

# Titanium Imido Complexes Supported by Amidinate Ligands: Synthesis, Solution Dynamics, and Solid State Structures

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Received February 26, 1997<sup>⊗</sup>

Reaction of Li[PhC(NSiMe<sub>3</sub>)<sub>2</sub>] with the complexes [Ti(NR)Cl<sub>2</sub>(py)<sub>3</sub>] affords the corresponding (*N,N'*-bis(trimethylsilyl)benzamidinato)titanium imido derivatives [Ti(NR){PhC(NSiMe<sub>3</sub>)<sub>2</sub>}Cl(py)<sub>2</sub>] [R = Bu<sup>t</sup> (**1**), 2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub> (**2**), 2,6-C<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub> (**3**)], which, in solution, exist in temperature-dependent, dynamic equilibrium with their mono(pyridine) homologues [Ti(NR){PhC(NSiMe<sub>3</sub>)<sub>2</sub>}Cl(py)] and free pyridine. Kinetic and thermodynamic data for these processes are reported, and the relative contributions of the  $\Delta H$  and  $\Delta S$  terms associated with all three equilibria are identified. The arylimido complexes **2** and **3** may also be prepared by treating **1** with the appropriate arylamine. Reaction of Li[MeC(NC<sub>6</sub>H<sub>11</sub>)<sub>2</sub>] with [Ti(NBu<sup>t</sup>)Cl<sub>2</sub>(py)<sub>3</sub>] gives the binuclear *N,N'*-bis(cyclohexyl)acetamidinato derivative [Ti<sub>2</sub>( $\mu$ -NBu<sup>t</sup>)<sub>2</sub>{MeC(NC<sub>6</sub>H<sub>11</sub>)<sub>2</sub>}<sub>2</sub>Cl<sub>2</sub>] (**4**). The X-ray structures of **2** and **4** have been determined. Crystal data for **2**: triclinic,  $P\bar{1}$ ,  $a = 11.219(5)$  Å,  $b = 12.131(6)$  Å,  $c = 13.208(7)$  Å,  $\alpha = 80.34(5)^\circ$ ,  $\beta = 87.41(4)^\circ$ ,  $\gamma = 75.13(3)^\circ$ ,  $V = 1722.1(15)$  Å<sup>3</sup>,  $Z = 2$ ,  $R = 0.054$ ,  $R_w = 0.056$ . Crystal data for **4**: triclinic,  $P\bar{1}$ ,  $a = 10.455(3)$  Å,  $b = 10.637(5)$  Å,  $c = 11.024(3)$  Å,  $\alpha = 90.52(4)^\circ$ ,  $\beta = 112.62(3)^\circ$ ,  $\gamma = 114.10(3)^\circ$ ,  $V = 1012.8(10)$  Å<sup>3</sup>,  $Z = 1$ ,  $R = 0.0453$ ,  $R_w = 0.0495$ .

## Introduction

The study of compounds containing one or more transition metal–ligand multiple bond(s) continues to be an area of substantial interest.<sup>1–8</sup> The impressive variety of structural types and, in particular, reactivity properties of such complexes is a testament to the wide range of ancillary ligand environments available to support these multiply bonded functional groups. In the course of our studies of group 4 transition metal imido chemistry, we recently described the complexes [Ti(NR)Cl<sub>2</sub>(L)<sub>*n*</sub>] ( $n = 2$ , L = py or 4-NC<sub>5</sub>H<sub>4</sub>Bu<sup>t</sup>, R = Bu<sup>t</sup>;  $n = 3$ , L = py, R = Bu<sup>t</sup> or aryl).<sup>9–11</sup> Simple metathesis reactions of these complexes with neutral ligands or their anions give ready access to a wide range of monomeric titanium imido derivatives whose ancillary ligand sets include the cyclopentadienyl, indenyl, and bis(cyclopentadienyl) fragments,<sup>12</sup> as well as the tris(pyrazolyl)hydroborate<sup>13</sup> and dibenzotetraaza[14]annulene<sup>11,14,15</sup>  $\eta^3$  and  $\eta^4$  N-donor ligands.

In contrast to some of these other supporting ligand sets, amidinate ligands<sup>16,17</sup> [having the general formula RC(NR')<sub>2</sub>] have been relatively little used in metal imido or oxo chemistry.<sup>18–24</sup> Several research groups have reported interesting and novel reaction chemistry of amidinate-supported early transition metal complexes,<sup>25–30</sup> and we were interested in developing synthetic routes to new amidinate complexes containing metal–ligand multiple bonds.<sup>24</sup> Here we describe the synthesis and properties of some mono- and binuclear titanium imido complexes supported by *N,N'*-bis(trimethylsilyl)benzamidinato and *N,N'*-bis(cyclohexyl)acetamidinato ligands.<sup>31</sup>

## 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 solvents and pyridine were

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, July 15, 1997.

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- (31) 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 3 (pseudo- $\sigma^2 \pi^4$ , triple bond) rather than as 2.<sup>2</sup>

predried over activated molecular sieves, refluxed over the appropriate drying agent under an atmosphere of dinitrogen, and collected by distillation.  $\text{CDCl}_3$  was dried over freshly ground calcium hydride at room temperature, distilled under vacuum, and stored under  $\text{N}_2$  in a Young ampule. Other reagents were used as received (Aldrich). NMR samples were prepared in the drybox in 5 mm Wilmad tubes equipped with a Young Teflon valve.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX 300 spectrometer. The spectra were referenced internally to residual protio solvent ( $^1\text{H}$ ) or solvent ( $^{13}\text{C}$ ) resonances and are reported relative to tetramethylsilane ( $\delta = 0$  ppm). Chemical shifts are quoted in  $\delta$  (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  $\text{cm}^{-1}$ . Samples were prepared in the drybox as Nujol mulls between CsBr plates, and data are quoted in wavenumbers ( $\nu$ ,  $\text{cm}^{-1}$ ). Elemental analyses were carried out by the analysis department of this laboratory or by Canadian Microanalytical Service Ltd.

**Literature Preparations.**  $\text{Li}[\text{PhC}(\text{NSiMe}_3)_2]$ ,<sup>32</sup>  $\text{Li}[\text{MeC}(\text{NC}_6\text{H}_{11})_2]$ ,<sup>33</sup> and  $[\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_3]$  ( $\text{R} = \text{Bu}^t$ , 2,6- $\text{C}_6\text{H}_3\text{Me}_2$ , or 2,6- $\text{C}_6\text{H}_3\text{Pr}^i_2$ )<sup>9,10</sup> were prepared according to literature methods.

**$[\text{Ti}(\text{NBu}^t)\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$  (**1**).** A solution of  $\text{Li}[\text{PhC}(\text{NSiMe}_3)_2]$  (0.693 g, 2.56 mmol) in THF (25 mL) was added over 15 min to a stirred solution of  $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{py})_3]$  (1.094 g, 2.56 mmol) in THF (30 mL) at  $-40^\circ\text{C}$ . The resulting solution was allowed to warm to room temperature and then stirred for 18 h. Volatiles were removed under reduced pressure, the resulting orange residue was dissolved in dichloromethane, and the mixture was filtered to remove  $\text{LiCl}$ . Evaporation of the solvent and recrystallization from hexane yielded bright orange crystals of **1**, which were washed with pentane ( $2 \times 10$  mL) and dried *in vacuo*. Yield: 0.914 g (62%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $-40^\circ\text{C}$ ): 9.39 (4 H, d,  $J = 4.7$  Hz, *o*- $\text{NC}_5\text{H}_5$ ), 7.91 (2 H, t,  $J = 7.6$  Hz, *p*- $\text{NC}_5\text{H}_5$ ), 7.50 (4 H, apparent t, apparent  $J = 7.0$  Hz, *m*- $\text{NC}_5\text{H}_5$ ), 7.25 (3 H, m, *o*- and *p*- $\text{C}_6\text{H}_5$ ), 6.82 (2 H, m, *m*- $\text{C}_6\text{H}_5$ ), 0.95 (9 H, s,  $\text{NBu}^t$ ), 0.18 (9 H, s,  $\text{SiMe}_3$ ),  $-0.49$  (9 H, s,  $\text{SiMe}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz,  $-40^\circ\text{C}$ ): 178.6 ( $\text{C}_6\text{H}_5\text{C}$ ), 150.9 (*o*- $\text{NC}_5\text{H}_5$ ), 142.3 (*ipso*- $\text{C}_6\text{H}_5$ ), 138.0 (*p*- $\text{NC}_5\text{H}_5$ ), 127.6, 125.2, 124.8 ( $3 \times$  *o*-, *m*- or *p*- $\text{C}_6\text{H}_5$ ), 123.7 (*m*- $\text{NC}_5\text{H}_5$ ), 67.8 ( $\text{NCMe}_3$ ), 31.0 ( $\text{NCMe}_3$ ), 2.4, 1.5 ( $2 \times$   $\text{SiMe}_3$ ). IR: 1735 (w), 1650 (w), 1603 (s), 1573 (m), 1515 (s), 1480 (s), 1468 (vs), 1454 (vs), 1445 (vs), 1245 (vs), 1215 (m), 1208 (m), 1173 (w), 1150 (w), 1134 (w), 1108 (w), 1071 (m), 1040 (m), 1030 (w), 1012 (m), 1001 (m), 983 (s), 924 (m), 842 (vs), 788 (s), 761 (s), 728 (m), 700 (s), 632 (m), 597 (w), 547 (w), 525 (w), 493 (w), 436 (w)  $\text{cm}^{-1}$ . Anal. Calcd (found) for  $\text{C}_{27}\text{H}_{42}\text{ClN}_5\text{Si}_2\text{Ti}$ : C, 56.3 (55.7); H, 7.4 (7.3); N, 12.2 (11.8).

