Inorg. Chem. **2000,** *39,* 2001−2005 **2001**

Titanium and Niobium Imido Complexes Derived from Diamidoamine Ligands

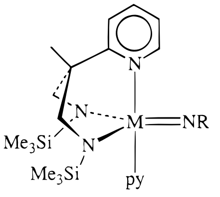
Philip E. Collier,[†] Stephen M. Pugh,[†]
Howard S. C. Clark,[‡] Jason B. Love,[‡]
Alexander J. Blake,[§] F. Geoffrey N. Cloke,[‡,||] and
Philip Mountford*,[†]

Inorganic Chemistry Laboratory, South Parks Road,
Oxford OX1 3QR, U.K., School of Chemistry, Physics and
Environmental Science, University of Sussex,
Brighton, BN1 9QJ, U.K., School of Chemistry, University
of Nottingham, Nottingham, NG7 2RD, U.K.

Received August 23, 1999

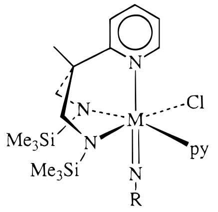
Introduction

Transition metal imido chemistry has attracted considerable interest, and a wide range of ancilliary ligand environments for the $M{=}NR$ functional group has been explored. Much of the recent activity in groups 4 and 5 imido chemistry has centered around reactions of the $M{=}NR$ functional group itself,[1−10] although the role of imides as supporting ligands (e.g., in olefin metathesis or polymerization catalysis) also continues to be developed.[11−14] As part of an ongoing research program in early transition metal imido chemistry,[2,15−20] we have described the synthesis and reactivity of complexes of the types **I** and **II**, which contain $M{=}NR$ groups supported in part by fac-coordinating diamidopyridine $MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2$ (N_2N_{py}) ligands (attempts to prepare vanadium(V) analogues lead to **III**).[21−24] A principal motivation for using these coligands was



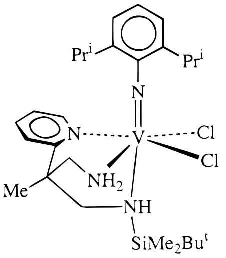
M = Ti, Zr; R = Bu^t, aryl

I



M = Nb, Ta; R = Bu^t, aryl

II



III

the reporting by Wolczanski and co-workers of highly reactive imido transients of the type $M(NR)X_2$ (X = sterically demanding amide or siloxide) generated in situ by alkane elimination from corresponding amidoalkyl precursors $[M(NHR)(R')(X)_2]$.[3,25−27] We envisaged that incorporation of a potentially labile donor group (e.g., pyridyl in N_2N_{py}) into a supporting diamide ligand set might allow for reversible generation of related reactive intermediates by dissociation of the labile donor.

We were therefore interested in preparing imido complexes with other tridentate diamide Lewis base donor ligands. A number of diamide Lewis donor ligand systems have been described recently,[28−36] especially in the context of the search for new olefin polymerization catalysts. The dianionic diamidoamine ligand $[Me_3SiN(CH_2CH_2NSiMe_3)_2]^{2-}$ (N_2N^{2-}) has

---

* To whom correspondence should be addressed. E-mail: Philip.Mountford@chemistry.oxford.ac.uk.

[†] Inorganic Chemistry Laboratory.

[‡] University of Sussex.

[§] University of Nottingham.

[||] E-mail: F.G.Cloke@sussex.ac.uk.

(1) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.
(2) Mountford, P. *Chem. Commun.* **1997**, 2127 (Feature Article).
(3) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1997**, *119*, 10696.
(4) Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.* **1993**, *32*, 131.
(5) Polse, J. L.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 13405.
(6) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705.
(7) Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 2669.
(8) Blake, R. E.; Antonelli, D. M.; Henling, L. M.; Schaefer, W. P.; Hardcastle, K. I.; Bercaw, J. E. *Organometallics* **1998**, *17*, 718.
(9) de With, J.; Horton, A. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 903.
(10) Gountchev, T. I.; Tilley, T. D. *J. Am. Chem. Soc.* **1997**, *119*, 12831.
(11) Antonelli, D. M.; Leins, A.; Stryker, J. M. *Organometallics* **1997**, *16*, 2500.
(12) Scheuer, S.; Fischer, J.; Kress, J. *Organometallics* **1995**, *14*, 2627.
(13) For imides in olefin polymerization catalysis. Coles, M. P.; Dalby, C. I.; Gibson, V. C.; Clegg, W.; Elsegood, M. R. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1709. Chan, M. C. W.; Chew, K. C.; Dalby, C. I.; Gibson, V. C.; Kohlmann, A.; Little, I. R.; Reed, W. *Chem. Commun.* **1998**, 1673.
(14) For imides in ring-opening metathesis polymerization catalysis. Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. Gibson, V. C. *Adv. Mater.* **1994**, *6*, 37.
(15) Wilson, P. J.; Blake, A. J.; Mountford, P.; Schröder, M. *Chem. Commun.* **1998**, 1007.
(16) Stewart, P. J.; Blake, A. J.; Mountford, P. *Organometallics* **1998**, *17*, 3271.
(17) McInnes, J. M.; Mountford, P. *Chem. Commun.* **1998**, 1669.
(18) Blake, A. J.; Dunn, S. C.; Green, J. C.; Jones, N. M.; Moody, A. G.; Mountford, P. *Chem. Commun.* **1998**, 1235.
(19) Swallow, D.; McInnes, J. M.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1998**, 2253.
(20) McInnes, J. M.; Swallow, D.; Blake, A. J.; Mountford, P. *Inorg. Chem.* **1998**, *37*, 5970.
(21) Blake, A. J.; Collier, P. E.; Gade, L. H.; McPartlin, M.; Mountford, P.; Schubart, M.; Scowen, I. J. *Chem. Commun.* **1997**, 1555.
(22) Collier, P. E.; Pugh, S. M.; Gade, L. H.; Mountford, P. Unpublished results.
(23) Bashall, A.; Collier, P. E.; Gade, L. H.; McPartlin, M.; Mountford, P.; Trösch, D. T. *Chem. Commun.* **1998**, 2555.
(24) Pugh, S. M.; Cloke, F. G. N.; Wilson, D. J.; Gade, L. H.; Nixon, J. F.; Mountford, P. Manuscript in preparation.
(25) Schaller, C. P.; Bonanno, J. B.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1994**, *116*, 4133.
(26) 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.
(27) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731.
(28) Guérin, F.; McConville, D. H.; Vittal, J. D.; Yap, G. A. P. *Organometallics* **1998**, *17*, 5172.
(29) Guérin, F.; McConville, D. H.; Vittal, J. D. *Organometallics* **1997**, *16*, 1491.
(30) Cai, S.; Schrock, R. R.; Kempe, R. R.; Davis, W. M. *Polyhedron* **1998**, *17*, 749.
(31) Schrock, R. R.; Seidel, S. W.; Schrodi, Y.; Davis, W. M. *Organometallics* **1999**, *18*, 428.
(32) Liang, L.-C.; Schrock, R. R.; Davis, W. M.; McConville, D. H. *J. Am. Chem. Soc.* **1999**, *121*, 5797.

