

A Non-Metallocene Hydride of Titanium(III)

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Abstract: Several titanium(III) complexes incorporating the chelating diamidoamine ligand $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_2\text{NSiMe}_3]^{2-}[\text{NN}_2]$ are described. The reaction between $\text{Li}_2[\text{NN}_2]$ and $\text{TiCl}_3(\text{THF})_3$ (THF = tetrahydrofuran) resulted in the formation of the dimeric titanium(III) chloride $\{\text{TiCl}[\text{NN}_2]\}_2$ **1**, from which the monomeric titanium(III) alkyl $\text{Ti}\{\text{CH}(\text{SiMe}_3)_2\}[\text{NN}_2]$ **2** could be synthesized via a salt metathesis route. The alkyl complex **2** was found to react with hydrogen gas to form the thermally stable, dimeric, diamagnetic titanium(III) hydride $\{\text{TiH}[\text{NN}_2]\}_2$ **3**; density functional calculations on a simplified model system of **3** indicated the presence of a weak Ti–Ti σ -interaction. The solid-state structures of **1**, **2**, and **3** are described.

The characterization and reactivity of titanium(III) hydride complexes has been a recurring theme of research over the past 30 years, in part due to the high reactivity of such species in a variety of catalytic processes such as alkene hydrogenation and isomerization,¹ imine hydrosilylation,^{2,3} and silane polymerization,^{4,5} and also because of the uncertainty in describing “titanocene”,^{6–11} only in 1992 was the original formulation of titanocene as the bridging fulvalene hydride confirmed by X-ray crystallography.¹² To date, however, all of the known titanium(III) hydridic species that have been reported have been based around cyclopentadienyl-derived ligands; employing C_5H_5 and other nonbulky cyclopentadienyl ligands causes dimeric species to be formed,^{6,11,13,14} whereas the more sterically crowded environments dictated by C_5Me_5 or alternatively $\text{C}_5\text{Me}_4\text{Ph}$ result in the formation of monomeric Ti(III) hydrides.^{15–19} Considering the recent upsurge in the chemistry of Group 4 complexes that

incorporate noncyclopentadienyl ligands^{20–28} and the high reactivity of Ti(IV) and Zr(IV) cations incorporating multidentate diamides toward processes such as alkene polymerization,^{29–36} it seemed appropriate to develop the Ti(III) chemistry of the polydentate diamidoamine ligand, $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_2\text{NSiMe}_3]^{2-}[\text{NN}_2]$. This ligand has been shown to stabilize Zr and Ti(IV) oxidation states^{37,38} and also to provide a suitable ligand

[†] University of Sussex.[‡] Inorganic Chemistry Laboratory.(1) Bochmann, M. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier Science Ltd, 1995; Vol. 4, Part 4.(2) Verdager, X.; Lange, U. E. W.; Reding, M. T.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 6784.(3) Verdager, X.; Lange, U. E. W.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 1103.(4) Aitkin, C. T.; Harrod, J. F.; Samuel, E. *J. Organomet. Chem.* **1985**, *279*, C11.(5) Aitkin, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059.(6) Bercaw, J. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1969**, *91*, 7301.(7) Fischer, A. K.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *2*, 149.(8) Watt, G. W.; Baye, L. J.; Drummond, F. O. *J. Am. Chem. Soc.* **1966**, *88*, 1138.(9) Toogood, G. E.; Wallbridge, M. G. H. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 267.(10) Salzmann, J. J.; Mossimann, P. *Helv. Chim. Acta* **1967**, *50*, 1831.(11) Samuel, E.; Harrod, J. F. *J. Am. Chem. Soc.* **1984**, *106*, 1859.(12) Troyanov, S. I.; Antropiusová, A.; Mach, K. *J. Organomet. Chem.* **1992**, *427*, 49.(13) Xin, S.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1994**, *116*, 11562.(14) Gyepes, R.; Mach, K.; Cisarova, I.; Loub, J.; Hiller, J.; Sindelar, P. *J. Organomet. Chem.* **1995**, *497*, 33.(15) De Wolf, J. M.; Blaauw, R.; Meetsma, A.; Teuben, J. H.; Gyepes, R.; Varga, V.; Mach, K.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 4977.(16) De Wolf, J. M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1995**, *14*, 5466.(17) Luinstra, G. A.; Teuben, J. H. *J. Am. Chem. Soc.* **1992**, *114*, 3361.(18) Teuben, J. H. In *Fundamental and Technological Aspects of Organof-Element Chemistry*; Marks, T. J., Fragalà, I. L., Reidel, D., Eds.; Dordrecht, Holland, 1985; pp 195 and references therein.(19) Pattiasina, J. W.; vanBolhuis, F.; Teuben, J. H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 330.(20) Black, D. G.; Swenson, D. C.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1995**, *14*, 3539.(21) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255.(22) Brand, H.; Arnold, J. *Organometallics* **1993**, *12*, 3655.(23) Brand, H.; Capriotti, J. A.; Arnold, J. *Organometallics* **1994**, *13*, 4469.(24) Brand, H.; Arnold, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 95.(25) Floriani, C.; Ciurli, S.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 70.(26) Giannini, L.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2204.(27) Giannini, L.; Solari, E.; Angelis, S. D.; Ward, T. R.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1995**, *117*, 5801.(28) Giannini, L.; Solari, E.; Zanotti-Gerosa, A.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 85.(29) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, *16*, 4415.(30) Cloke, F. G. N.; Geldbach, T. J.; Hitchcock, P. B.; Love, J. B. *J. Organomet. Chem.* **1996**, *506*, 343.(31) Horton, A. D.; DeWith, J. *J. Chem. Soc., Chem. Commun.* **1996**, 1375.(32) Horton, A. D.; De With, J. *Organometallics* **1997**, *16*, 5424.(33) Horton, A. D.; De With, J.; Van de Linden, A. J.; Van de Weg, H. *Organometallics* **1996**, *15*, 2672.(34) Baumann, R.; Davies, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830.(35) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008.(36) Scollard, J. D.; McConville, D. H.; Vittal, J. J.; Payne, N. C. *J. Mol. Catal.* **1998**, *128*, 201.(37) Clark, H. C. S.; Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B.; Wainwright, A. P. *J. Organomet. Chem.* **1995**, *503*, 333.(38) Cloke, F. G. N.; Love, J. B.; Hitchcock, P. B. *J. Chem. Soc., Dalton Trans.* **1995**, 25.

environment for Ti(IV) imido³⁹ and cationic Al(III) complexes.^{40–42} Herein, we report the characterization of a series of titanium-(III) species ligated by [NN₂] leading to the first noncyclopentadienyl titanium(III) hydride, {TiH[NN₂]}₂.

Experimental Details.