$^1\text{H}$  NMR data for  $[\text{Ti}(\text{NBu}^t)\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})]$  (**1'**) ( $\text{CDCl}_3$ , 300 MHz,  $-15^\circ\text{C}$ ): 8.96 (2 H, d,  $J = 4.7$  Hz, *o*- $\text{NC}_5\text{H}_5$ ), 7.98 (1 H, t,  $J = 7.7$  Hz, *p*- $\text{NC}_5\text{H}_5$ ), 7.58 (2 H, apparent t, apparent  $J = 6.7$  Hz, *m*- $\text{NC}_5\text{H}_5$ ), 7.38 (3 H, m, *o*- and *p*- $\text{C}_6\text{H}_5$ ), 7.31 (2 H, m, *m*- $\text{C}_6\text{H}_5$ ), 1.15 (9 H, s,  $\text{NBu}^t$ ),  $-0.26$  (18 H, s,  $\text{SiMe}_3$ ).

**$[\text{Ti}(\text{N-2,6-C}_6\text{H}_3\text{Me}_2)\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$  (**2**).** A solution of  $\text{Li}[\text{PhC}(\text{NSiMe}_3)_2]$  (0.108 g, 0.40 mmol) in THF (15 mL) was added over 15 min to a stirred solution of  $[\text{Ti}(\text{N-2,6-C}_6\text{H}_3\text{Me}_2)\text{Cl}_2(\text{py})_3]$  (0.190 g, 0.40 mmol) in THF (15 mL) at  $-40^\circ\text{C}$ . The resulting solution was allowed to warm to room temperature and then stirred for 18 h. The volatiles were removed under reduced pressure, and the resulting orange residue was dissolved in hexane. After filtration, concentration, and cooling overnight at  $-25^\circ\text{C}$ , orange-red crystals of **2** formed; these were washed with pentane ( $2 \times 5$  mL) and dried *in vacuo*. Yield: 0.159 g (64%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $-40^\circ\text{C}$ ): 9.31 (4 H, d,  $J = 6.4$  Hz, *o*- $\text{NC}_5\text{H}_5$ ), 7.93 (2 H, t,  $J = 7.6$  Hz, *p*- $\text{NC}_5\text{H}_5$ ), 7.49 (4 H, apparent t, apparent  $J = 7.0$  Hz, *m*- $\text{NC}_5\text{H}_5$ ), 7.29 (3 H, m, *o*- and *p*- $\text{C}_6\text{H}_5$ ), 6.82 (2 H, m, *m*- $\text{C}_6\text{H}_5$ ), 6.74 (2 H, d,  $J = 7.4$  Hz, *m*- $\text{C}_6\text{H}_3\text{Me}_2$ ), 6.50 (1 H, t,  $J = 7.4$  Hz, *p*- $\text{C}_6\text{H}_3\text{Me}_2$ ), 2.09 (6 H, s,  $\text{C}_6\text{H}_3\text{Me}_2$ ),  $-0.18$  (9 H, s,  $\text{SiMe}_3$ ),

$-0.44$  (9 H, s,  $\text{SiMe}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz,  $-40^\circ\text{C}$ ): 180.3 ( $\text{C}_6\text{H}_5\text{C}$ ), 156.5 (*ipso*- $\text{C}_6\text{H}_3\text{Me}_2$ ), 150.9 (*o*- $\text{NC}_5\text{H}_5$ ), 141.7 (*ipso*- $\text{C}_6\text{H}_5$ ), 138.5 (*p*- $\text{NC}_5\text{H}_5$ ), 133.8 (*o*- $\text{C}_6\text{H}_3\text{Me}_2$ ), 128.0 (*o*-, *m*- or *p*- $\text{C}_6\text{H}_5$ ), 127.8 (*p*- $\text{C}_6\text{H}_3\text{Me}_2$ ), 126.7, 125.1 ( $2 \times$  *o*-, *m*- or *p*- $\text{C}_6\text{H}_5$ ), 123.7 (*m*- $\text{NC}_5\text{H}_5$ ), 119.1 (*m*- $\text{C}_6\text{H}_3\text{Me}_2$ ), 18.8 ( $\text{C}_6\text{H}_3\text{Me}_2$ ), 2.6, 1.2 ( $2 \times$   $\text{SiMe}_3$ ). IR: 1650 (w), 1603 (s), 1589 (m), 1568 (m), 1504 (s), 1470 (vs), 1446 (vs), 1403 (s), 1295 (s), 1247 (s), 1216 (m), 1167 (w), 1152 (w), 1138 (w), 1094 (w), 1072 (m), 1042 (m), 1029 (w), 1012 (m), 1001 (m), 987 (s), 959 (s), 918 (m), 846 (vs), 786 (s), 757 (s), 699 (s), 634 (m), 587 (w), 574 (w), 508 (w), 498 (w), 436 (w)  $\text{cm}^{-1}$ . Anal. Calcd (found) for  $\text{C}_{31}\text{H}_{42}\text{ClN}_5\text{Si}_2\text{Ti}$ : C, 59.7 (59.6); H, 6.8 (6.9); N, 11.2 (11.4).

NMR data for  $[\text{Ti}(\text{N-2,6-C}_6\text{H}_3\text{Me}_2)\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})]$  (**2'**) are as follows.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $-10^\circ\text{C}$ ): 9.00 (2 H, d,  $J = 4.9$  Hz, *o*- $\text{NC}_5\text{H}_5$ ), 7.92 (1 H, t,  $J = 7.7$  Hz, *p*- $\text{NC}_5\text{H}_5$ ), 7.58 (2 H, apparent t, apparent  $J = 6.4$  Hz, *m*- $\text{NC}_5\text{H}_5$ ), 7.41 (3 H, s, *o*- and *p*- $\text{C}_6\text{H}_5$ ), 7.33 (2 H, m, *m*- $\text{C}_6\text{H}_5$ ), 6.88 (2 H, d,  $J = 7.8$  Hz, *m*- $\text{C}_6\text{H}_3\text{Me}_2$ ), 6.62 (1 H, t,  $J = 8.4$  Hz, *p*- $\text{C}_6\text{H}_3\text{Me}_2$ ), 2.60 (6 H, s,  $\text{C}_6\text{H}_3\text{Me}_2$ ),  $-0.31$  (18 H, s,  $\text{SiMe}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz,  $20^\circ\text{C}$ ): 179.5 ( $\text{C}_6\text{H}_5\text{C}$ ), 159.6 (*ipso*- $\text{C}_6\text{H}_3\text{Me}_2$ ), 151.4 (*o*- $\text{NC}_5\text{H}_5$ ), 139.6 (*p*- $\text{NC}_5\text{H}_5$ ), 133.3 (*o*- $\text{C}_6\text{H}_3\text{Me}_2$ ), 128.8, 128.0, 126.8 ( $3 \times$  *o*-, *m*- or *p*- $\text{C}_6\text{H}_5$ ), 126.3 (*p*- $\text{C}_6\text{H}_3\text{Me}_2$ ), 125.0 (*m*- $\text{NC}_5\text{H}_5$ ), 120.2 (*m*- $\text{C}_6\text{H}_3\text{Me}_2$ ), 19.1 ( $\text{C}_6\text{H}_3\text{Me}_2$ ), 1.8 ( $\text{SiMe}_3$ ); the  $\text{PhC}(\text{NSiMe}_3)_2$  ligand *ipso* carbon was not observed.