10.1021/ic991014c CCC: $19.00

previously been used by us[37,38] and others[39] in nonimido Group 4 chemistry. Like its diamidopyridine N_2N_{py} analogue,[40,41] the N_2N ligand can adopt a *fac*-coordination mode. We describe here new imido complexes derived from the N_2N ligand system.

Experimental Section

General Methods and Instrumentation. General methods used in our group have been described previously.[16,20] ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker DPX 300 or a Varian Unity Plus 500 spectrometer at ambient temperature. IR spectra were recorded on either a Perkin-Elmer 1600 Series or a Mattson Polaris FT-IR spectrometer in the range 4000−400 cm^{-1}. Mass spectra were recorded on a AEI MS902 mass spectrometer. Elemental analyses were carried out by the analysis laboratory of these departments.

Literature Preparations. $Li_2[N_2N]$,[37,38] $[Ti(NR)Cl_2(py)_3]$ (R = Bu^t, 2,6-$C_6H_3Pr^i{}_2$),[42] and $[Nb(NBu^t)Cl_3(py)_2]$[43] were prepared according to literature methods.

$[Ti(NBu^t)(N_2N)py)]$ (1). To a solution of $[Ti(NBu^t)Cl_2(py)_3]$ (561 mg, 1.31 mmol) in benzene (35 cm^3) was added $Li_2[N_2N]$ (435 mg, 1.31 mmol) in benzene (40 cm^3) at room temperature. After being stirred for 16 h, the solution was filtered and the volatiles were removed under reduced pressure. Subsequent extraction of the brown solid into pentane (20 cm^3) was followed by filtration. Recrystallization of the solution from a saturated pentane solution (6 cm^3) at −25 °C yielded yellow crystals of **1** that were dried in vacuo. Yield: 280 mg (41%).

^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): δ 8.89 (2 H, d, J = 6.6 Hz, 2-NC_5H_5), 6.85 (1 H, t, J = 6.6 Hz, 4-NC_5H_5), 6.52 (2 H, apparent t, apparent J = 8.0 Hz, 3-NC_5H_5), 3.27, 3.14, 2.78, 2.33 (4 × 2 H, 4 × m, CH_2CH_2), 1.53 (9 H, s, Bu^t), 0.41 (9 H, s, $SiMe_3$ trans to py), 0.19 (18 H, s, $SiMe_3$ cis to py). $^{13}C-\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 298 K): δ 151.0 (2-NC_5H_5), 137.3 (4-NC_5H_5), 123.2 (3-NC_5H_5), 68.7 (CMe_3), 59.8, 47.2 (2 × CH_2), 34.2 (CMe_3), 1.9 ($SiMe_3$ cis to py), 0.2 ($SiMe_3$ trans to py). IR (CsBr plates, Nujol, cm^{-1}): 1602 (w), 1350 (w), 1251 (m), 1237 (m), 1229 (m), 1211 (w), 1150 (w), 1130 (w), 1115 (w), 1075 (w), 1034 (w), 946 (m), 909 (w), 872 (m), 841 (m), 779 (w), 740 (w), 696 (w), 680 (w), 633 (w), 531 (w), 516 (w), 490 (w), 415 (w), 404 (w). Anal. Found (calcd for $C_{22}H_{49}N_5Si_3Ti$): C, 50.8 (51.2);H, 9.9 (9.6); N, 13.5 (13.6).