All experiments were carried out under pure argon using Schlenk techniques or in a MBraun glovebox under an atmosphere of dinitrogen (<2 ppm H₂O, <1 ppm O₂). Diethyl ether, tetrahydrofuran (thf), and *n*-pentane were predried over sodium wire, distilled from sodium/potassium alloy, and stored over potassium mirrors. Deuterated solvents (C₆D₆, C₆D₅CD₃) were refluxed over potassium and trap-to-trap distilled prior to use. The compounds [TiCl₃(thf)₃],⁴³ Li₂[NN₂],³⁷ and LiCH(SiMe₃)₂⁴⁴ were prepared according to literature methods. NMR spectra were recorded on Bruker AMX WM, 360 DMX 300, and AC 250 instruments at 298 K unless otherwise stated and were referenced internally to residual solvent resonances. EPR spectra were recorded using a Varian E104A spectrometer. Samples for solid-state magnetic measurements were prepared in a Vacuum Atmospheres glovebox and data recorded on the SHE 905 SQUID magnetometer at Berkeley by Dr. N. M. Edelstein. Infrared spectra were recorded as Nujol mulls using a Perkin-Elmer 1720 FTIR spectrometer. The mass spectra were recorded on solid samples using a Kratos MS80RF spectrometer. Elemental analyses were carried out by the Canadian Microanalytical Service Ltd, Canada.

Synthesis of {TiCl[NN₂]}₂ **1.** A colorless solution of [Li₂(N'N₂)] (2.2 g, 6.7 mmol) in diethyl ether (20 mL) was added dropwise to a pale green stirred suspension of [TiCl₃(thf)₃] (2.5 g, 6.8 mmol) in diethyl ether (30 mL) at -78 °C. The resultant blue reaction mixture was stirred at room temperature for 2 h, after which the solvent was removed in vacuo and the solid residues were extracted with toluene (100 mL) and filtered through Celite on a glass frit. The dark green filtrate was concentrated in vacuo to ~20 mL and stored in a freezer at -50 °C overnight to afford 1.49 g, 55%, of **1** as green microcrystals.

Anal. calcd for C₂₆H₇₀Cl₂N₆Si₆Ti₂: C, 38.93%; H, 8.80%; N, 10.48%. Found: C, 38.95%; H, 8.55%; N, 10.40%. Mass spectrum (EI): *m/z* 400 (62%, [TiCl[NN₂]]⁺). EPR spectrum (120 K), dilute toluene solution, *g* = 1.990, 1.931, 1.872.

Synthesis of Ti{CH(SiMe₃)₂}[NN₂] **2.** A colorless solution of Li[CH(SiMe₃)₂] (0.13 g, 0.78 mmol) in diethyl ether (20 mL) was added dropwise to a stirred, green solution of **1** (0.30 g, 0.38 mmol) in diethyl ether (20 mL) at -78 °C. Upon warming to room temperature a blue coloration developed along with the formation of a colorless precipitate. The mixture was stirred for 18 h, after which the solvents were removed in vacuo, the residue was extracted into pentane and filtered through Celite, and the filtrates were concentrated in vacuo until small blue crystals were seen to form on the sides of the Schlenk (~5 mL). These crystals were redissolved by warming, and the solution was then cooled to -50 °C overnight affording 0.38 g, 92%, of **2** as large blue needles.

Anal. calcd for C₂₀H₅₄N₃Si₅Ti: C, 45.75%; H, 10.37%; N, 8.00%. Found: C, 44.80%; H, 9.70%; N, 8.00%. Mass spectrum (EI): *m/z* 524 [45%, (M)⁺], 365 [100, {M-CH(SiMe₃)₂}⁺]. EPR spectrum (120 K), dilute toluene solution, *g* = 1.991, 1.930, 1.871; $\mu(293\text{ K}) = 1.01\ \mu_{\text{B}}$

Synthesis of {TiH[NN₂]}₂ **3.** A solution of **2** (0.26 g, 0.49 mmol) in pentane (50 mL) in a high-pressure ampule was placed under a partial vacuum and then pressurized with dihydrogen gas (99.999%, 2 bar). The mixture was stirred for 24 h, during which the initial blue coloration slowly changed to dark green. The green solution was transferred to a Schlenk flask, concentrated in vacuo to ~10 mL and then slowly cooled to -50 °C for 16 h affording 0.18 g, 83%, of **3** as dark green crystals.

Anal. calcd for C₂₆H₇₂N₆Si₆Ti₂: C, 42.59%; H, 9.90%; N, 11.46%. Found: C, 42.34%; H, 9.79%; N, 11.44%. ¹H (C₆D₆): δ_{H} 4.84 (br.s, 4H, CH₂), 3.33 (br.s, 4H, CH₂), 1.66 (br.s, 4H, CH₂), 1.17 (br.s, 4H, CH₂), 0.79 (s, 9H, SiMe₃), 0.19 (s, 9H, SiMe₃), -35.9 (br.s, 2H, *w*_{1/2} 1920 Hz, TiH₂Ti); ¹³C{¹H} (C₆D₅-CD₃): δ_{C} 65.8 (CH₂), 9.40 (SiMe₃), 6.16 (SiMe₃); ²⁹Si{¹H} (C₆D₅CD₃): δ_{Si} 21.74 (SiMe₃), -2.66 (SiMe₃). Mass spectrum (EI): *m/z* 732 [50%, (M)⁺], 365 [85, (Ti[N'N₂])⁺]. IR (Nujol): 1274 (m, br.sh.), 1253 (s), 1242 (s), 1111 (m, sh.), 1098 (m), 1071 (s), 1036 (m), 1020 (m), 933 (s), 906 (s), 887 (m), 838 (vs, br.), 807 (s), 752 (m), 743 (m), 673 (m).

Synthesis of {Ti(μ -²H)[NN₂]}₂ **3-(²H).** In a manner similar to that of **3**, a solution of **2** (0.27 g, 0.51 mmol) in pentane (30 mL) in a high-pressure ampule was placed under a partial vacuum and then pressurized with deuterium gas (5 bar). The mixture was stirred for 48 h, during which the initial blue coloration slowly changed to dark green. The green solution was transferred to a Schlenk flask, concentrated in vacuo to ~10 mL, and then slowly cooled to -50 °C for 16 h affording 0.12 g, 63%, of **3-(²H)** as dark green crystals.

