Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Novel titanium complexes of a mulidentate dicarbollide ligand. Synthesis and structural characterization of the constrained geometry complex

Young-Joo Lee,[a] Jong-Dae Lee,[a] Jaejung Ko,[a] Sang-Hern Kim,[b] Minserk Cheong,[c] and Sang Ook Kang*,[a]

[a]Department of Chemistry, Korea University, 208 Seochang, Chochiwon, Chung-nam 339-700, Korea.

[b]Department of Chemistry, Department of Fine Chemistry, Hanbat University, Daejeon 300-717, Korea.

[c]Department of Chemistry and Research Institute for Basic Sciences, Kyung Hee University, Seoul 130-701, Korea

Experimentals

General Procedures. All manipulations were performed under a dry, oxygen-free, nitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmosphere HE-493 dry box. THF was freshly distilled over potassium benzophenone. Toluene , n-hexane, n-pentane was dried and distilled from sodium benzophenone. Dichloromethane and hexane were dried and distilled over CaH_2. ^1H, ^{11}B, and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1, 96.3, and 75.4 MHz respectively. All boron-11 chemical shifts were referenced to $BF_3{\cdot}O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All proton and carbon chemical shifts were measured relative to internal residual benzene from the lock solvent (99.5% C_6D_6) and then referenced to Me_4Si (0.00 ppm). IR spectra were recorded on a Biorad FTS-165 spectrophotometer spectrometer. High-resolution mass spectra were measured at the Korea Basic Science Institute. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA1108 analyzer. All melting points were uncorrected. *o*-Carborane was purchased from the Katechem and used without purification. All other reagents were obtained from commercial suppliers (Aldrich and TCI) and used as received.

Preparation of [*closo*-1,2-$(CH_2NMe_2)_2$-1,2-$C_2B_{10}H_{10}$] 1. To a stirred solution of *o*-carborane (0.72 g, 5 mmol) in toluene (100 mL) was added 2.5 M *n*-BuLi (4.4 mL) via a syringe through a serum cap at 0 °C. The resulting white suspension was stirred at 25 °C for 10 min and then placed in an ice bath. When the toluene solution was cold, the Eschenmoser's salt, $CH_2{=}NMe_2^+I^-$ (2.03 g, 11.1 mmol) was added to the lithio-*o*-carborane. The reaction temperature was maintained at 0 °C for 1 h. The reaction mixture was then slowly warmed to room temperature. After stirring for an additional 12 h at refluxing temperature, the reaction mixture was filtered and then dried in vacuo to give a white crystalline powder. The resulting residue was taken up in a minimum of *n*-pentane and then recrystallized from this solution by cooling it to –5 °C to afford **1** as colorless crystals. Yield 86 % (1.1 g, 4.3 mmol); mp 87 °C; IR spectrum (KBr pellet, cm^{-1}) ν(C-H) 3001(m), 2984 (s), 2955 (m), 2855 (m), 2829 (vs), 2781 (s), ν(B-H) 2640 (s), 2580 (s); ^1H NMR ($CDCl_3$) δ 3.11 (s, 4H, NC*H*$_2$), 2.32 (s, 12H, N*Me*); $^{13}C\{^1H\}$NMR ($CDCl_3$) δ 62.6 (N*C*H$_2$), 46.7 (N*Me*); $^{11}B\{^1H\}$NMR ($CDCl_3$) δ -3.9 (4B), –10.8 (6B). Anal. Calcd for $C_8H_{26}B_{10}N_2$: C, 37.18; H, 10.14; N, 10.84. Found: C, 37.30; H, 10.12; N, 10.80.