$[Ti(N\text{-}2,6\text{-}C_6H_3Pr^i{}_2)(N_2N)(py)]$ (2). A solution of $[Ti(N\text{-}2,6\text{-}C_6H_3\text{-}Pr^i{}_2)Cl_2(py)_3]$ (535 mg, 0.99 mmol) was dissolved in benzene (20 cm^3) and cooled to 5 °C. To this was added a solution of $Li_2[N_2N]$ (329 mg, 0.99 mmol) in benzene (40 cm^3) also at 5 °C. The solution was allowed to warm to room temperature and was stirred for 17 h. The volatiles were removed under reduced pressure, and the solid was extracted into pentane (25 cm^3). The solution was concentrated, and recrystallization at −80 °C produced dark-orange crystals of **2** that were dried in vacuo. Yield: 281 mg (46%).

^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): δ 8.77 (2 H, br. s, 2-NC_5H_5), 7.16 (2 H, d, J = 7.5 Hz, 3-$C_6H_3Pr^i{}_2$), 6.92 (1 H, t, J = 7.5 Hz, 4-C_6H_3-$Pr^i{}_2$), 6.77 (1 H, t, J = 7.6 Hz, 4-NC_5H_5), 6.45 (2 H, t, J = 6.7 Hz, 3-NC_5H_5), 4.79 (2 H, sept, J = 6.8 Hz, $CHMe_2$), 3.78, 3.26, 2.96, 2.42 (4 × 2 H, 4 × m, CH_2CH_2), 1.41 (12 H, d, J = 6.8 Hz, $CHMe_2$), 0.18 (9 H, s, $SiMe_3$ trans to py), 0.03 (18 H, s, $SiMe_3$ cis to py). $^{13}C-\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 298 K): δ 156.2 (1-$C_6H_3Pr^i{}_2$), 152.5 (2-NC_5H_5), 143.4 (2-$C_6H_3Pr^i{}_2$), 138.5 (4-NC_5H_5), 123.9 (3-NC_5H_5), 123.0 (3-$C_6H_3Pr^i{}_2$), 120.7 (4-$C_6H_3Pr^i{}_2$), 58.2, 48.3 (2 × CH_2), 26.8 ($CHMe_2$), 25.9 ($CHMe_2$), 1.5 ($SiMe_3$ cis to py), −1.0 ($SiMe_3$ trans to py). IR (CsBr plates, Nujol mull, cm^{-1}): 3041 (w), 2360 (w), 1601 (w), 1584 (w), 1444 (s), 1418 (m), 1323 (m), 1269 (s), 1253 (s), 1212 (w), 1152 (w), 1127 (w), 1104 (w), 1068 (m), 1041 (w), 1024 (w), 946 (s), 931 (s), 910 (m), 870 (s), 840 (vs), 782 (m), 753 (s), 696 (m), 680 (w), 636 (w), 557 (w), 525 (w), 504 (w), 434 (w). Anal. Found (calcd for $C_{30}H_{57}N_5Si_3Ti$): C, 57.0 (58.1); H, 9.4 (9.3); N, 11.1 (11.3).

Synthesis of $[Nb(NBu^t)Cl_2\{Me_3SiN(CH_2)_2NH(CH_2)_2N(SiMe_3)_2\}$-(py)] (3) and $[Nb(NBu^t)(N_2N)Cl]_x$ (4, x = 1 or 2). To a cooled (10 °C) solution of $[Nb(NBu^t)Cl_3(py)_2]$ (268 mg, 0.65 mmol) in benzene (30 cm^3) was added $Li_2[N_2N]$ (215 mg, 0.65 mmol) in benzene (20 cm^3). The solution was stirred for 17 h at room temperature, becoming yellow-brown during this time, before being filtered and the volatiles removed under reduced pressure. The brown residues were extracted into pentane (5 cm^3). White crystals of $[Nb(NBu^t)Cl_2\{Me_3SiN(CH_2)_2NH(CH_2)_2N(SiMe_3)_2\}(py)]$ (**3**) formed from the solution over 48 h at room temperature; these were collected by filtration and dried in vacuo. Yield of **3**: 55 mg (13%). Evaporation of the volatiles from the mother liquors afforded **4** as a light-orange oil that could not be crystallized. Yield: 67%.

Data for **3**. ^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): δ 9.67 (2 H, br. s, 2-NC_5H_5), 6.83 (1 H, t, J = 7.5 Hz, 4-NC_5H_5), 6.58 (2 H, apparent t, apparent J = 6.8 Hz, 3-NC_5H_5), 3.80, 3.02, 2.75, 2.19 (2 × 2 H, 4 × br m, CH_2CH_2), 1.27 (9 H, s, Bu^t), 0.62 (9 H, s, $NSiMe_3$), −0.05 (18 H, s, $N(SiMe_3)_2$). $^{13}C-\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 298 K): δ 152.9 (2-NC_5H_5), 137.9 (4-NC_5H_5), 124.0 (3-NC_5H_5), 53.0, 52.4, 50.4, 43.7 (4 × CH_2), 31.0 (CMe_3), 3.0 ($NSiMe_3$), 2.0 [$N(SiMe_3)_2$]; the quaternary $NCMe_3$ resonance was not observed. IR (CsBr plates, Nujol mull, cm^{-1}): 3237 (m), 1603 (m), 1488 (m), 1401 (w), 1307 (w), 1260 (s), 1247 (s), 1215 (m), 1152 (m), 1142 (m), 1128 (w), 1075 (s), 1050 (s), 1075 (w), 1029 (w), 1006 (m), 972 (s), 915 (s), 874 (s), 841 (s), 792 (s), 765 (m), 700 (m), 682 (m), 626 (w), 596 (w), 559 (w), 542 (m), 466 (w), 433 (w). Anal. Found (calcd for $C_{22}H_{50}N_5Cl_2NbSi_3$): C, 56.1 (56.2); H, 8.4 (8.0); N, 9.5 (9.7).