Mass spectrum (EI): *m/z* 734 (M⁺, 5%), 704 (M⁺-2CH₃, 20%), 589 (M⁺-2SiMe₃, 85%), 367 (Ti{²H}[NN₂]⁺, 25%), 73 (SiMe₃, 100%). ¹H NMR (C₆D₆, 300 MHz): δ_{H} 4.80 (br.s, 4H, CH₂), 3.35 (br.s, 4H, CH₂), 1.74 (br.s, 4H, CH₂), 1.26 (br.s, 4H, CH₂), 0.77 (s, 9H, SiMe₃), 0.17 (s, 9H, SiMe₃). ²H NMR (toluene): δ -36.8 (br.s, *w*_{1/2} 70 Hz). IR (Nujol): 1253 (s), 1241 (s), 1157 (w), 1111 (m, sh.), 1098 (m), 1072 (s), 1039 (m), 1019 (m), 1013 (w), 941 (s, sh.), 933 (s), 909 (s), 890 (m), 837 (vs, br.), 807 (s), 751 (m), 673 (m).

Crystal Structure Determinations of **1, **2**, and **3**.** See Table 1 for crystal data, Tables 2, 3, and 4 for atomic coordinates and equivalent isotropic displacement parameters for **1**, **2**, and **3** respectively. Full crystallographic data is available in the Supporting Information.

Data were collected on an Enraf-Nonius CAD4 diffractometer using crystals mounted in a Lindemann capillary under nitrogen in the case of **1** and in mineral oil at 173 K for **2** and **3**. Reflections with $|F^2| > 2\sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04i)^2]^{0.5}/L_p$. Absorption corrections were applied. The structures were solved using SHELXS-86 and refined using SHELXL-93 with non-H atoms anisotropic by full-matrix least squares on all F^2 . Hydrogen atoms were refined in riding mode with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ for CH₂ or 1.5 $U_{\text{eq}}(\text{C})$ for Me. In the case of **3**, the hydride H atom was located on a difference map and freely refined. Other H atoms were included in the riding mode. Molecules **1** and **3** lie on crystallographic inversion centers.

Computational Details. All calculations were carried out using the Amsterdam Density Functional (ADF) program system, version 2.3.⁴⁵ The electronic configurations of the

(39) Mountford, P. *J. Chem. Soc., Chem. Commun.* **1997**, 2127.

(40) Emig, N.; Réau, R.; Krautscheid, H.; Fenske, D.; Bertrand, G. *J. Am. Chem. Soc.* **1996**, *118*, 5822.

(41) Emig, N.; Gabbai, F. P.; Krautscheid, H.; Réau, R.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 989.

(42) Emig, N.; Nguyen, H.; Krautscheid, H.; Reau, R.; Cazaux, J. B.; Bertrand, G. *Organometallics* **1998**, *17*, 3599.

(43) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

(44) Davidson, D. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268.

(45) Te Velde, G.; Baerends, E. J. *J. Chem. Phys.* **1992**, *99*, 84.

Table 1. Crystal Data for **1**, **2**, and **3**

	1	2	3
formula	C ₂₆ H ₇₀ Cl ₂ N ₆ Si ₆ Ti ₂	C ₂₀ H ₅₄ N ₃ Si ₅ Ti	C ₂₆ H ₇₂ N ₆ Si ₆ Ti ₂
formula weight	802.1	525.0	733.2
temperature, K	293(2)	173(2)	173(2)
wavelength, Å	0.71073	0.71073	0.71073
crystal system	triclinic	monoclinic	monoclinic
space group	<i>P</i> 1	<i>C</i> c (No.9)	<i>P</i> 2 _{1/n}
unit cell dimensions, Å, deg	<i>a</i> = 10.835(4) <i>b</i> = 10.971(2) <i>c</i> = 12.089(1) α = 106.290(10) β = 96.49(2) γ = 119.05(3)	<i>a</i> = 17.667(8) <i>b</i> = 11.799(5) <i>c</i> = 15.233(5) α = 90.00 β = 94.84(3) γ = 90.00	<i>a</i> = 9.756(2) <i>b</i> = 11.198(3) <i>c</i> = 19.38(2) α = 90.00 β = 90.23(4) γ = 90.00
volume, Å ³	1151.4(5)	3164(2)	2117(2)
<i>Z</i>	1	4	2
Density (calcd.), mgm ⁻³	1.16	1.10	1.15
absorption coefficient, mm ⁻¹	0.64	0.47	0.57
<i>F</i> (000)	430	1148	796
crystal size, mm	0.40 × 0.25 × 0.25	0.40 × 0.40 × 0.20	0.40 × 0.40 × 0.30
theta range, deg	2.18–29.97	2–25	2–30
reflections collected	6686	2860	6480
independent reflections	6686 [<i>R</i> (int) = 0.0000]	2860 [<i>R</i> (int) = 0.0000]	6163 [<i>R</i> (int) = 0.0371]
<i>I</i> > 2 σ <i>I</i>	3947	2605	4188
data/restraints/parameters	6684/0/190	2860/2/262	6162/0/185
good on <i>F</i> ²	0.941	0.814	0.969
<i>R</i> indices [<i>I</i> > 2 σ <i>I</i>]	<i>R</i> = 0.0546, <i>wR</i> = 0.1361	<i>R</i> = 0.047, <i>wR</i> = 0.130	<i>R</i> = 0.053, <i>wR</i> = 0.114
absorption correction, (<i>T</i> _{max} , <i>T</i> _{min})	1.00, 0.96	1.00, 0.85	1.00, 0.93

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^5$) for **1**^a

complex 1	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Ti	710.2(6)	321.1(6)	1588.4(5)	45(1)
Cl	1308(1)	-252(1)	-302(1)	63(1)
Si(1)	3881(1)	-31(1)	2185(1)	62(1)
Si(2)	-2093(1)	-2889(1)	1657(1)	68(1)
Si(3)	1170(1)	3582(1)	3291(1)	72(1)
N(1)	2702(3)	494(3)	2826(2)	51(1)
N(2)	-417(3)	-1178(3)	2217(2)	56(1)
N(3)	1772(3)	2449(3)	2646(2)	53(1)
C(1)	1923(4)	-522(5)	3450(3)	66(1)
C(2)	447(4)	-690(5)	3461(3)	67(1)
C(3)	3570(4)	2108(4)	3686(3)	66(1)
C(4)	3377(4)	3065(4)	3088(4)	65(1)
C(5)	5036(4)	1345(5)	1558(4)	79(1)
C(6)	2729(6)	-1975(5)	1013(4)	86(1)
C(7)	5146(6)	31(7)	1317(5)	98(2)
C(8)	-2934(7)	-3457(6)	45(5)	145(3)
C(9)	-3355(6)	-2792(7)	2552(6)	140(3)
C(10)	-1813(8)	-4391(6)	1774(7)	144(3)
C(11)	2076(8)	4535(8)	4952(6)	163(3)
C(12)	-807(6)	2478(7)	3145(6)	158(3)
C(13)	1623(15)	5062(12)	2717(12)	284(8)

^a *U*(eq) is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

molecular systems were described by an uncontracted triple- ζ basis set of Slater type orbitals (STO). Hydrogens and carbons were given an extra polarization function, 2p on H and 3d on C. The cores of the atoms were frozen, C up to 1s and Ti up to 2p. Energies were calculated using Vosko, Wilk, and Nusair's local exchange correlation potential⁴⁶ with nonlocal-exchange corrections by Becke⁴⁷ and nonlocal correlation corrections by Perdew.^{48,49}

Results and Discussion

The dithiodiamidoamine Li₂[NN₂] was found to react with TiCl₃(THF)₃ resulting in the formation of the green, base-free,

(46) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(47) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 2398.