**$[\text{Ti}(\text{N-2,6-C}_6\text{H}_3\text{Pr}^i_2)\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$  (**3**).** A solution of  $\text{Li}[\text{PhC}(\text{NSiMe}_3)_2]$  (0.236 g, 0.87 mmol) in THF (30 mL) was added over 10 min to a stirred solution of  $[\text{Ti}(\text{N-2,6-C}_6\text{H}_3\text{Pr}^i_2)\text{Cl}_2(\text{py})_3]$  (0.464 g, 0.87 mmol) in THF (20 mL) at  $-45^\circ\text{C}$ . The resulting solution was allowed to warm to room temperature and then stirred for 17 h. The volatiles were removed under reduced pressure, and the resulting orange oil was dissolved in pentane (30 mL). After filtration, concentration, and cooling overnight at  $-25^\circ\text{C}$ , orange-brown crystals of **3** formed; these were washed with cold pentane ( $2 \times 5$  mL) and dried *in vacuo*. Yield: 0.174 g (29%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $-43^\circ\text{C}$ ): 9.27 (4 H, d,  $J = 5.1$  Hz, *o*- $\text{NC}_5\text{H}_5$ ), 7.91 (2 H, t,  $J = 7.6$  Hz, *p*- $\text{NC}_5\text{H}_5$ ), 7.49 (4 H, apparent t, apparent  $J = 7.0$  Hz, *m*- $\text{NC}_5\text{H}_5$ ), 7.43 (1 H, m, *p*- $\text{C}_6\text{H}_5$ ), 7.33 (2 H, m, *o*- $\text{C}_6\text{H}_5$ ), 6.99 (2 H, m, *m*- $\text{C}_6\text{H}_5$ ), 6.93 (2 H, d,  $J = 7.6$  Hz, *m*- $\text{C}_6\text{H}_3\text{Pr}^i_2$ ), 6.74 (1 H, t,  $J = 7.6$  Hz, *p*- $\text{C}_6\text{H}_3\text{Pr}^i_2$ ), 4.13 (2 H, sept,  $J = 6.6$  Hz,  $\text{CHMe}_2$ ), 0.91 (12 H, br s,  $\text{CHMe}_2$ ),  $-0.14$  (9 H, s,  $\text{SiMe}_3$ ),  $-0.50$  (9 H, s,  $\text{SiMe}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz,  $-43^\circ\text{C}$ ): 180.1 ( $\text{C}_6\text{H}_5\text{C}$ ), 153.0 (*ipso*- $\text{C}_6\text{H}_3\text{Pr}^i_2$ ), 150.5 (*o*- $\text{NC}_5\text{H}_5$ ), 145.1 (*o*- $\text{C}_6\text{H}_3\text{Pr}^i_2$ ), 141.9 (*ipso*- $\text{C}_6\text{H}_5$ ), 138.4 (*p*- $\text{NC}_5\text{H}_5$ ), 128.2 (*o*-, *m*- or *p*- $\text{C}_6\text{H}_5$ ), 127.9 (*p*- $\text{C}_6\text{H}_3\text{Pr}^i_2$ ), 125.1 (*o*-, *m*- or *p*- $\text{C}_6\text{H}_5$ ), 124.1 (*m*- $\text{NC}_5\text{H}_5$ ), 122.5 (*o*-, *m*- or *p*- $\text{C}_6\text{H}_5$ ), 120.0 (*m*- $\text{C}_6\text{H}_3\text{Pr}^i_2$ ), 27.1 ( $\text{CHMe}_2$ ), 24.5 ( $\text{CHMe}_2$ ), 2.6, 0.8 ( $2 \times$   $\text{SiMe}_3$ ). IR: 1590 (w), 1570 (w), 1504 (w), 1249 (m), 1137 (w), 1071 (w), 1042 (w), 922 (m), 844 (s), 754 (m), 743 (m), 722 (m), 700 (m), 633 (w), 516 (w), 461 (w), 404 (w). Anal. Calcd (found) for  $\text{C}_{35}\text{H}_{50}\text{ClN}_5\text{Si}_2\text{Ti}$ : C, 61.8 (61.0); H, 7.4 (7.6); N, 10.3 (9.9).

NMR data for  $[\text{Ti}(\text{N-2,6-C}_6\text{H}_3\text{Pr}^i_2)\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})]$  (**3'**) are as follows.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $25^\circ\text{C}$ ): 8.98 (2 H, d,  $J = 4.8$  Hz, *o*- $\text{NC}_5\text{H}_5$ ), 7.98 (1 H, t,  $J = 7.6$  Hz, *p*- $\text{NC}_5\text{H}_5$ ), 7.57 (2 H, apparent t, apparent  $J = 7.0$  Hz, *m*- $\text{NC}_5\text{H}_5$ ), 7.41 (2 H, m, *o*- $\text{C}_6\text{H}_5$ ), 7.30 (3 H, m, *m*- and *p*- $\text{C}_6\text{H}_5$ ), 6.94 (2 H, d,  $J = 7.6$  Hz, *m*- $\text{C}_6\text{H}_3\text{Pr}^i_2$ ), 6.79 (1 H, m, *p*- $\text{C}_6\text{H}_3\text{Pr}^i_2$ ), 4.38 (2 H, sept,  $J = 6.8$  Hz,  $\text{CHMe}_2$ ), 1.31 (6 H, d,  $J = 6.6$  Hz,  $\text{CHMe}_2$ ), 1.28 (6 H, d,  $J = 6.7$  Hz,  $\text{CHMe}_2$ ),  $-0.27$  (18 H, s,  $\text{SiMe}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz,  $25^\circ\text{C}$ ): 179.8 ( $\text{C}_6\text{H}_5\text{C}$ ), 157.2 (*ipso*- $\text{C}_6\text{H}_3\text{Pr}^i_2$ ), 151.4 (*o*- $\text{NC}_5\text{H}_5$ ), 143.7 (*o*- $\text{C}_6\text{H}_3\text{Pr}^i_2$ ), 139.8 (*p*- $\text{NC}_5\text{H}_5$ ), 135.9 (*ipso*- $\text{C}_6\text{H}_5$ ), 128.9 (*o*-, *m*- or *p*- $\text{C}_6\text{H}_5$ ), 128.1 (*p*- $\text{C}_6\text{H}_3\text{Pr}^i_2$ ), 126.7, 125.1 ( $2 \times$  *o*-, *m*- or *p*- $\text{C}_6\text{H}_5$ ), 123.7 (*m*- $\text{NC}_5\text{H}_5$ ), 121.8 (*m*- $\text{C}_6\text{H}_3\text{Pr}^i_2$ ), 27.7 ( $\text{CHMe}_2$ ), 24.3, 23.7 ( $2 \times$   $\text{CHMe}_2$ ), 1.8 ( $\text{SiMe}_3$ ).

**NMR-Scale Reaction of  $[\text{Ti}(\text{NBu}^t)\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$  (**1**) with 2,6-Dimethylaniline.** A solution of **1** (9.0 mg, 0.016 mmol) in  $\text{CDCl}_3$  (0.6 mL) in a 5 mm NMR tube was treated with *ca.* 1.5 equiv of 2,6-dimethylaniline at room temperature. The  $^1\text{H}$  NMR spectrum after 6 d showed quantitative formation of **2** together with a new resonance attributable to  $\text{Bu}^t\text{NH}_2$ .

**NMR-Scale Reaction of  $[\text{Ti}(\text{NBu}^t)\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$  (**1**) with 2,6-Diisopropylaniline.** A solution of **1** (6.6 mg, 0.011 mmol) in  $\text{CDCl}_3$  (0.5 mL) in a 5 mm NMR tube was treated with *ca.* 1.2 equiv of 2,6-diisopropylaniline at room temperature. The  $^1\text{H}$  NMR spectrum after 6 d showed quantitative formation of **3** together with a new resonance attributable to  $\text{Bu}^t\text{NH}_2$ .