Data for **4**. Actual intensities are given assuming that the compound is monomeric. ^{1}H NMR (C_6D_6, 500.0 MHz, 298 K): δ 3.32, 2.81, 2.40 (4 H and 2 × 2 H, 3 × m, CH_2CH_2), 1.55 (9 H, s, Bu^t), 0.40 (9 H, s, amino $SiMe_3$), 0.22 (18 H, s, amido $SiMe_3$). $^{13}C-\{^1H\}$ NMR (C_6D_6, 125.7 MHz, 298 K): δ 67.6 (CMe_3), 50.9, 50.7 (2 × CH_2), 32.2 (CMe_3), 2.8 (amino $SiMe_3$), −0.1 (amido $SiMe_3$). EI-MS (assignments assume that M corresponds to a monomeric unit): m/z 516 (M^+), 501 ($M^+ - Me$).

Crystal Structure Determination of $[Ti(NBu^t)(N_2N)(py)]$ (1) and $[Nb(NBu^t)Cl_2\{Me_3SiN(CH_2)_2NH(CH_2)_2N(SiMe_3)_2\}(py)]$ (3). 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.[44] Data were collected using $\omega-\theta$ scans with Mo Kα radiation (λ = 0.710 73 Å), and absorption corrections were applied to the data. Equivalent reflections were merged, and the structures were solved by direct methods (SIR92[45]). Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms.

For **1** all H atoms were placed geometrically and refined in a riding model, and all non-H atoms were refined anisotropically. For **3** the methyl carbons of the Si(2) $SiMe_3$ group were disordered. The two sets of carbons were refined with 50% site occupancy factors in an isotropic model with each set of three carbons having a common isotropic U. Similarity restraints were applied to the Si−C bond lengths and angles subtended at Si. All other non-H atoms were freely refined

---

(33) Schrock, R. R.; Schattenmann, F.; Aizenberg, M.; Davis, W. M. *Chem. Commun.* **1998**, 199.

(34) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830.

(35) Schattenmann, F. J.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 989.

(36) Male, N. A. H.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2487.

(37) Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B. *J. Chem. Soc., Dalton Trans.* **1995**, 25.

(38) Clark, H. C. S.; Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B.; Wainwright, A. P. *J. Organomet. Chem.* **1995**, *501*, 333.

(39) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672.

(40) Friedrich, S.; Schubart, M.; Gade, L. H.; Scowen, I. J.; Edwards, A. J.; McPartlin, M. *Chem. Ber.-Recueil* **1997**, *130*, 1751.

(41) Friedrich, S.; Gade, L. H.; Edwards, A. J.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1993**, 2861.

(42) Blake, A. J.; Collier, P. E.; Dunn, S. C.; Li, W.-S.; Mountford, P.; Shishkin., O. V. *J. Chem. Soc., Dalton Trans.* **1997**, 1549.

(43) Sundermeyer, J.; Putterlik, J.; Foth, M.; Field, J. S.; Ramesar, N. *Chem. Ber.* **1994**, *127*, 1201.

(44) Cosier, J.; Glazer, A. M. *J. Appl. Crystallogr.* **1986**, *19*, 105.

(45) Altomare, A.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

anisotropically. The amino N−H H(1) and the pyridine and methylene H atoms were located from Fourier difference syntheses; other H atoms were placed geometrically. H atoms were refined in a riding model except for H(1), which was refined isotropically.

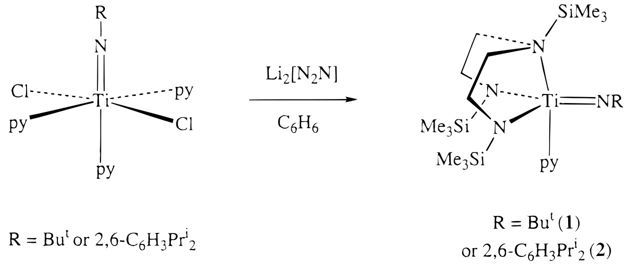
Both structures were refined against F^2 using a Chebychev weighting scheme.[46] Examination of the refined secondary extinction parameter[47] and an agreement analysis suggested that no extinction correction was required for either structure. The maximum residual electron density in the final Fourier difference syntheses of **3** lies close to the disordered carbon atoms with the closest contact being 0.22 Å from one of them.

All crystallographic calculations were performed using SIR92[45] and CRYSTALS-PC.[48] A full listing of atomic coordinates, bond lengths and angles, and displacement parameters for **1** and **3** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, issue 1.

Results and Discussion

The diamidopyridine complexes **I** and **II** are readily prepared[21,22] in fair to good yields by reaction of the appropriate imidometal complex [M(NR)Cl$_2$(py)$_3$] (M = Ti or Zr; R = Bu^t or 2,6-C$_6$H$_3$Pr$^i{}_2$)[42,49] or [M(NR)Cl$_3$(py)$_2$] (M = Nb or Ta; R = Bu^t or 2,6-C$_6$H$_3$Pr$^i{}_2$)[43,50] with Li$_2$[N$_2$N$_{py}$].[40] We have therefore used analogous routes for trying to prepare the diamidoamine analogues.