(48) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(49) Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7046.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^5$) for **2**^a

complex 2	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Ti	3011.4(5)	2057.2(7)	945.5(5)	20(1)
Si(1)	2407(1)	-792(1)	856(1)	35(1)
Si(2)	3848(1)	3288(1)	2737(1)	28(1)
Si(3)	4412(1)	2744(1)	-310(1)	31(1)
Si(4)	1231(1)	2972(1)	1474(1)	30(1)
Si(5)	1694(1)	3509(1)	-427(1)	27(1)
N(1)	3188(3)	185(4)	1048(3)	27(1)
N(2)	3615(3)	2146(4)	2071(3)	27(1)
N(3)	3678(3)	1903(4)	-28(3)	26(1)
C(1)	1859(3)	2638(5)	586(4)	28(1)
C(2)	3538(4)	79(5)	1983(4)	36(1)
C(3)	4027(4)	1085(5)	2250(4)	36(1)
C(4)	3786(3)	-66(5)	412(4)	33(1)
C(5)	3701(3)	743(5)	-350(4)	32(1)
C(6)	2034(4)	-674(7)	-317(5)	51(2)
C(7)	1643(4)	-413(6)	1571(6)	53(2)
C(8)	2739(5)	-2249(5)	1110(5)	54(2)
C(9)	3666(4)	2949(5)	3901(4)	38(1)
C(10)	4870(4)	3681(7)	2734(5)	50(2)
C(11)	3245(4)	4504(6)	2316(6)	52(2)
C(12)	5338(4)	2137(6)	123(7)	58(2)
C(13)	4327(5)	4186(6)	135(6)	52(2)
C(14)	4434(6)	2828(8)	-1530(5)	64(2)
C(15)	1581(4)	2431(7)	2519(4)	41(2)
C(16)	258(4)	2349(8)	1212(5)	51(2)
C(17)	1082(4)	4522(7)	1626(5)	49(2)
C(18)	2039(4)	2760(8)	-1392(4)	53(2)
C(19)	660(4)	3802(6)	-729(4)	38(2)
C(20)	2163(4)	4929(7)	-301(6)	58(2)

^a *U*(eq) is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

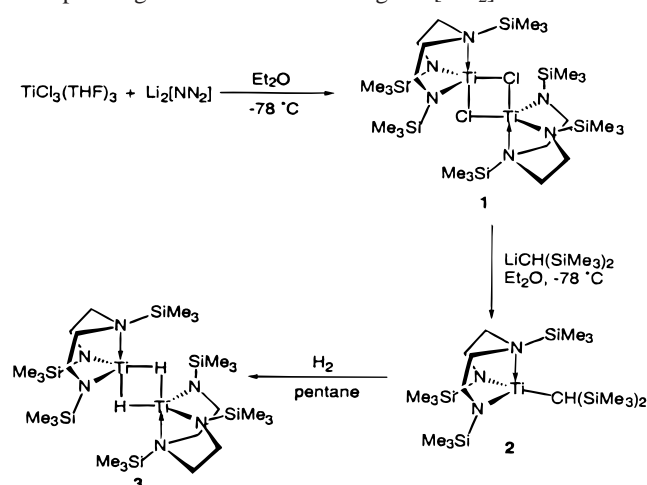
dimeric titanium(III) chloride {TiCl[NN₂]}₂, **1**, which was isolated from cold pentane in moderate yield (Scheme 1). The elemental analysis is consistent with the proposed formulation, and the dimeric nature of **1** in the solid state was confirmed by a single-crystal X-ray diffraction study and is shown in Figure 1, with selected bond lengths and angles detailed in Table 5. The solid-state structure shows that the two titanium centers are asymmetrically bridged by the chlorine atoms [Ti-Cl(1) =

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3**

complex 3	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Ti	503.8(5)	-222.5(4)	701.6(2)	16(1)
Si(1)	2117.6(8)	2407.7(7)	1058.6(4)	23(1)
Si(2)	-2027.0(8)	57.8(7)	1998.0(4)	22(1)
Si(3)	2685.1(8)	-2457.1(7)	485.8(4)	23(1)
N(1)	1277(2)	1094(2)	1256(1)	21(1)
N(2)	-477(2)	-686(2)	1729(1)	19(1)
N(3)	1177(2)	-1870(2)	818(1)	21(1)
C(1)	1203(3)	883(3)	2009(1)	27(1)
C(2)	739(3)	-383(3)	2166(1)	25(1)
C(3)	-681(3)	-2007(2)	1674(2)	23(1)
C(4)	567(3)	-2613(3)	1364(2)	27(1)
C(5)	1279(4)	3712(3)	1495(2)	38(1)
C(6)	3938(3)	2339(3)	1373(2)	36(1)
C(7)	2120(4)	2678(3)	112(2)	34(1)
C(8)	-2074(3)	1626(3)	1692(2)	30(1)
C(9)	-2129(4)	39(3)	2961(2)	35(1)
C(10)	-3535(3)	-753(3)	1645(2)	32(1)
C(11)	2306(4)	-3680(3)	-145(2)	42(1)
C(12)	3763(3)	-1263(3)	98(2)	32(1)
C(13)	3758(4)	-3151(3)	1183(2)	40(1)
H(1)	1026(29)	23(26)	-217(14)	20

^a *U*(eq) is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

Scheme 1 The Synthesis of Titanium(III) Complexes Incorporating the Diamidoamine Ligand [NN₂]



2.4414(10) Å, Ti-Cl' = 2.4921(12) Å], bond distances that are similar to those observed in the Ti(III)-Ti(III) chloride bridged dimers [Ti(η -C₅H₅)₂Cl]₂^{50a} and [TiCl₃(dippe)]₂.^{50b} The diamidoamine ligand is coordinated in a facial manner with all three nitrogen atoms interacting with the metal, resulting in the metal atom sitting in a distorted trigonal-bipyramidal environment, with N(2), N(3), and Cl equatorial and N(1) and Cl' in the axial positions. The metal-N_{amido} bond lengths of 1.932(3) and 1.947(3) Å in **1** are comparable to those observed for other Ti(III) amide complexes [range 1.896(2)–2.036(8) Å].^{52–54} In contrast, the metal-amino bond length [Ti-N(1)] of 2.376(3) Å is significantly longer than those seen in TiCl₃{NMe(CH₂CH₂-