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[Ti( $\mu$ -NBu<sup>t</sup>)<sub>2</sub>{MeC(NC<sub>6</sub>H<sub>11</sub>)<sub>2</sub>}<sub>2</sub>Cl<sub>2</sub>] (**4**). A solution of Li[MeC(NC<sub>6</sub>H<sub>11</sub>)<sub>2</sub>]·OEt<sub>2</sub> (0.261 g, 0.86 mmol) in THF (20 mL) was added over 10 min to a stirred solution of [Ti(NBu<sup>t</sup>)Cl<sub>2</sub>(py)<sub>3</sub>] (0.368 g, 0.86 mmol) in THF at -60 °C. The resulting solution was allowed to warm to room temperature and then stirred for 18 h. Volatiles were removed under reduced pressure, the resulting orange residue was dissolved in dichloromethane, and the mixture was filtered to remove LiCl. Evaporation of the solvent and recrystallization from ether yielded red crystals of **4**, which were washed with cold ether (2 × 5 mL) and dried *in vacuo*. Yield: 0.166 g (51%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, 25 °C): 4.68, 3.21 (2 × 2 H, 2 × m, 2 × NCHC<sub>5</sub>H<sub>10</sub>), 2.17 (6 H, s, overlapping 2 × MeCN<sub>2</sub>), 2.2–1.1 (40 H, series of multiplets corresponding to NCHC<sub>5</sub>H<sub>10</sub> of two inequivalent cyclohexyl rings), 1.19 (18 H, s, NBu<sup>t</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75.5 MHz, 25 °C): 178.9 (MeCN<sub>2</sub>), 73.7 (NCMe<sub>3</sub>), 59.9, 58.3 (2 × NCHC<sub>5</sub>H<sub>10</sub>), 34.0 (NCHC<sub>5</sub>H<sub>10</sub>), 31.0 (NCMe<sub>3</sub>), 26.6, 26.3, 26.2, 25.5 (some signals overlapping, NCHC<sub>5</sub>H<sub>10</sub>), 15.1 (overlapping 2 × MeCN<sub>2</sub>). IR: 1735 (w), 1650 (m), 1495 (s), 1454 (vs), 1415 (s), 1360 (vs), 1258 (m), 1195 (vs), 1185 (vs), 1141 (w), 1075 (m), 1027 (w), 1003 (m), 937 (w), 892 (m), 819 (w), 802 (w), 791 (w), 768 (w), 745 (m), 722 (w), 634 (vs), 563 (w), 533 (m), 505 (m), 408 (s). Anal. Calcd (found) for C<sub>36</sub>H<sub>68</sub>Cl<sub>2</sub>N<sub>6</sub>Ti<sub>2</sub>: C, 57.5 (58.1); H, 9.1 (8.8); N, 11.2 (11.5).

**Variable-Temperature NMR Experiments for [Ti(NR){PhC(NSiMe<sub>3</sub>)<sub>2</sub>}Cl(py)<sub>2</sub>] [R = Bu<sup>t</sup> (**1**), 2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub> (**2**), 2,6-C<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub> (**3**)].** Detailed procedures for **2** only are given here by way of example. Similar procedures were used for obtaining the corresponding rate and/or equilibrium constants for **1** and **3**.

A 0.05 mol·dm<sup>-3</sup> sample of [Ti(N-2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>){PhC(NSiMe<sub>3</sub>)<sub>2</sub>}Cl(py)<sub>2</sub>] (**2**) in CDCl<sub>3</sub> was prepared in the drybox. NMR integration yielded relative concentrations of **2**, **2'**, and free py at each temperature. The relative concentrations were converted to absolute concentrations by assuming that [**2**] + [**2'**] = 0.05 mol·dm<sup>-3</sup> and that [py] = [**2'**]. Kinetic parameters for the **2** → **2'** + py and **2'** + py → **2** processes were obtained from five <sup>1</sup>H NMR spectra of **2/2'** + py in the range 248 ≤ *T* ≤ 268 K in the intermediate-exchange regime. Lorentzian curve fitting of the *ortho* methyl group resonances afforded  $\nu_{1/2}$  (bandwidth at half-height) values from which were subtracted the estimated natural line widths (1.8 Hz at 228 K) to give corrected  $\nu_{1/2}$  values. The first-order (for **2** → **2'** + py) and pseudo-first-order rate constants (for **2'** + py → **2**) were calculated according to the expression  $k = \pi\nu_{1/2}$ .<sup>34</sup> The second-order rate constant  $k_{2'+py-2}$  for **2'** + py → **2** was obtained from the pseudo-first-order rate constant ( $k_{obs}$ ) and [py] at each temperature by assuming  $k_{obs} = k_{2'+py-2}$ [py]. Standard Eyring plots afforded the activation parameters listed in Table 3 according to standard procedures.<sup>35</sup> Further measurements of [**2**], [**2'**], and [py] were made in the range 228 ≤ *T* ≤ 243 K, but at these temperatures line-broadening contributions from **2** → **2'** + py are less than or comparable to the natural line width.

For **3**, a lineshape analysis to obtain rate constants and activation parameters was not possible due to the complex, overlapping multiplet nature of the <sup>1</sup>H resonances. For **1–3**, equilibrium constants were measured and plots of ln *K*<sub>eq</sub> vs 1/*T* afforded  $\Delta H$  and  $\Delta S$  values. To confirm that solvent effects are not significant, we found the equilibrium  $\Delta H$  and  $\Delta S$  (and hence the derived  $\Delta G_{258}$ ) values in toluene-*d*<sub>8</sub> solution showed the same trends and as those found in CDCl<sub>3</sub>.

**Crystal Structure Determination of [Ti(N-2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>){PhC(NSiMe<sub>3</sub>)<sub>2</sub>}Cl(py)<sub>2</sub>] (**2**) and [Ti<sub>2</sub>( $\mu$ -NBu<sup>t</sup>)<sub>2</sub>{MeC(NC<sub>6</sub>H<sub>11</sub>)<sub>2</sub>}<sub>2</sub>Cl<sub>2</sub>] (**4**).** Crystal data collection and processing parameters are given in Table 1. Crystals were mounted in a film of RS3000 oil on a glass fiber and transferred to a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.<sup>36</sup> An absorption correction based on  $\psi$  scans was applied to the data, and equivalent reflections were merged. The structures were solved by direct methods (SIR92<sup>37</sup>). Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms; these were refined aniso-

**Table 1.** Crystallographic Data for [Ti(N-2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>){PhC(NSiMe<sub>3</sub>)<sub>2</sub>}Cl(py)<sub>2</sub>] (**2**) and [Ti<sub>2</sub>( $\mu$ -NBu<sup>t</sup>)<sub>2</sub>{MeC(NC<sub>6</sub>H<sub>11</sub>)<sub>2</sub>}<sub>2</sub>Cl<sub>2</sub>] (**4**)

	<b>2</b>	<b>4</b>
empirical formula	C <sub>31</sub> H <sub>42</sub> ClN <sub>5</sub> Si <sub>2</sub> Ti	C <sub>36</sub> H <sub>68</sub> Cl <sub>2</sub> N <sub>6</sub> Ti <sub>2</sub>
fw	624.24	751.66
temp/°C	-53(1)	-53(1)
wavelength/Å	0.710 73	0.710 73
space group	<i>P</i> 1̄ (No. 2)	<i>P</i> 1̄ (No. 2)
<i>a</i> /Å	11.219(5)	10.455(3)
<i>b</i> /Å	12.131(6)	10.637(5)
<i>c</i> /Å	13.208(7)	11.024(3)
$\alpha$ /deg	80.34(5)	90.52(4)
$\beta$ /deg	87.41(4)	112.62(3)
$\gamma$ /deg	75.13(3)	114.10(3)
<i>V</i> /Å <sup>3</sup>	1722.1(15)	1012.8(10)
<i>Z</i>	2	1
<i>d</i> (calcd)/Mg·m <sup>-3</sup>	1.20	1.23
abs coeff/mm <sup>-1</sup>	0.417	0.550
<i>R</i> ( <i>F</i> <sub>o</sub> ) <sup>a</sup>	0.054	0.0453
<i>R</i> <sub>w</sub> ( <i>F</i> <sub>o</sub> ) <sup>b</sup>	0.056	0.0495

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

tropically. For compound **2**, H atoms were placed in estimated positions with C–H = 0.96 Å and *U*<sub>iso</sub> = 1.3 × *U*<sub>equiv</sub> or *U*<sub>iso</sub> of the atom to which each was bonded and were refined “riding” on their respective supporting atoms. For compound **4**, all H atoms could be located from difference syntheses and were refined isotropically. For both structures, examination of the refined secondary extinction parameter and |*F*<sub>o</sub>| and |*F*<sub>c</sub>| for the strongest reflections and an agreement analysis suggested that no extinction correction or weighting scheme needed to be applied.

All crystallographic calculations were performed using SIR92<sup>37</sup> and CRYSTALS-PC.<sup>38</sup> Full listings of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See also paragraph at end of paper regarding Supporting Information.

## Results and Discussion

Although a variety of amidinate ligands of the general formula RC(NR')<sub>2</sub> have been described in the literature,<sup>16,17</sup> we were particularly attracted by the *N,N'*-bis(trimethylsilyl)benzamido-nato [PhC(NSiMe<sub>3</sub>)<sub>2</sub>] and *N,N'*-bis(cyclohexyl)acetamidinato [MeC(NC<sub>6</sub>H<sub>11</sub>)<sub>2</sub>] species because of the ease of preparation of their lithium salts<sup>31–33</sup> and the stabilizing properties they generally impart to their metal complexes.