Preparation of [*nido*-7,8-$(NMe_2CH_2)_2$-7,8-$C_2B_9H_{10}$] 2. Yield 95 % (0.95 g, 3.8 mmol);

mp 294 °C (dec.); IR spectrum (KBr pellet, cm^{-1}) ν(C-H) 3025 (w), 2989 (w), 2963 (w), 2886 (w), 2852 (w), ν(B-H) 2593 (m), 2509 (vs); ^{1}H NMR (C_5D_5N) δ 3.53 (d, 2H, *J* = 13.5 Hz, NC*H*$_2$), 3.49 (s, 1H, N-*H*-N), 3.07 (d, 2H, *J* = 13.5 Hz, NC*H*$_2$), 2.69 (s, 12H, N*Me*), –2.05 (br, 1H, B-*H*-B); ^{13}C{^{1}H} NMR ($(CD_3)_2CO$)) δ 65.0 (N*Me*), 43.4 (N*C*H$_2$); ^{11}B{^{1}H} NMR ($(CD_3)_2CO$)) δ -7.5 (3B), -15.5 (2B), -19.5 (2B), -34.1 (1B), –36.8 (1B); Anal. Calcd for $C_8H_{27}B_9N_2$: C, 38.65; H, 10.95; N, 11.25. Found: C, 38.52; H, 10.98; N, 11.30.

Preparation of [η^5:η^1-($NMe_2CH_2C_2B_9H_9CH_2NMe_2$)]Ti($NMe_2$)$_2$ 3. Over a period of 30 min, a 20 mL toluene solution of Ti(NMe_2)$_4$ (0.22 g, 1 mmol) was added to a stirred solution of **2** (0.25 g, 1 mmol) in toluene (20 mL) at 0 °C. After addition was complete, the cold bath was removed and the solution was stirred at room temperature for 36 h. Solvent was removed in vacuo and the residue purified by recrystallization with CH_2Cl_2/toluene mixture at –35 ºC. Yield 84 % (0.32 g, 0.84 mmol); mp 131 °C (dec.); IR (KBr, pellet, cm^{-1}) ν(C-H) 2989 (w), 2964 (w), 2855 (w), ν(B-H) 2593 (m), 2520 (s), 2510 (s); ^{1}H NMR ($CDCl_3$) δ 4.12 (d, 1H, *J* = 15.9 Hz, NC*H*$_2$, *N*-coordinated), 3.66 (s, 6H, TiNC*H*$_3$), 3.56 (d, 2H, NC*H*$_2$), 3.48 (s, 6H, TiN*Me*), 2.93 (d, 1H, *J* = 15.9 Hz, NC*H*$_2$, *N*-coordinated), 2.86 (s, 3H, N*Me*, *N*-coordinated), 2.54 (s, 3H, N*Me*, *N*-coordinated), 2.33 (s, 6H, N*Me*); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 69.6 (N*C*H$_2$, *N*-coordinated), 64.4 (N*C*H$_2$), 53.3 (N*Me*, *N*-coordinated), 52.6 (TiN*Me*), 52.3 (N*Me*, *N*-coordinated), 47.8 (N*Me*), 47.2 (TiN*Me*); ^{11}B{^{1}H} NMR ($CDCl_3$) δ –3.9 (1B), -11.5 (2B), -18.6 (2B), -24.7 (1B), -29.2 (1B), -43.1 (1B), -46.1 (1B); HRMS *m/z* calcd 384.3335, obsd 384.3322. Anal. Calcd for $C_{12}H_{37}B_9N_4Ti$: C, 37.67; H, 9.75; N, 14.64. Found: C, 37.74; H, 9.77; N, 14.69.

Preparation of {[η^5:η^1-($NMe_2CH_2C_2B_9H_9CH_2NMe_2$)]Ti($NMe_2$)$_2$-$\mu^3$-O-Ti 4. A solution of Ti(NMe_2)$_4$ (0.11 g, 0.5 mmol) in toluene (10 mL) was slowly dropped into the toluene solution (10 mL) of **3** (0.38 g, 1 mmol). To this solution, precooled to -20 °C, was added the toluene solution (10 mL) of distilled water (0.03 g, 1.6 mmol) for 1 h. The resultant orange mixture was allowed to warm to 25 °C and stirred for 2 h. ^{1}H NMR spectroscopy demonstrated that **4** was formed after 5 min at room temperature. The mixture was concentrated to ca. 5 mL and placed at -10 °C, giving a yellow precipitate of **4** which was filtered and dried in vacuo. Suitable crystals for X-ray diffraction analysis were obtained from a saturated toluene solution at -10 °C. Yield 48 % (0.38 g, 0.48 mmol); mp 294 °C (dec.); IR (KBr pellet, cm^{-1}) ν(C-H) 2964 (w), 2886 (w), ν(B-H) 2592 (m), 2510 (s); ^{1}H NMR ($CDCl_3$) δ 4.72 (s, 3H, μ-N*Me*), 4.37 (s, 3H, μ-N*Me*), 4.21 (d, 1H, *J* = 14.1 Hz, NC*H*$_2$, *N*-coordinated), 3.84 (d, 1H, *J* = 16.2 Hz, NC*H*$_2$, *N*-coordinated), 3.73 (d, 2H, NC*H*$_2$), 3.59 (d,