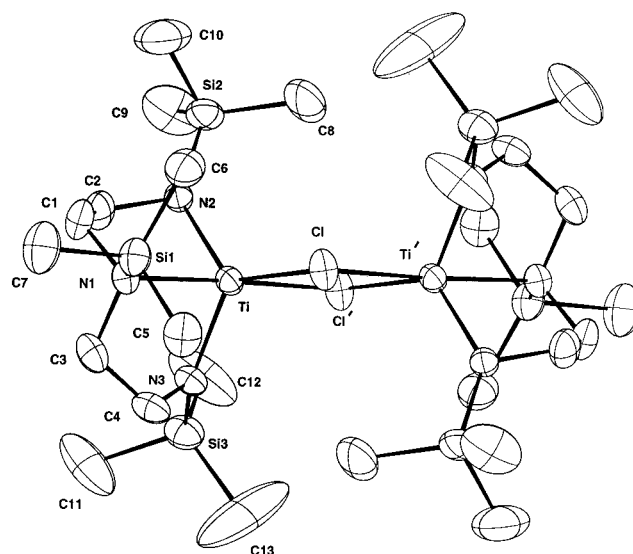
(50) (a) Jungst, R.; Sekutowski, D.; Davis, J.; Luly, M.; Stucky, J. *Inorg. Chem.*, **1977**, *16*, 1645. (b) Hermes, A. R.; Girolami, G. S. *Inorg. Chem.* **1990**, *29*, 313.

(51) Barker, G. K.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1978**, 734.

(52) Johnson, A. R.; Davies, W. M.; Cummins, C. C. *Organometallics* **1996**, *15*, 3825.

(53) Scoles, L.; Minhas, R.; Duchateau, R.; Jubb, J.; Gambarotta, S. *Organometallics* **1994**, *13*, 4978.

(54) Putzer, M. A.; Magull, J.; Goesmann, H.; Neumüller, B.; Dehnicke, K. *Chem. Ber.* **1996**, *129*, 1401.

**Figure 1.** ORTEP⁷³ view of {TiCl[NN₂]}₂, **1** (thermal ellipsoids at 50%).**Table 5.** Selected Bond Lengths (Å) and Angles (deg) for **1**

Ti-N(1)	2.376(3)	N(2)-Ti-Cl	124.03(9)
Ti-N(2)	1.932(3)	N(3)-Ti-Cl	116.22(9)
Ti-N(3)	1.947(3)	N(1)-Ti-Cl	97.00(7)
Ti-Cl(1)	2.4414(10)	N(2)-Ti-Cl'	100.84(9)
Ti-Cl'	2.4921(12)	N(3)-Ti-Cl'	97.06(9)
N(2)-Ti-N(3)	118.59(12)	N(1)-Ti-Cl'	177.60(7)
N(2)-Ti-N(1)	81.29(11)	Cl-Ti-Cl'	82.75(4)
N(3)-Ti-N(1)	80.90(11)	Ti-Cl-Ti'	97.25(4)

[C₅H₅N]₂] [N_{amino} = 2.212(16) Å and N_{pyridyl} = 2.269(14)–2.243(16) Å];⁵⁵ similar M-N_{amino} bond lengthening was observed for Ti(IV) and Zr(IV) complexes supported by this ligand and is probably a consequence of the constrained nature of the chelate.^{37,38} The EPR spectrum of a dilute toluene solution of **1** is broad and complex; the spectrum recorded at 120 K displays three signals at *g* = 1.990, 1.931, and 1.872 (compare with *g* = 1.99, 1.98, 1.95 for Cp₂Ti{NMe₂}), and is characteristic of a low symmetry species.⁵⁶ There was no evidence of any hyperfine coupling to titanium or nitrogen.

Attempts to prepare Ti(III) alkyl complexes of the general formula TiR[NN₂] by salt metathesis with alkyllithium reagents were hindered by the thermal instability of the final products; for the compounds where R = Me or CH₂SiMe₃, the initial highly colored solutions formed at low temperature rapidly decomposed upon warming to yield intractable brown oils after workup.⁵² However, by utilizing the sterically demanding alkyl group CH(SiMe₃)₂, the thermally stable, blue Ti(III) alkyl Ti{CH(SiMe₃)₂}[NN₂] **2** could be prepared in high yield according to Scheme 1 and is a rare example of a noncyclopentadienyl, Ti(III) alkyl.^{51,52,53,57,58} The low-temperature, solid-state structure of **2** is shown in Figure 2, with selected bond lengths and angles detailed in Table 6. The geometry at the 4-coordinate metal center is unusual and appears heavily influenced by the chelate constraints imposed by the diamidoamine ligand. The arrangement of alkyl and [NN₂] ligand tends away from the tetrahedral toward a geometry reminiscent of the structurally characterized trigonal-monopyramidal V(III) complex V(NN₃) (NN₃ = [(Bu⁻Me₂Si)NCH₂CH₂]₃N).⁵⁹ Similar geometries have been observed

(55) Collins, R. K.; Drew, M. G. B.; Rodgers, J. J. *J. Chem. Soc., Dalton Trans.* **1972**, 899.

(56) Alyea, E. C.; Bradley, D. C.; Lappert, M. F.; Sanger, A. R. *J. Chem. Soc., Chem. Commun.* **1969**, 1064.

(57) Hagadorn, J. R.; Arnold, J. J. *J. Am. Chem. Soc.* **1996**, *118*, 893.

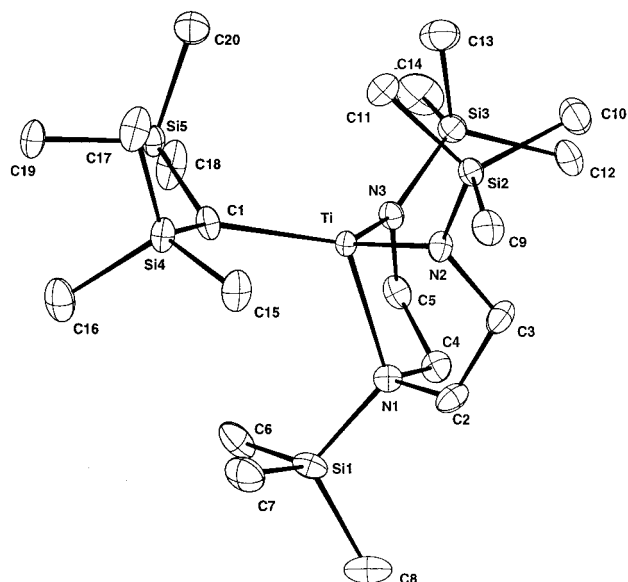


Figure 2. ORTEP⁷³ view of $\text{Ti}[\text{CH}(\text{SiMe}_3)_2][\text{NN}_2]$, **2** (thermal ellipsoids at 50%).