Reaction of Li[PhC(NSiMe<sub>3</sub>)<sub>2</sub>] with the complex [Ti(NBu<sup>t</sup>)Cl<sub>2</sub>(py)<sub>3</sub>] at -40 °C in THF gave the mono(*N,N'*-bis(trimethylsilyl)benzamido)nitrogen imido derivatives [Ti(NBu<sup>t</sup>){PhC(NSiMe<sub>3</sub>)<sub>2</sub>}Cl(py)<sub>2</sub>] (**1**) in 62% yield after standard workup and recrystallization from hexane. Similarly the 2,6-disubstituted arylimido homologues [Ti(NAr){PhC(NSiMe<sub>3</sub>)<sub>2</sub>}Cl(py)<sub>2</sub>] [Ar = 2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub> (**2**), 2,6-C<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub> (**3**)] may also be prepared by simple metathesis reactions. The red compounds **1–3** are highly soluble in hydrocarbon solvents, and these solutions are very air- and moisture-sensitive. A summary of the syntheses and proposed structures for all the new compounds are shown in Scheme 1; full characterization data are listed in the Experimental Section.

Cooling of a hexane solution of [Ti(N-2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>){PhC(NSiMe<sub>3</sub>)<sub>2</sub>}Cl(py)<sub>2</sub>] (**2**) afforded X-ray-quality crystals. The molecular structure of **2** is shown in Figure 1, and selected bond lengths and angles are given in Table 2.

Compound **2** has a six-coordinate titanium(4+) center with two mutually *trans* py ligands both bonded *cis* to the N-2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub> and Cl moieties. The PhC(NSiMe<sub>3</sub>)<sub>2</sub> ligand thus has

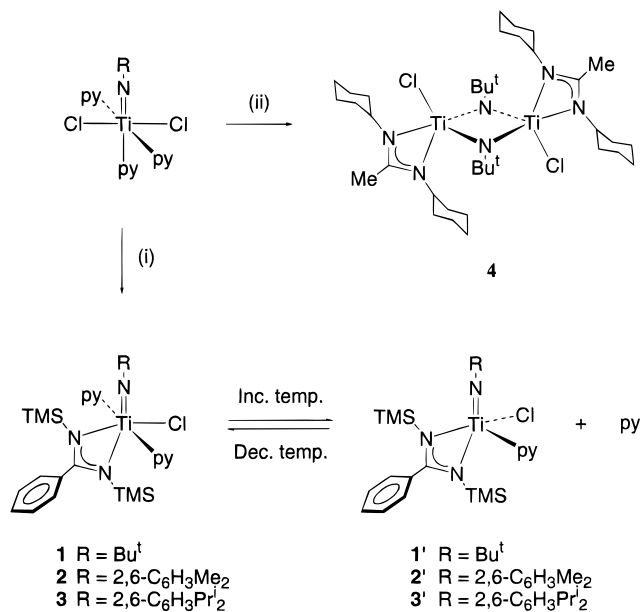
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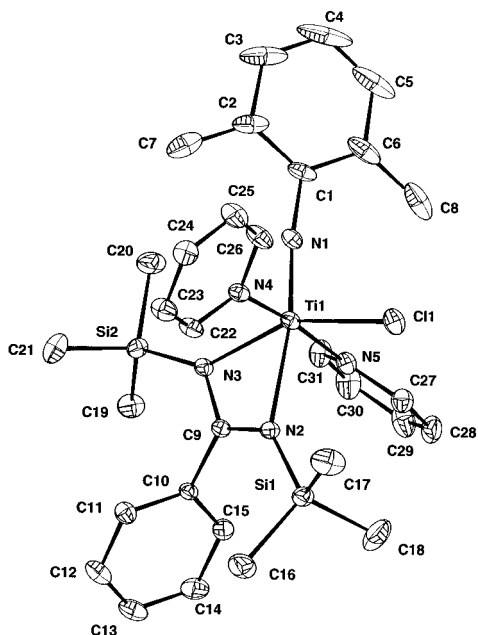
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Scheme 1<sup>a</sup>

<sup>a</sup> Reagents and conditions: (i) Li[PhC(NSiMe<sub>3</sub>)<sub>2</sub>] (1 equiv); THF; 18 h; for **1**, 62%, for **2**, 64%, and, for **3**, 29%. (ii) Li[MeC(NC<sub>6</sub>H<sub>11</sub>)<sub>2</sub>] (1 equiv); THF; 18 h, 51%.



**Figure 1.** CAMERON<sup>57</sup> plot of [Ti(N-2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>){PhC(NSiMe<sub>3</sub>)<sub>2</sub>}-Cl(py)<sub>2</sub>] (**2**). Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 20% probability level.

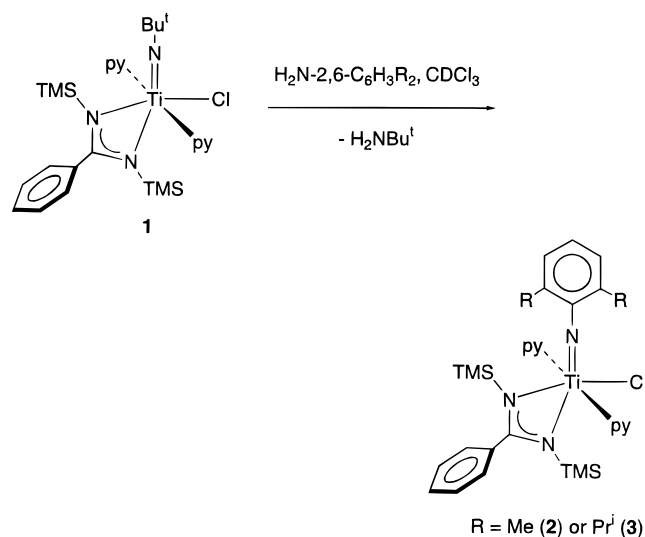
one N donor atom *cis* [N(3)] and one approximately *trans* [N(2)] to the imido nitrogen atom [N(1)]. The titanium–imido nitrogen bond length in **2** [Ti(1)–N(1) = 1.727(4) Å] is somewhat longer than those in the six-coordinate arylimido complexes [Ti(N-4-C<sub>6</sub>H<sub>4</sub>R)Cl<sub>2</sub>(py)<sub>3</sub>] [R = H, Ti=N = 1.714(2) Å; R = Me, Ti=N = 1.705(4) Å],<sup>9,10</sup> possibly indicative of steric interactions between the *ortho*-methyl of the arylimido ligand and the nearby SiMe<sub>3</sub> groups. In addition, the longer Ti=N bond length in **2** may also reflect a better net  $\sigma$ -donor ability of the PhC(NSiMe<sub>3</sub>)<sub>2</sub> ligand as compared to the {Cl(py)} ligand set in [Ti(N-4-C<sub>6</sub>H<sub>4</sub>R)Cl<sub>2</sub>(py)<sub>3</sub>], although this does not appear to result in a significant lengthening of the Ti–Cl bond in **2**. The *cis* (with respect to the imido group) Ti–N(benzamidinate) [Ti(1)–N(3) = 2.114(4) Å] bond length is similar to that found in other inorganic and organometallic titanium(4+) PhC(NSiMe<sub>3</sub>)<sub>2</sub>

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for [Ti(N-2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>){PhC(NSiMe<sub>3</sub>)<sub>2</sub>}Cl(py)<sub>2</sub>] (**2**)

Ti(1)–Cl(1)	2.403(2)	N(1)–C(1)	1.385(6)
Ti(1)–N(1)	1.727(4)	N(2)–Si(1)	1.737(4)
Ti(1)–N(2)	2.288(4)	N(2)–C(9)	1.304(6)
Ti(1)–N(3)	2.114(4)	N(3)–Si(2)	1.760(4)
Ti(1)–N(4)	2.250(4)	N(3)–C(9)	1.354(6)
Ti(1)–N(5)	2.247(4)	C(9)–C(10)	1.501(6)
Cl(1)–Ti(1)–N(1)	99.2(1)	Cl(1)–Ti(1)–N(5)	89.3(1)
Cl(1)–Ti(1)–N(2)	91.2(1)	N(1)–Ti(1)–N(5)	95.0(2)
N(1)–Ti(1)–N(2)	169.6(2)	N(2)–Ti(1)–N(5)	84.9(1)
Cl(1)–Ti(1)–N(3)	152.8(1)	N(3)–Ti(1)–N(5)	86.0(1)
N(1)–Ti(1)–N(3)	107.9(2)	N(4)–Ti(1)–N(5)	171.2(2)
N(2)–Ti(1)–N(3)	61.7(1)	Ti(1)–N(1)–C(1)	170.4(4)
Cl(1)–Ti(1)–N(4)	86.5(1)	N(2)–C(9)–N(3)	116.7(4)
N(1)–Ti(1)–N(4)	93.3(2)	N(2)–C(9)–C(10)	122.2(4)
N(2)–Ti(1)–N(4)	87.4(1)	N(3)–C(9)–C(10)	120.9(4)
N(3)–Ti(1)–N(4)	94.2(1)		

complexes [range 1.986(2)–2.177(2) Å for four examples],<sup>22,23,39,40</sup> whereas the *trans* Ti–N bond length [Ti(1)–N(2) = 2.288(4) Å] appears to be relatively long. This difference of 0.174(6) Å between the *cis* and *trans* bond lengths in **2** is indicative of the well-known, strong *trans* influence of multiply bonded ligands such as imido or oxo.<sup>1,10,41–43</sup>