Reaction of Li$_2$[N$_2$N] with [Ti(NBu^t)Cl$_2$(py)$_3$] in benzene at room temperature gave [Ti(NBu^t)(N$_2$N)(py)] (**1**) as yellow crystals in 41% yield after recrystallization from pentane (eq 1):



N$_2$N = Me$_3$SiN(CH$_2$CH$_2$NSiMe$_3$)$_2$ (1)

Similarly, reaction of Li$_2$[N$_2$N] with [Ti(N-2,6-C$_6$H$_3$Pr$^i{}_2$)Cl$_2$(py)$_3$] gave dark-orange crystals of the arylimido analogue [Ti(N-2,6-C$_6$H$_3$Pr$^i{}_2$)(N$_2$N)(py)] (**2**) in 46% yield. Attempts to prepare a zirconium analogue by reaction of Li$_2$[N$_2$N] with [Zr(N-2,6-C$_6$H$_3$Pr$^i{}_2$)Cl$_2$(py)$_3$] in benzene lead to complex mixtures. The ^{1}H and ^{13}C NMR spectra for **1** and **2** show resonances for coordinated N$_2$N, NR (R = Bu^t or 2,6-C$_6$H$_3$Pr$^i{}_2$), and pyridine ligands; the symmetry of the spectra implies the presence of a molecular mirror plane. To establish unambiguously the coordination environment, an X-ray structure determination of **1** was carried out (Figure 1, Table 2).

The solid-state structure of [Ti(NBu^t)(N$_2$N)(py)] (**1**) is consistent with its solution NMR data. Molecules of **1** contain a fac-coordinated N$_2$N ligand, and the titanium center possesses an approximately trigonal bipyramidal geometry. The imido and N$_2$N amido nitrogens occupy the equatorial positions, while the N$_2$N amino and pyridine nitrogens are situated at the axial sites. The titanium−imido [Ti(1)−N(1) = 1.718(3) Å] and amido [Ti(1)−N(2) = 1.983(3), Ti(1)−N(4) = 2.033(3) Å] bond lengths reflect the different degrees of metal−ligand multiple bonding in these linkages and are very similar to those in the

Table 1. X-ray Data Collection and Processing Parameters for [Ti(NBu^t)(N$_2$N)(py)] (**1**) and [Nb(NBu^t)Cl$_2${Me$_3$SiN(CH$_2$)$_2$NH(CH$_2$)$_2$N(SiMe$_3$)$_2$}(py)] (**3**)

	1	**3**
empirical formula	C$_{22}$H$_{49}$N$_5$Si$_3$Ti	C$_{22}$H$_{50}$Cl$_2$N$_5$NbSi$_3$
fw	515.83	632.75
temp/°C	−123(1)	−123(1)
wavelength/Å	0.710 73	0.710 73
space group	$P2_1/c$	$P2_1/n$
a/Å	9.857(4)	9.0658(11)
b/Å	19.382(4)	25.139(2)
c/Å	16.339(5)	15.185(2)
β/°	102.26(4)	104.989(10)
V/Å^3	3050.4(14)	3342.9(5)
Z	4	4
d(calcd)/Mg m^{-3}	1.12	1.26
abs coeff/mm^{-1}	0.41	0.63
R indices [$I > 2\sigma(I)$]^a	R_1 = 0.062 wR2 = 0.111	R_1 = 0. 042 wR2 = 0.0430
R indices (all data)	R_1 = 0.0722 wR2 = 0.1231	R_1 = 0.0512 wR2 = 0.0479

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. wR2 = $\{\sum w(F_o{}^2 - F_c{}^2)^2/\sum(w(F_o{}^2)^2\}^{1/2}$.

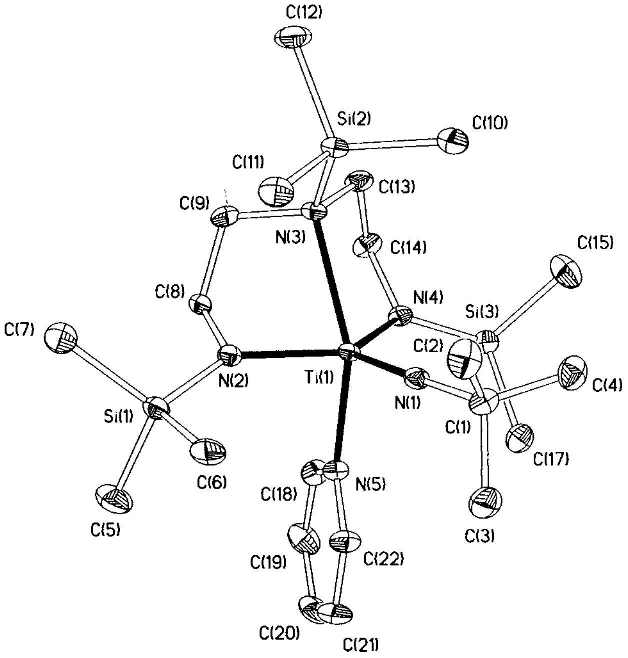


Figure 1. Displacement ellipsoid plot of [Ti(NBu^t)(N$_2$N)(py)] (**1**). Hydrogen atoms are omitted, and displacement ellipsoids are drawn at the 35% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Ti(NBu^t)(N$_2$N)(py)] (**1**)