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **2**

Ti–C(1)	2.175(5)	N(2)–Ti–C(1)	129.6(2)
Ti–N(1)	2.234(4)	N(3)–Ti–C(1)	116.4(2)
Ti–N(2)	1.944(5)	N(2)–Ti–N(1)	85.9(2)
Ti–N(3)	1.978(4)	N(3)–Ti–N(1)	82.7(2)
N(2)–Ti–N(3)	110.4(2)	C(1)–Ti–N(1)	116.8(2)

in aluminum complexes incorporating the same diamidoamine $[\text{NN}_2]$ ligand, namely, the neutral $\text{AlCl}[\text{NN}_2]$ and the cationic $\text{AlCl}[\text{NN}_2\text{H}]^+$.⁴⁰ Steric repulsion between the silyl groups of the amide ligand and the alkyl group appears to be fairly limited, since there is no abnormal extension of the Ti–C bond length [2.175(5) Å], compared to other amido-supported titanium(III) alkyl species [range 2.137(7)–2.235(5)].^{52,53,57,58} As with **1**, the “frozen toluene” solution of **2** displays three separate signals in its EPR spectrum at $g = 1.991$, 1.930 , and 1.871 , with no evidence for any hyperfine coupling.

The general route to early transition metal and f-element hydrido complexes by σ -bond metathesis of a metal alkyl with hydrogen gas was found to be applicable in this case;¹⁸ the reaction between **2** and H_2 in pentane gave a high yield of dark green crystalline $\{\text{TiH}[\text{NN}_2]\}_2$ **3** upon cooling to -50°C . To our knowledge, this is the first example of a noncyclopentadienyl Ti(III) hydride complex. The parent ion for **3** at 732 amu with an isotopic pattern attributable to two titanium atoms was observed in the mass spectrum; a satisfactory microanalysis was also obtained. The low-temperature, solid-state structure of **3** is shown in Figure 3, with selected bond lengths and angles detailed in Table 7, and is isostructural with the chloride **1**, with N(1), N(3), and H(1) equatorial and N(2) and H(1) axial; the bridging hydride atoms were located from the difference Fourier map and refined isotropically. The decrease in the Ti–N_{amino} bond length from 2.376(3) in **1** to 2.272(3) Å in **3** may be attributed to the increased electrophilicity of the metal center in the latter. The Ti···Ti distance in **3**, [Ti···Ti' = 2.931(3) Å] may indicate a degree of metal–metal interaction, being significantly shorter than that observed in the chloro complex **1** [Ti···Ti' = 3.702(1) Å], and the related titanium(III) hydrides

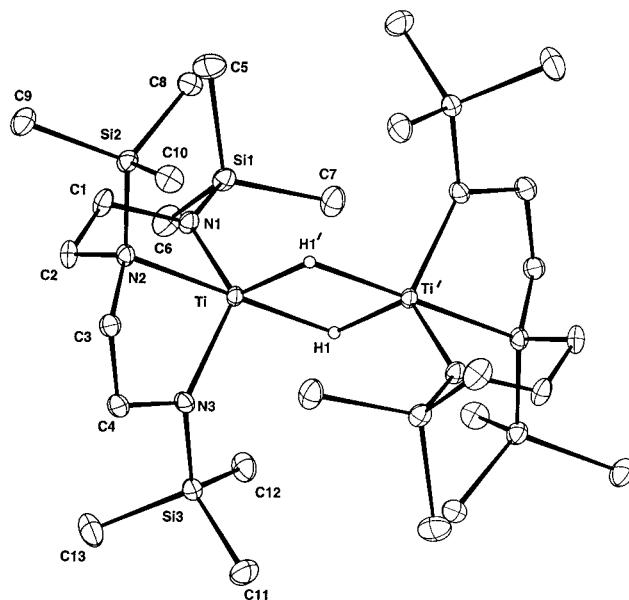


Figure 3. ORTEP⁷³ view of $\{\text{TiH}[\text{NN}_2]\}_2$, **3** (thermal ellipsoids at 50%).

Table 7. Selected Bond Lengths (Å) and Angles (deg) for **3**

Ti–N(1)	1.973(2)	N(3)–Ti–N(2)	80.06(9)
Ti–N(2)	2.272(3)	N(1)–Ti–N(2)	81.67(10)
Ti–N(3)	1.971(2)	N(3)–Ti–H(1)	99(1)
Ti–H(1)	1.88(3)	N(1)–Ti–H(1)	108(1)
Ti–H'(1)	1.77(3)	N(2)–Ti–H(1)	169(1)
Ti···Ti'	2.931(3)	H(1)–Ti–H'(1)	73(2)
N(3)–Ti–N(1)	120.73(10)	Ti–H(1)–Ti'	107(2)

$\text{rac}\{-\text{C}_2\text{H}_4(\eta^5\text{-tetrahydroindenyl})_2\text{Ti}(\mu\text{-H})_2\}_2$ [3.2288(13) Å]¹³ and $\{\{\eta\text{-C}_5\text{H}_5\text{Ti}\}_2(\mu\text{-}\eta^5\text{-fulvalene})(\mu\text{-H})_2$ [2.989(1) Å].¹² However, only a weak interaction is implied, as significant Ti···Ti bonding would presumably result in a substantially shorter distance as observed for $[(\text{Bu}^t_3\text{SiNH})\text{Ti}]_2(\mu\text{-NSiBu}^t_3)_2$ (Ti···Ti = 2.442(1) Å)⁶⁰ and $\{[(\text{Me}_3\text{Si})_3\text{C}_5\text{H}_2]\text{TiCl}(\mu\text{-O})\}_2$ (Ti···Ti = 2.7071(4) Å).⁶¹ The Ti–H bridge is symmetric, with Ti–H bond lengths of 1.77(3) and 1.88(3) Å; these Ti(III)–H bond lengths are comparable to those observed in monomeric^{15,16,19,62} and the dimeric cyclopentadienyl-based Ti(III) hydrides described above and in the structurally characterized, Ti(III)–borohydride complexes with ancillary amide ligands $\text{Ti}(\text{BH}_4)(\text{THF})\text{-}[\text{N}(\text{SiMe}_3)_2]$, $\text{Ti}(\text{BH}_4)_2(\text{THF})[\text{N}(\text{SiMe}_3)_2]$, and $\text{Ti}(\text{BH}_4)[\text{PhC}\{-\text{N}(\text{SiMe}_3)_2\}_2]$.⁶³ The presence of the hydride was corroborated by infrared spectroscopy. The IR spectrum of **3** displayed a broad absorption at 1274 cm^{-1} , overlapping with those due to the $[\text{NN}_2]$ ligand and which can be assigned to the asymmetric stretch of the bridging hydride by comparison with absorptions previously observed for the dimeric titanocenes $[\mu\text{-}\eta^5\text{-}(\text{C}_5\text{H}_4)_2\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\mu\text{-H})_2]$,⁶⁴ $[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(\text{C}_5\text{HMe}_3)_2][(\eta^5\text{-C}_5\text{H}_2\text{Me}_3)\text{Ti}(\mu\text{-H})_2]$,⁶⁵ and $\{[\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2(\mu\text{-CH}_2[\text{Mg}, \text{Mg}])][\eta^5\text{-C}_5\text{Me}_4\text{-SiMe}_3]\text{Ti}(\mu\text{-H})_2\text{Mg}(\text{THF})\}_2$.⁶⁶ To confirm this assignment, we

(60) 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.
 (61) Okuda, J.; Herdtweck, E. *Inorg. Chem.* **1991**, *30*, 1516.