NMR-scale reactions in CDCl<sub>3</sub> show that complexes **2** and **3** are also accessible by reaction of **1** with the appropriate arylamine. These imido exchange reactions are qualitatively



considerably slower than those reported previously for the [Ti-(NBu<sup>t</sup>)Cl<sub>2</sub>(py)<sub>3</sub>] system,<sup>9,10</sup> requiring *ca.* 6 d to go to completion.

The room-temperature <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1–3** are broad, indicating that one or more fluxional processes take place in solution. Examination of the variable-temperature NMR spectra showed that the behaviors of the three complexes are qualitatively the same, and so we shall discuss mainly the data for [Ti(N-2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>){PhC(NSiMe<sub>3</sub>)<sub>2</sub>}Cl(py)<sub>2</sub>] (**2**) by way of example. The variable-temperature <sup>1</sup>H NMR spectra of **2** in CDCl<sub>3</sub> between 243 and 296 K are reproduced in Figure 2.

The NMR spectra of **2** are consistent with the temperature-dependent, dynamic equilibrium between [Ti(N-2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>)-

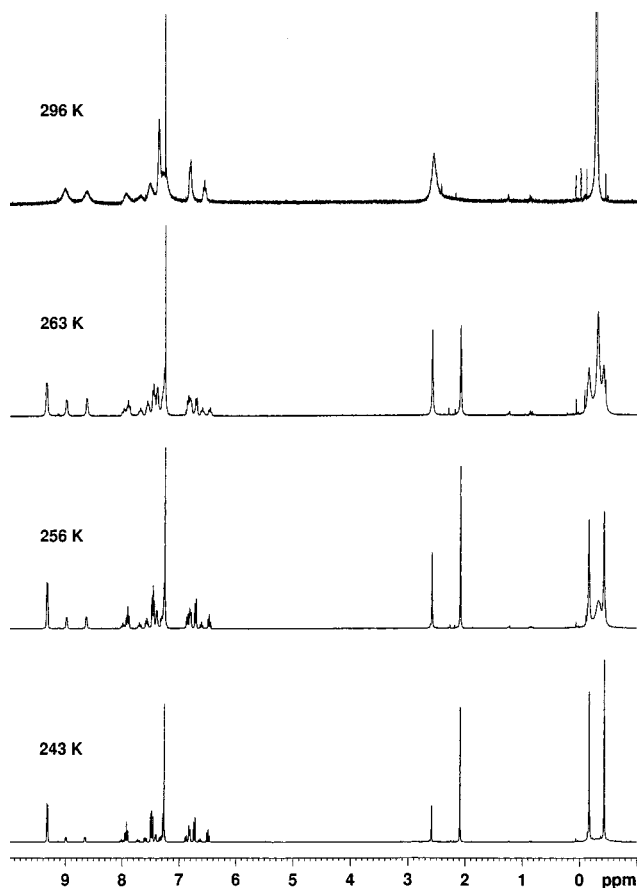
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**Figure 2.** Variable-temperature 300 MHz  $^1\text{H}$  NMR spectra for  $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$  (**2**) in  $\text{CDCl}_3$  in the range 243–296 K. The sharp singlet at  $\delta$  7.26 ppm is due to residual  $\text{CHCl}_3$ .

$\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$  (**2**) and the mono(pyridine) adduct  $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})]$  (**2'**) shown in Scheme 1. At intermediate temperatures, the relative concentrations of **2** and **2'** change with the amount of added pyridine in a way that is consistent with the dissociative equilibrium illustrated. The equilibrium constant associated with this process is therefore defined as  $K_{\text{eq}} = [\text{2}'][\text{py}]/[\text{2}]$ . Furthermore, the line widths of the *ortho*-methyl group resonances for **2** are independent of added py, whereas those of **2'** broaden as py is added, also consistent with the proposed equilibrium. At temperatures below 260 K, the signals assigned to **2** are relatively sharp and are consistent with the solid state structure. The remaining signals are assignable to **2'** and free pyridine. The structures proposed in Scheme 1 for **1'**–**3'** are the “least-motion” possibilities derived from **1**–**3**. I.e., the titanium atom has a pseudo trigonal bipyramidal geometry, with the imido nitrogen and one benzamidinate nitrogen occupying the apical sites and the remaining pyridine, chloride, and other benzamidinate nitrogen lying in the equatorial plane. A square-based pyramidal geometry with both benzamidinate nitrogen atoms and the Cl and py ligands *cis* to the imido ligand may also be possible. However, because the diastereotopic methyl groups of the *ortho*-isopropyl ring substituents in **3'** appear as a *pair* of doublets, we can rule out an alternative pseudo trigonal bipyramidal geometry (with the Cl or py ligand *trans* to the imido group), since this would have a molecular mirror plane containing the  $\text{Ti}=\text{N}(\text{imido})$  vector.

The  $^1\text{H}$  NMR  $\text{SiMe}_3$  resonances for **1'** and **2'** appear as broad singlets which broaden further into the baseline in the low-temperature spectra, and only for **3'** can two different  $\text{SiMe}_3$  resonances be resolved at low temperature. This fluxional behavior is consistent with rapid exchange of the inequivalent

**Table 3.** Thermodynamic and Kinetic Parameters for the Dissociative Equilibria of  $[\text{Ti}(\text{NR})\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$  [ $\text{R} = \text{Bu}^t$  (**1**), 2,6- $\text{C}_6\text{H}_3\text{Me}_2$  (**2**), 2,6- $\text{C}_6\text{H}_3\text{Pr}^i_2$  (**3**)]<sup>a</sup>

R	Thermodynamic Parameters		
	$\Delta H/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\Delta G_{258}/\text{kJ}\cdot\text{mol}^{-1}$
$\text{Bu}^t$ ( <b>1</b> )	$38.7 \pm 1.5$	$108 \pm 5$	$10.8 \pm 2.8$
2,6- $\text{C}_6\text{H}_3\text{Me}_2$ ( <b>2</b> )	$47.3 \pm 1.9$	$142 \pm 5$	$10.7 \pm 3.2$
2,6- $\text{C}_6\text{H}_3\text{Pr}^i_2$ ( <b>3</b> )	$45.7 \pm 2.0$	$172 \pm 5$	$1.2 \pm 3.3$
Kinetic Parameters			
	$\Delta H^\ddagger/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S^\ddagger/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\Delta G^\ddagger_{258}/\text{kJ}\cdot\text{mol}^{-1}$
$\text{R} = \text{Bu}^t$			
$\mathbf{1} \rightarrow \mathbf{1}' + \text{py}$	$90.5 \pm 3.4$	$108 \pm 7$	$62.5 \pm 5.2$
$\mathbf{1}' + \text{py} \rightarrow \mathbf{1}$	$39.3 \pm 1.5$	$-45 \pm 3$	$51.0 \pm 2.3$
$\text{R} = 2,6\text{-C}_6\text{H}_3\text{Me}_2$			
$\mathbf{2} \rightarrow \mathbf{2}' + \text{py}$	$75.7 \pm 2.9$	$60 \pm 4$	$60.3 \pm 3.9$
$\mathbf{2}' + \text{py} \rightarrow \mathbf{2}$	$21.3 \pm 0.8$	$-108 \pm 7$	$49.2 \pm 2.6$

<sup>a</sup> See text for further details.