Ti(1)−N(1)	1.718(3)	N(1)−C(1)	1.456(5)
Ti(1)−N(2)	1.983(3)	N(2)−Si(1)	1.708(3)
Ti(1)−N(3)	2.381(3)	N(3)−Si(2)	1.783(3)
Ti(1)−N(4)	2.033(3)	N(4)−Si(3)	1.713(3)
Ti(1)−N(5)	2.228(3)		
N(1)−Ti(1)−N(2)	113.8(1)	N(4)−Ti(1)−N(5)	87.9(1)
N(1)−Ti(1)−N(3)	112.6(1)	Ti(1)−N(1)−C(1)	175.2(3)
N(2)−Ti(1)−N(3)	78.2(1)	Ti(1)−N(2)−Si(1)	141.1(2)
N(1)−Ti(1)−N(4)	116.3(1)	Ti(1)−N(2)−C(8)	99.6(2)
N(2)−Ti(1)−N(4)	129.6(1)	Si(1)−N(2)−C(8)	118.5(2)
N(3)−Ti(1)−N(4)	78.7(1)	Ti(1)−N(4)−Si(3)	129.1(2)
N(1)−Ti(1)−N(5)	99.1(1)	Ti(1)−N(4)−C(14)	114.1(2)
N(2)−Ti(1)−N(5)	88.9(1)	Si(3)−N(4)−C(14)	114.6(2)
N(3)−Ti(1)−N(5)	148.3(1)		

---

(46) Carruthers, J. R.; Watkin, D. J. *Acta Crystallogr., Sect. A* **1979**, *35*, 698.

(47) Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664.

(48) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS*; Chemical Crystallography Laboratory: University of Oxford, U.K., 1996; Issue 10.

(49) Arney, D. J.; Bruck, M. A.; Huber, S. R.; Wigley, D. E. *Inorg. Chem.* **1992**, *31*, 3749.

(50) Chao, Y.-W.; Wexler, P. A.; Wigley, D. A. *Inorg. Chem.* **1989**, *28*, 3860.

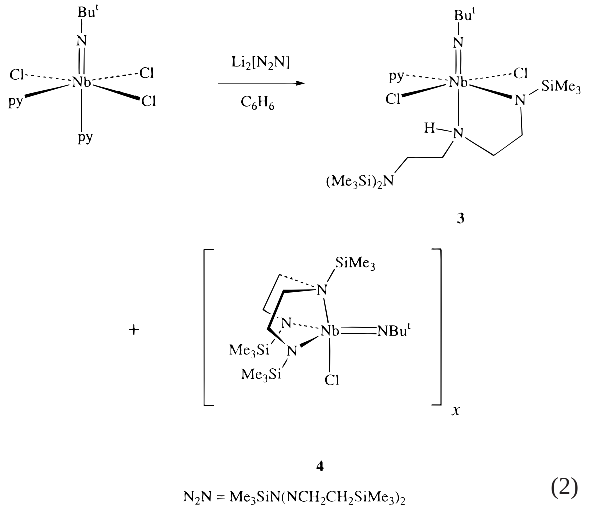
diamidopyridine homologue [Ti(NBu^t)(N$_2$N$_{py}$)(py)] [1.724(2), 1.983(2), and 2.025(2) Å, respectively].[21] The sums of angles subtended at the amido nitrogens N(2) and N(4) are 359.2 and 357.8°, showing that they are, in principle, capable of π-donating lone pair electron density to the otherwise 14-valence-electron metal center.

The axial Ti−N bond lengths in **1** indicate that the N$_2$N amino donor nitrogen is considerably less tightly bound [Ti(1)−N(3) = 2.381(3) Å] than the pyridine ligand for which Ti(1)−N(5) = 2.228(3) Å. The pyridine ligand in **1** is more strongly coordinated than in [Ti(NBu^t)(N$_2$N$_{py}$)(py)] for which Ti−N(py) = 2.278(2) Å, reflecting both the nature (i.e., tertiary silylamine versus pyridyl) and the orientation of the donor group trans to pyridine. In compound **1** the N$_2$N ligand gives rise to two five-membered chelate rings [i.e., Ti(1),N(2)C(8),C(9),N(3) and Ti(1),N(4),C(14),C(13),N(3)] and consequently the amino donor cannot attain a strictly trans position with respect to the pyridine giving N(3)−Ti(1)−N(5) = 148.3(1)°. In [Ti(NBu^t)(N$_2$N$_{py}$)-(py)] the diamidopyridine ligand forms two six-membered rings and the angle subtended at titanium between the two axial donors is 175.10(17)°.

Two other Ti(IV) complexes of N$_2$N have previously been crystallographically characterized, namely, [Ti(N$_2$N)Me$_2$] and [Ti(N$_2$N)Cl{CH(SiMe$_3$)$_2$}].[38] In these complexes the amino donor nitrogen is not coordinated [Ti$\cdots$N(amine) = 2.732(2) and 2.909(6) Å]. The amido nitrogens are more tightly bound [ave Ti−N(amide) = 1.904; range = 1.894(5)−1.910(2) Å] than in **1**.

