinate complexes.^{8,61} The line widths of the SiMe₃ and Bu^t resonances were unaffected by addition of ca. 1.5 equiv of free pyridine to a CDCl₃ 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 molecules⁶²). It is, therefore, likely that the SiMe₃ 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 SiMe₃ group exchange, at least two mechanisms are possible. These include either a process involving in-place rotation of the benzamidinate ligand about the Ti···C(N₂) axis⁸ or one

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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 ΔS^{\ddagger} and would also be consistent with the large value for ΔH^{\ddagger} , as such a process would involve bond-breaking in the transition state.

In conclusion, it appears that the correlated SiMe₃ 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 SiMe₃ groups in 9, 10, or 12. However, it is likely that the readily frozen out exchange in the bis(trimethvlsilyl)amido complex 9 also involves some degree of Ti-N(benzamidinate) bond cleavage.⁶³ In **10** and **12**, the SiMe₃ group exchange activation energy appears to be much lower⁶³ so a mechanism involving in-place benzamidinate ligand rotation about the Ti…C(N₂) axis may be the more probable and the SiMe₃ 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 complexes⁶⁴). 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)(η -C₅-Me₅){CH₂SiMe₃}(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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⁽⁶⁴⁾ Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. J. Chem. Soc., Dalton Trans. 1992, 367.