*N*- and *N'*- $\text{SiMe}_3$  groups as commonly observed for other transition metal bis(trimethylsilyl)benzamidinates. The mechanism of  $\text{SiMe}_3$  group exchange is unknown, and both an in-place rotation process and initial dissociation to a monodentate  $\text{PhC}(\text{NSiMe}_3)_2$  followed by a rearrangement process have been considered as possibilities.<sup>26,44</sup> Exchange between the  $\text{SiMe}_3$  groups in the bis(pyridine) complexes **1**–**3** is more easily “frozen out”. This implies<sup>35</sup> a greater steric hindrance to  $\text{SiMe}_3$  group exchange in the six-coordinate species, since the chemical shift differences between the two  $\text{SiMe}_3$   $^1\text{H}$  NMR resonances (of **3** and **3'**) are comparable in the slow-exchange regime.

The signals attributable to **1**–**3** increase in intensity relative to those of py and **1'**–**3'** as the temperature is lowered. Careful integration of signal intensities for variable-temperature  $^1\text{H}$  NMR spectra of solutions of  $[\text{Ti}(\text{NR})\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$  [ $\text{R} = \text{Bu}^t$  (**1**), 2,6- $\text{C}_6\text{H}_3\text{Me}_2$  (**2**), 2,6- $\text{C}_6\text{H}_3\text{Pr}^i_2$  (**3**)] of known concentration afforded equilibrium constants ( $K_{\text{eq}}$ ) at different temperatures. Table 3 lists the corresponding  $\Delta S$ ,  $\Delta H$ , and  $\Delta G_{258}$  values extracted from plots of  $\ln K_{\text{eq}}$  vs  $1/T$  shown in Figure 3.

The general magnitude of the  $\Delta G_{258}$  values ( $10.8 \pm 2.8$ ,  $10.7 \pm 3.2$ , and  $1.2 \pm 3.3$   $\text{kJ}\cdot\text{mol}^{-1}$  for  $\mathbf{1} \rightarrow \mathbf{1}' + \text{py}$ ,  $\mathbf{2} \rightarrow \mathbf{2}' + \text{py}$ , and  $\mathbf{3} \rightarrow \mathbf{3}' + \text{py}$ , respectively) shows that all three equilibria are effectively thermochemically neutral. This results in part from the large positive  $\Delta S$  (also consistent with the dissociative equilibrium as written), which nearly compensates for the endothermic  $\Delta H$  term as the temperature is increased. The values of  $\Delta H$  and  $\Delta S$  in Table 3 are within the ranges previously found for pyridine dissociation from first-row transition metal complexes.<sup>45</sup>

The trends in  $\Delta H$ ,  $\Delta S$ , and  $\Delta G_{258}$  for **1**–**3** merit discussion. The X-ray structures of homologous pairs of *tert*-butylimido and arylimido complexes generally show that the former group has a greater bond-lengthening (and, presumably, bond-weakening) effect on other ligands present.<sup>48,10,46–52</sup> The values of  $\Delta H$  for **2** and **3** are comparable within error but are significantly

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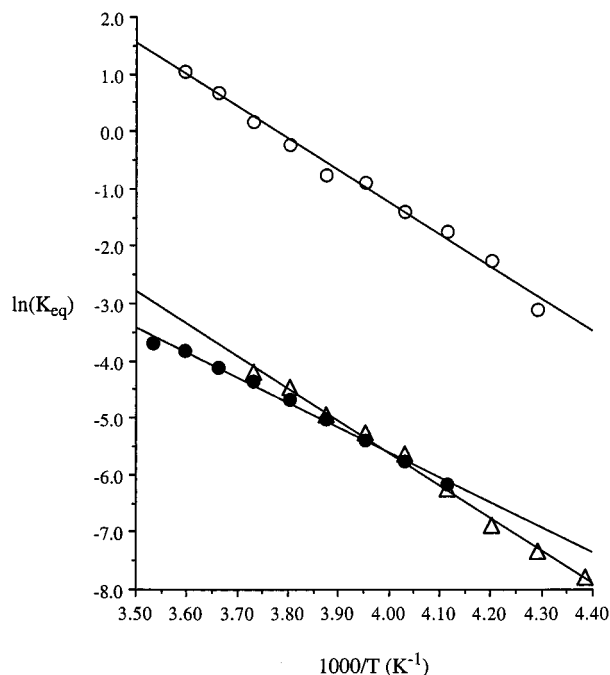
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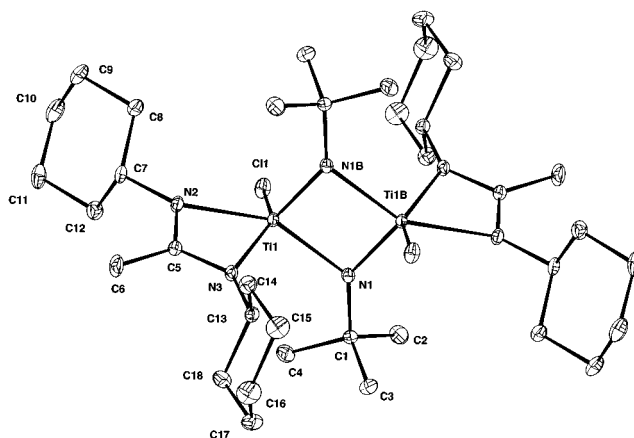
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**Figure 3.** Plots of  $\ln(K_{\text{eq}})$  vs  $1000/T$  for  $[\text{Ti}(\text{NR})\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$ . Key: NR =  $\text{NBu}^t$  (**1**, ●),  $\text{N-2,6-C}_6\text{H}_3\text{Me}_2$  (**2**, △),  $\text{N-2,6-C}_6\text{H}_3\text{-Pr}^t_2$  (**3**, ○).

larger than that for **1**. This would be consistent with the Ti–pyridine bonds being slightly weaker in **1** than in **2** and **3**, although one cannot rule out nonbonded (steric) effects on the enthalpy terms as the imido N-substituent is varied. Interestingly,  $\Delta S$  for the dissociation of pyridine from **1**–**3** increases with the steric demands of the imido substituent. Indeed the  $\Delta H$  values for  $\mathbf{2} \rightarrow \mathbf{2}' + \text{py}$  and  $\mathbf{3} \rightarrow \mathbf{3}' + \text{py}$  are very similar, and so the *ca.* 60-fold difference in  $K_{\text{eq}}$  at 258 K (and associated *ca.* 10  $\text{kJ}\cdot\text{mol}^{-1}$  difference in  $\Delta G_{258}$ ) is mostly attributable to entropy effects. We interpret the increase in  $\Delta S$  from  $\mathbf{1} \rightarrow \mathbf{1}' + \text{py}$  to  $\mathbf{3} \rightarrow \mathbf{3}' + \text{py}$  as reflecting increased steric hindrance to internal rotation etc. in the six-coordinate complexes as compared with that in the five-coordinate  $\mathbf{1}'$ – $\mathbf{3}'$ .

We have also extracted kinetic parameters for the dynamic equilibria of **1** and **2**.  $^1\text{H}$  NMR spectra of solutions of **1** and **2** with known concentrations were recorded at 5 K intervals between 248 and 278 K and between 248 and 268 K, respectively, in the intermediate-exchange regime. Standard procedures (see Experimental Section) afforded the rate constants for  $\mathbf{1} \rightarrow \mathbf{1}' + \text{py}$  and  $\mathbf{2} \rightarrow \mathbf{2}' + \text{py}$  (and for the reverse processes,  $\mathbf{1}' + \text{py} \rightarrow \mathbf{1}$  and  $\mathbf{2}' + \text{py} \rightarrow \mathbf{2}$ ). Table 3 lists the corresponding  $\Delta S^\ddagger$ ,  $\Delta H^\ddagger$ , and  $\Delta G_{258}^\ddagger$  values extracted from Eyring plots. For the purposes of discussion, we shall refer only to the data for **2**. The difference (*ca.* 11  $\text{kJ}\cdot\text{mol}^{-1}$ ) between the (activation)  $\Delta G_{258}^\ddagger$  values for  $\mathbf{2} \rightarrow \mathbf{2}' + \text{py}$  and for  $\mathbf{2}' + \text{py} \rightarrow \mathbf{2}$  compares well with the (thermodynamic)  $\Delta G_{258}$  value of  $10.7 \pm 3.2 \text{ kJ}\cdot\text{mol}^{-1}$  obtained from the equilibrium constants. These results are consistent with a single transition state, and the  $\Delta S^\ddagger$  values imply dissociative and associative activation for the  $\mathbf{2} \rightarrow \mathbf{2}' + \text{py}$  and  $\mathbf{2}' + \text{py} \rightarrow \mathbf{2}$  processes, respectively. The activation enthalpy for py loss from **2** ( $\Delta H^\ddagger = 75.7 \pm 2.9 \text{ kJ}\cdot\text{mol}^{-1}$ ) is substantially greater than that for py addition to  $\mathbf{2}'$  ( $\Delta H^\ddagger = 21.3 \pm 0.8 \text{ kJ}\cdot\text{mol}^{-1}$ ). This is consistent with early Ti–py bond formation along the  $\mathbf{2}' + \text{py} \rightarrow \mathbf{2}$  reaction



**Figure 4.** CAMERON<sup>57</sup> plot of  $[\text{Ti}_2(\mu\text{-NBu}^t)_2\{\text{MeC}(\text{NC}_6\text{H}_{11})_2\}_2\text{Cl}_2]$  (**4**). Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 20% probability level. Atoms carrying the suffix “B” are related to their counterparts by the symmetry operator  $[2 - x, 1 - y, 1 - z]$ .

coordinate or/and minimal preorganization of  $\mathbf{2}'$  before pyridine coordination occurs. The data for **1** show trends similar to those for **2**.