The diamidoamine complex [Ti(NBu^t)(N$_2$N)py)] (**1**) is readily sublimed without loss of coordinated pyridine or decomposition at 75 °C/1 × 10^{-6} mbar. This is contrast to the diamidopyridine analogues [Ti(N$_2$N$_{py}$)(NR)(py)] (R = Bu^t or 2,6-C$_6$H$_3$Pr$^i{}_2$), which sublime with loss of pyridine to form [Ti(N$_2$N$_{py}$)(NR)].[22] The differing behavior of the N$_2$N and N$_2$N$_{py}$ systems is consistent with the different Ti−N(pyridine) bond strengths indicated by the crystal structures.

We were also interested in preparing group 5 imido complexes of the N$_2$N ligand. Reaction of Li$_2$[N$_2$N] with [V(N-2,6-C$_6$H$_3$Pr$^i{}_2$)Cl$_3$(thf)] failed to produce an isolable product. Reaction of Li$_2$[N$_2$N] with [Nb(Bu^t)Cl$_3$(py)$_2$] in benzene gave two different imidoniobium(V) products, namely, [Nb(NBu^t)Cl$_2${Me$_3$SiN(CH$_2$)$_2$NH(CH$_2$)$_2$N(SiMe$_3$)$_2$}(py)] (**3**) and [Nb(NBu^t)(N$_2$N)-Cl]$_x$ (**4**, x = 1 or 2) in 13% and 67% yield, respectively (eq 2):



N$_2$N = Me$_3$SiN(NCH$_2$CH$_2$SiMe$_3$)$_2$ (2)

Both products were reproducibly formed. Compound **3** was isolated as white crystals from pentane at room temperature, but compound **4** could only be obtained as an orange oil and was characterized by NMR spectroscopy and electron-impact mass spectrometry.

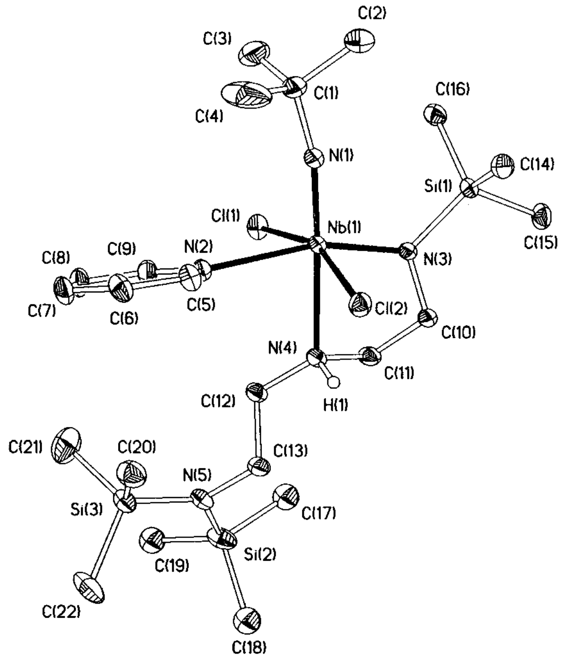


Figure 2. Displacement ellipsoid plot of [Nb(NBu^t)Cl$_2${Me$_3$SiN(CH$_2$)$_2$-NH(CH$_2$)$_2$N(SiMe$_3$)$_2$}(py)] (**3**). Carbon-bound hydrogen atoms are omitted, displacement ellipsoids are drawn at the 35% probability level, and the H atom is drawn as a sphere of arbitrary radius.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [Nb(NBu^t)Cl$_2${Me$_3$SiN(CH$_2$)$_2$NH(CH$_2$)$_2$N(SiMe$_3$)$_2$}(py)] (**3**)

Nb(1)−Cl(1)	2.4434(8)	N(5)−Si(3)	1.743(2)
Nb(1)−Cl(2)	2.4678(7)	N(1)−C(1)	1.458(3)
Nb(1)−N(1)	1.768(2)	N(3)−Si(1)	1.757(2)
Nb(1)−N(2)	2.442(2)	N(4)−H(1)	0.961(7)
Nb(1)−N(3)	1.995(2)	N(5)−Si(2)	1.732(2)
Nb(1)−N(4)	2.413(2)		
Cl(1)−Nb(1)−Cl(2)	159.24(3)	N(2)−Nb(1)−N(4)	85.14(7)
Cl(1)−Nb(1)−N(1)	97.58(8)	N(3)−Nb(1)−N(4)	79.51(8)
Cl(2)−Nb(1)−N(1)	99.33(8)	Nb(1)−N(1)−C(1)	167.1(2)
Cl(1)−Nb(1)−N(2)	84.79(6)	Nb(1)−N(3)−Si(1)	125.0(1)
Cl(2)−Nb(1)−N(2)	82.87(6)	Nb(1)−N(3)−C(10)	115.5(2)
N(1)−Nb(1)−N(2)	91.26(9)	Si(1)−N(3)−C(10)	117.9(2)
Cl(1)−Nb(1)−N(3)	96.56(6)	Nb(1)−N(4)−C(11)	102.3(1)
Cl(2)−Nb(1)−N(3)	90.96(7)	Nb(1)−N(4)−C(12)	125.0(2)
N(1)−Nb(1)−N(3)	104.02(9)	C(11)−N(4)−C(12)	112.4(2)
N(2)−Nb(1)−N(3)	164.29(8)	Nb(1)−N(4)−H(1)	100.83(6)
Cl(1)−Nb(1)−N(4)	83.13(6)	C(11)−N(4)−H(1)	106.8(2)
Cl(2)−Nb(1)−N(4)	79.25(6)	C(12)−N(4)−H(1)	107.9(1)
N(1)−Nb(1)−N(4)	176.26(9)	Si(2)−N(5)−Si(3)	126.4(1)
Si(2)−N(5)−C(13)	114.3(2)	Si(3)−N(5)−C(13)	119.0(2)