(62) Frerichs, S. R.; Stein, B. K.; Ellis, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 5558.

(63) Dick, D. G.; Duchateau, R.; Edema, J. J. H.; Gambarotta, S. *Inorg. Chem.* **1993**, *32*, 2, 1959. Scoles, L.; Gambarotta, S. *Inorg. Chim. Acta* **1995**, *235*, 375.

(64) Brintzinger, H. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 6182.
 (65) Varga, V.; Mach, K.; Polasek, M.; Sedmera, P.; Hiller, J.; Thewalt, U.; Troyanov, S. I. *J. Organomet. Chem.* **1996**, *506*, 241.

(66) Horacek, M.; Hiller, J.; Thewalt, U.; Polasek, M.; Mach, K. *Organometallics* **1997**, *16*, 4185.

(58) Rosset, J.-M.; Floriani, C.; Mazzanti, M.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1990**, *29*, 3991.

(59) Cummins, C. C.; Lee, J.; Schrock, R. R.; Davies, W. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1501.

synthesized the deuteride **3**-(²H) in a manner similar to that of the hydride **3**; in the mass spectrum, the molecular ion of the deuteride was observed at 734 amu along with an appropriate fragmentation pattern. The absorption at 1274 cm⁻¹ was absent in the IR spectrum of **3**-(²H), although no absorption due to the Ti-²H-Ti asymmetric stretch could be confidently assigned due to problems of overlap with ligand absorptions.

Despite the presence of two formally d¹ titanium(III) centers, NMR spectra in the normal chemical shift range were obtained for **3**. The silyl-amino and -amido groups are displayed in the ¹H NMR spectrum at δ 0.79 and 0.19 respectively, but together with the four signals for the "backbone" protons, displayed at δ 4.84, 3.33, 1.66, and 1.17, these signals are broader than might be expected ($\nu_{1/2}$ = 23 Hz) and appear slightly paramagnetically shifted. A further very broad peak at δ -35.9 ($\nu_{1/2}$ = 1920 Hz) can be attributed to the hydridic protons by careful integration. Also, the ¹H NMR spectrum of the deuteride **3**-(²H) shows no hydridic resonance, whereas the resonances for the [NN₂] ligand are similar to those observed for the hydride **3**; the ²H NMR spectrum confirms the presence of the Ti-(²H)₂-Ti unit, resonating as a less broad feature at δ -36.8 ppm ($\nu_{1/2}$ = 70 Hz). The decrease in the line width of this signal is associated with the decrease in gyromagnetic ratio from H to D, resulting in less interaction of the single Ti-based electron with the deuterium nucleus;⁶⁷ a similar effect was observed for the Ti(III) alkyl complex Cp*₂TiMe, in which the width of the resonance due to the methyl protons decreased from 1730 to 34 Hz upon perdeuteration of the methyl group.⁶⁸ The broad resonance for the hydridic protons of **3** undergoes normal Curie behavior, with the chemical shift inversely related to temperature. Variation of chemical shift and line broadness via a potential monomer-dimer equilibrium route can be discounted, as the dimeric nature of **3** is retained in solution as determined by cryoscopy in cyclohexane. In light of the observation of NMR spectra for **3**, it is unsurprising that the EPR spectrum displays only very weak signals from 120 to 300 K. The solution magnetic moments of **3** and **3**-(²H) between 300 and 180 K were determined by Evans' method.⁶⁹ In both cases, the magnetic moment was observed to be essentially invariant with temperature over the range observed, averaging to 1.65 μ_B for **3** and 1.32 μ_B for **3**-(²H), that is, values at or less than one unpaired electron per titanium dimer. The lower than expected magnetic moments for **3** and **3**-(²H) are consistent with the NMR characteristics observed for these complexes. Similar features were seen in the temperature-dependent ¹H NMR spectra of the original "titanocene" complex, $\{(\eta^5\text{-C}_5\text{H}_5)\text{Ti}\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-fulvalene})(\mu\text{-H})_2$, in which the cyclopentadienyl resonances were observed in the usual chemical shift range with the bridging hydrides appearing as a broad feature at -21.2 ppm at -60 °C.⁷⁰ In this case it was postulated that a thermal equilibrium exists between the singlet ground state and triplet excited state, although the triplet state was thought to be insignificantly populated at room temperature; such an explanation is seemingly viable in the case of **3**, with the lower magnetic moment observed for **3**-(²H) a consequence of a small increase in energy between singlet and triplet states. However, in the solid-state magnetic susceptibility measurements on **3** show weak temperature-independent paramagnetism, or possible diamagnetism, over the temperature range of 5-300 K; **3** is also esr silent in the solid state. At present we have no reasonable

(67) Reuben, J.; Fiat, D. *J. Am. Chem. Soc.* **1969**, *91*, 1242.

(68) Luinstra, G. A.; Ten Cate, L. C.; Heeres, H. J.; Pattiasina, J. W.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 3227.

(69) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(70) Lemenovskii, D. A.; Urazowski, I. F.; Grishin, Y. U. K.; Roznyatovsky, V. A. *J. Organomet. Chem.* **1985**, *290*, 301.

Table 8. One-Electron Energies and Bonding Type Calculated for **4**

orbital symmetry	orbital energy	orbital type
a _u LUMO	-2.05	Ti Ti π bond
a _g HOMO	-2.09	Ti Ti σ bond
b _u	-4.93	N $p\pi$ nonbonding
a _g	-4.93	N $p\pi$ nonbonding
a _u	-5.15	N $p\pi$ bonding
b _g	-5.16	N $p\pi$ bonding
a _g	-6.12	H bridge
b _u	-6.45	H bridge

explanation for the difference between the solution and solid-state magnetic behavior of **3**; a similar disparity was also observed for the related cyclopentadienyl-based Ti(III) dimers with accessible triplet states.⁷⁰

The above data suggests that **3** is magnetically similar to cyclopentadienyl-based Ti(III) hydrides, in that a triplet excited state is accessible from a singlet ground state (at least in solution).^{70,71} To understand more fully the diamagnetism of **3**, density functional calculations were undertaken to investigate the electronic structure of this bridged dimer. Calculations were carried out on the model compound [TiH(NH(CH₂CH₂NH)₂)₂]₂, **4**, with distances and angles taken from the crystal structure, but idealized to C_{2h} symmetry in order to reduce computational time.