While this work was in progress, Hagadorn and Arnold reported the bis(benzamidinato)titanium imido complexes  $[\text{Ti}(\text{NSiMe}_3)\{\text{PhC}(\text{NSiMe}_3)_2\}_2]$ <sup>18</sup> and  $[\text{Ti}(\text{NBu}^t)\{\text{PhC}(\text{NSiMe}_3)_2\}_2]$ .<sup>53</sup> We attempted to prepare bis(benzamidinato) imido derivatives from our mono(benzamidinato) complexes but could not isolate a pure product. The binuclear group 4  $\mu$ -imido amidinates  $[\text{Ti}_2(\mu\text{-NPh})_2\{\mu\text{-HC}(\text{NPh})_2\}_2\{\text{HC}(\text{NPh})_2\}_2]$ <sup>19</sup> and  $[\text{Zr}_2(\mu\text{-NSiMe}_3)_2(\eta^2\text{-PhCNSiMe}_3)_2\{\text{PhC}(\text{NSiMe}_3)_2\}_2]$ <sup>21</sup> were also recently described. So far in our studies, we have only found evidence for mononuclear terminal titanium imido species when using the *N,N'*-bis(trimethylsilyl)benzamidinate ligand.

We were also interested in preparing titanium imido complexes supported by the *N,N'*-bis(cyclohexyl)acetamidinate group so as to explore the effects of modifying the steric requirements of the supporting amidinate ligand in these titanium imido systems. Thus reaction of  $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{py})_3]$  with 1 equiv of  $\text{Li}[\text{MeC}(\text{NC}_6\text{H}_{11})_2]$  in THF at  $-60^\circ\text{C}$  gave a color change to dark orange after 18 h. Subsequent workup and crystallization from diethyl ether afforded dark red crystals of the binuclear complex  $[\text{Ti}_2(\mu\text{-NBu}^t)_2\{\text{MeC}(\text{NC}_6\text{H}_{11})_2\}_2\text{Cl}_2]$  (**4**; see Scheme 1) which were suitable for X-ray diffraction analysis. The molecular structure of **4** is shown in Figure 4, and selected bond lengths and angles are given in Table 4.

The solution  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR data for **4** are consistent with the solid state structure, which shows a crystallographically-imposed centrosymmetric, binuclear geometry with five-coordinate titanium centers, each possessing a terminal chloride and *N,N'*-bis(cyclohexyl)acetamidinate ligand. The titanium atoms are bridged by two *tert*-butylimido groups, each having a trigonal planar nitrogen atom. A search of the Cambridge Structural Database<sup>54,55</sup> showed the geometry of the central  $\{\text{Ti}_2(\mu\text{-NBu}^t)_2\}$  core in **4** to be similar to that found in a number of other complexes (with a range of different terminal ligand types) containing this fragment. There is a significant asymmetry in the Ti–( $\mu$ -N) bond lengths of **4** [ $\text{Ti}(1)\text{--N}(1) = 1.835(3) \text{ \AA}$ ;  $\text{Ti}(1)\text{--N}(1\text{B}) = 1.997(3) \text{ \AA}$ ]. The electronic origins of substantially asymmetric M–( $\mu$ -N) bond lengths in certain group 6 complexes possessing a central  $\{\text{M}_2(\mu\text{-NR})_2\}$  fragment have

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**Table 4.** Selected Bond Lengths (Å) and Angles (deg) for  $[\text{Ti}_2(\mu\text{-NBu}^t)_2\{\text{MeC}(\text{NC}_6\text{H}_{11})_2\}_2\text{Cl}_2]$  (**4**)<sup>a</sup>

Ti(1)⋯Ti(1B)	2.803(1)	N(2)–C(5)	1.332(5)
Ti(1)–Cl(1)	2.321(1)	N(2)–C(7)	1.469(4)
Ti(1)–N(1)	1.835(3)	N(3)–C(5)	1.330(4)
Ti(1)–N(1B)	1.997(3)	N(3)–C(13)	1.477(4)
Ti(1)–N(2)	2.112(3)	C(5)–C(6)	1.502(5)
Ti(1)–N(3)	2.076(3)	Ti(1)–Cl(1)	2.403(2)
N(1)–C(1)	1.471(4)		
Ti(1)⋯Ti(1B)–Cl(1B)	108.66(4)	N(1)–Ti(1)–N(2)	114.9(1)
Ti(1)⋯Ti(1B)–N(1B)	45.30(9)	Ti(1)–N(1)–C(1)	138.8(2)
Ti(1)⋯Ti(1B)–N(2B)	154.95(9)	Cl(1)–Ti(1)–N(3)	143.03(9)
Ti(1)⋯Ti(1B)–N(3B)	104.24(8)	N(1)–Ti(1)–N(3)	106.7(1)
Cl(1)–Ti(1)–N(1)	108.31(9)	N(1B)–Ti(1)–N(2)	152.2(1)
Cl(1)–Ti(1)–N(1B)	99.24(8)	N(1B)–Ti(1)–N(3)	94.7(1)
N(1)–Ti(1)–N(1B)	86.1(1)	N(2)–Ti(1)–N(3)	62.9(1)
Cl(1)–Ti(1)–N(2)	91.41(9)	Ti(1)–N(1)–Ti(1B)	93.9(1)

<sup>a</sup> Atoms carrying the suffix “B” are related to their counterparts by the symmetry operator  $[2 - x, 1 - y, 1 - z]$ .

been discussed in detail previously by Nugent and co-workers.<sup>56</sup> These researchers suggested that a substantial distortion of the  $\text{M}(\mu\text{-N})$  bond lengths in *four*-coordinate group 4  $\{\text{M}_2(\mu\text{-NR})_2\}$ -containing complexes, however, is not expected on electronic grounds. Our interpretation of Nugent and co-workers’ theoretical model suggests that *five*-coordinate complexes having a geometry of the type shown by **4** should also be free of such distortions—according to electronic arguments at least. We therefore attribute the difference in the  $\text{Ti}(1)\text{--}$

$\text{N}(1)$  and  $\text{Ti}(1)\text{--N}(1\text{B})$  bond lengths in **4** mainly to steric effects arising from the cyclohexyl rings lying somewhat asymmetrically over the  $\{\text{Ti}_2(\mu\text{-NBu}^t)_2\}$  unit.

The contrasting structures of  $[\text{Ti}(\text{NR})\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$  (**1–3**) and  $[\text{Ti}_2(\mu\text{-NBu}^t)_2\{\text{MeC}(\text{NC}_6\text{H}_{11})_2\}\text{Cl}_2]$  (**4**) show the importance of the amidinate N-substituent in these systems. We have also attempted to prepare (arylimido)titanium complexes containing the *N,N'*-bis(cyclohexyl)acetamidinate ligand, but these reactions have so far only provided complex, inseparable mixtures.

## Summary and Conclusions

We have prepared and characterized some novel benzamidinato- and acetamidinato-supported titanium imido complexes. The solution dynamic equilibrium processes in the mononuclear titanium imido complexes **1–3** have been fully analyzed and show a substantial entropic contribution to the equilibrium constants. We are currently exploring the reaction chemistry of these and other early transition metal amidinates containing metal–ligand multiple bonds.

**Acknowledgment.** This work was supported by grants (to P.M.) from the EPSRC, Leverhulme Trust, and Royal Society. We thank the EPSRC for a studentship (to P.J.S.) and the provision of an X-ray diffractometer. We acknowledge the use of the EPSRC Chemical Database Service at Daresbury Laboratory.

**Supporting Information Available:** Eyring plots for **1** and **2** and  $\ln K_{\text{eq}}$  vs  $1/T$  plots for **1–3** (7 pages). X-ray crystallographic files, in CIF format, for **2** and **4** are available on the Internet only. Ordering and access information is given on any current masthead page.

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