The NMR spectra of **3** show resonances for a coordinated pyridine ligand, a *tert*-butylimido group, two types of SiMe$_3$ group (ratio 2:1 with respect to NBu^t), and four methylene groups. Diffraction-quality crystals were grown from pentane at room temperature (Figure 2, Table 3).

Molecules of **3** contain a pseudo-octahedral niobium(V) center with a terminal *tert*-butylimido group and two mutually trans chloride ligands and a pyridine ligand cis to it. The coordination sphere is completed by a bidentate (Me$_3$Si)NCH$_2$CH$_2$N(H)CH$_2$-CH$_2$NSiMe$_3$ monoamidodiamine ligand. The bond lengths from niobium to the imide, pyridine, and chloride groups are within previously reported ranges.[51,52] The angles subtended at niobium between the equatorial donors and the imido nitrogen are all greater than 90°; this is a manifestation of the trans influence of multiply bonded ligands such as imide.[53,54] The former N_2N ligand in **3** has undergone a rearrangement leading to the transfer of a central $SiMe_3$ group to a terminal nitrogen, as well as gaining an additional hydrogen atom on the central nitrogen. The mechanism of the rearrangement and H-atom abstraction is unclear. Apart from possible trace hydrolysis and associated decomposition processes, the origin of **3** could be attributed to competing redox side reactions as previously found in the synthesis of the vanadium complex **III**.[22] Six-coordinate group 5 imido complexes have been structurally characterized previously.[1,51,52,55]

The NMR spectra of the major product $[Nb(NBu^t)(N_2N)Cl]_x$ (**4**) also show resonances for *tert*-butyl and two trimethylsilyl groups (ratio of 2:1 with respect to NBu^t), but unlike **3** there are only two types of methylene group, the hydrogens of which appear as an ABCD spin system. Compound **4** does not contain pyridine, and the quaternary and methyl ^{13}C resonances of the NBu^t ligand appear at 67.6 and 32.2 ppm, respectively. These resonances are very close to those of the *tert*-butyl group in the crystallographically characterized $[Nb(NBu^t)(N_2N_{py})Cl(py)]$ (67.5 and 32.6 ppm, respectively)[22] and are therefore consistent with **4** possessing a terminal $Nb{=}NBu^t$ linkage.

We are unable to distinguish between a five-coordinate mononuclear $[Nb(NBu^t)(N_2N)Cl]$ or six-coordinate binuclear $[Nb_2(NBu^t)_2(N_2N)_2(\mu\text{-}Cl)_2]$ structure for **4**. The electron impact mass spectrum of **4** shows the correct isotopic distribution envelope and m/z ratio for monomeric $[Nb(NBu^t)(N_2N)Cl]^+$, and no fragments with higher m/z ratio were observed. This suggests that **4** is monomeric in the gas phase but could also be consistent with a binuclear species that readily fragments under EI conditions. Group 5 metal complexes of the N_2N ligand have not been described previously, but the zirconium dichloride derivative $[Zr_2(N_2N)_2Cl_2(\mu\text{-}Cl)_2]$ exists as a six-coordinate dimer in the solid state, whereas the monoalkyl derivative $[Zr(N_2N)Cl\{CH(SiMe_3)_2\}]$ is five-coordinate and monomeric.[37] The N_2N_{py} homologues of **4** (namely, $[M(NBu^t)(N_2N_{py})Cl(py)]$ (M = Nb, Ta), **II**) are six-coordinate monomers. It is not apparent that **4** would prefer a monomeric, five-coordinate $[Nb(NBu^t)(N_2N)Cl]$ structure in preference to a six-coordinate $[Nb(NBu^t)(N_2N)Cl(py)]$ (pyridine is present in the reaction mixtures), and on balance we favor a binuclear $[Nb_2(NBu^t)_2(N_2N)_2(\mu\text{-}Cl)_2]$ formulation for **4**.

In summary, we have described the synthesis and structures of three types of new diamidoamine complexes of groups 4 and 5. The compounds show some significant differences from the homologues **I**−**III** that may be attributed to the formation of five- as opposed to six-membered chelate rings in the case of N_2N.

Acknowledgment. This work was supported by the EPSRC, Leverhulme Trust and Royal Society. P. Mountford is the Royal Society of Chemistry Sir Edward Frankland Fellow for 1998-1999. We acknowledge the use of the EPSRC Chemical Database Service at Daresbury Laboratory.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC991014C

---

(51) Fletcher, D. A.; McMeeking, R. F.; Parkin, D. The United Kingdom Chemical Database Service. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 746.

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

(53) Kaltsoyannis, N.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1999**, 781.

(54) Lyne, P. D.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1995**, 1635.

(55) Korolev, A. V.; Rheingold, A. L.; Williams, D. S. *Inorg. Chem.* **1997**, *36*, 2647.