If the approximately trigonal bipyramidal coordination of the Ti atoms in **3** is considered (see Figure 4a), it is clear that, of the d orbitals, the z², xy, and x² - y² are involved in σ -bond formation. The chelate rings more or less constrain the amido-N $p\pi$ orbitals to lie in the xy plane, so they are only able to interact with the xy and x² - y² orbitals. The Ti 3d electron has therefore a choice of the xz and yz orbitals. In the absence of the constraint of the chelate rings, the amido groups would be expected to orient so as to utilize the xz and yz orbitals in π -bond formation.^{72,73}

SCF convergence was achieved for **4** with a singlet configuration; the calculation gave as the highest occupied orbital (HOMO) a Ti-Ti σ bonding orbital of a_g symmetry. The orbital energies and orbital type are given in Table 8. Inspection of the one electron energies showed a very small energy gap between the highest occupied and lowest unoccupied molecular orbital (LUMO). The LUMO was a Ti-Ti π bonding orbital of a_u symmetry. The contribution of the bridging hydrogens to the HOMO and LUMO is less than 5%. Representations of the a_g HOMO and a_u LUMO are given in Figure 4b. Here, the coordinate system is that appropriate to the symmetry assumed for the whole molecule with z' as the C₂ axis. The combination of the two d orbitals which were xz in the local framework gives the a_g orbital, and the combination of the two d orbitals, yz in the local framework, gives the a_u orbital. The two yz orbitals are not well oriented to overlap, as they are tilted with respect to one another as indicated in Figure 4b. The corresponding antibonding orbitals of b_u and b_g symmetry were also close in energy, lying 0.5 and 0.7 eV above the HOMO. At a distance of 2.93 Å, any Ti-Ti bonding is likely to be weak. The closeness of energy of these four orbitals suggests that the molecule is not well described by a single configuration and that configuration interaction is likely to be needed to give a

(71) Jungst, R.; Sekutowski, D.; Davis, J.; Luly, M.; Stucky, G. *Inorg. Chem.* **1977**, *16*, 6, 1645.

(72) Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: New York, 1987; Vol. 2; Chapter 13.4.5.

(73) Johnson, C. K. ORTEP II, Report ORNL-5738; Oak Ridge National Laboratory: Oakridge, TN, 1976.

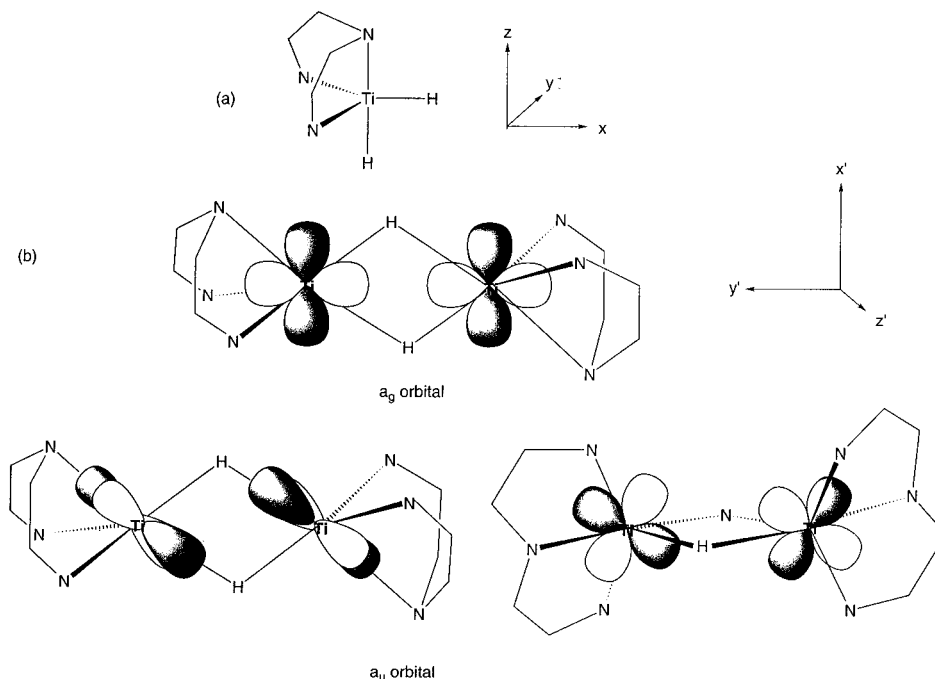


Figure 4. Schematic representations of the a_g HOMO and a_u LUMO of **4**. Two orientations are shown for the LUMO. The coordinate system shown for the a_g orbital is that adopted for the calculation in C_{2h} symmetry and differs from the local coordinate system given in 4a.

good representation of the electronic structure. Such a description would increase electron correlation, and the molecular energy would be lowered.

Geometry optimization of **4** with C_{2h} symmetry gave a considerably shorter Ti–Ti distance than that found in the crystal structure, 2.63 Å, as opposed to the experimental value of 2.93 Å. However, it is clear that, from a space-filling model of the optimized framework structure to which the bulky SiMe₃ groups were added, that steric interaction across the bridge would prevent such a short metal–metal distance from being adopted. Indeed, the crystal structure shows interleaving of the methyl groups between opposing SiMe₃ substituents. We thus conclude that the substituents control the bridge geometry.

Given the closeness of the HOMO and LUMO, we also calculated the energy of a triplet configuration for the model compound with each of these two orbitals singly occupied; it lay 0.18 eV below the singlet. Thus the modeling suggests that the singlet and triplet states lie close in energy as is suggested by the magnetic measurements. A further calculation was carried out in which the symmetry of the molecule was broken. A

singlet state was assumed but with the spins unrestricted and the start potential polarizing the spin density with a spin up on one Ti and a spin down on the other. The energy of this calculation was 0.02 eV lower than the triplet state. The final spin density of the Ti atoms was 0.85.

The conclusion is that the most appropriate simple physical picture of the d electrons in the molecule is of each d electron being largely localized on a Ti atom with weak anti-ferromagnetic coupling between the two.

Acknowledgment. The authors thank the EPSRC, and ICI and Zeneca for funding (J.B.L. and H.C.S.C., respectively) and Professor Norman Edelstein of the University of California at Berkeley for the solid-state magnetic moment study of **3**.

Supporting Information Available: Listings of crystallographic data and solution magnetic moment measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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