2H, NCH_2), 3.36 (s, 12H, TiN*Me*), 3.13 (d, 1H, *J* = 14.1 Hz, NCH_2, *N*-coordinated), 3.02 (d, 1H, *J* = 16.2 Hz, NCH_2, *N*-coordinated), 2.80 (s, 6H, N*Me*, *N*-coordinated), 2.59 (s, 6H, N*Me*, *N*-coordinated), 2.41 (s, 12H, N*Me*); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ71.3 (*μ*-N*Me*), 68.8 (NCH_2, *N*-coordinated), 65.2 (NCH_2, *N*-coordinated), 63.3 (N*Me*, *N*-coordinated), 61.2 (N*Me*, *N*-coordinated), 53.6 (TiN*Me*), 47.5 (N*Me*), 46.2 (TiN*Me*); $^{11}B\{^1H\}$ NMR ($CDCl_3$) -18.8 (3H), -27.0 (2B), -31.0 (2B), -45.4 (1B), –47.9 (1B); HRMS *m/z* calcd 802.5629, obsd 802.5663. Anal. Calcd for $C_{22}H_{68}B_{18}N_8OTi_3$: C, 33.07; H, 8.58; N, 14.02. Found: C, 32.99; H, 8.54; N, 14.05.

Table 1. Crystal data and structure refinement for **2.**

Identification code	kor250
Empirical formula	$C_8 B_9H_{27} N_2$
Formula weight	248.61
Temperature	293(2) K
Wavelength	0.71070 Å
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 8.3868(5) Å
	b = 17.6878(8) Å β = 99.485(6) deg.
	c = 10.6643(9) Å
Volume	1560.36(18) $Å^3$
Z, Calculated density	4, 1.058 g/cm^3
μ	0.053 mm^{-1}
F(000)	536
Crystal size	0.4 x 0.5 x 0.5 mm
θ range for data collection	2.25 to 25.97 deg.
Index ranges	0<=h<=10, -1<=k<=21, -13<=l<=12
Reflections collected / unique	3308 / 3061 [R(int) = 0.0375]
Completeness to 2θ = 51.94	96.6%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3061 / 0 / 193
Goodness-of-fit on F^2	1.260
Final R indices [I>2σ (I)]	$^aR_1$ = 0.0663, $^bwR_2$ = 0.1862
R indices (all data)	$^aR_1$ = 0.1159, $^bwR_2$ = 0.2070
Largest diff. peak and hole	0.389 and -0.334 e. $Å^{-3}$

$^aR_1 = \sum||F_o|-|F_c|| / \sum|F_o|$ (based on reflections with $F_o^2>2\sigma F^2$)

$^bwR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(0.095P)^2]$;

$P = [\max(F_o^2, 0)+2F_c^2]/3$(also with $F_o^2>2\sigma F^2$)

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **2.** U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	3038(2)	1322(1)	3712(2)	37(1)
N(2)	5348(3)	1214(1)	2277(2)	41(1)
C(1)	3853(3)	2690(1)	3551(2)	32(1)
C(2)	5203(3)	2633(1)	2667(2)	33(1)
C(3)	3588(3)	2032(1)	4408(2)	36(1)
C(4)	1425(3)	1382(2)	2906(3)	50(1)
C(5)	3069(4)	695(1)	4651(3)	49(1)
C(6)	6243(3)	1920(1)	2684(2)	41(1)
C(7)	4661(4)	1211(2)	913(3)	56(1)
C(8)	6438(4)	553(2)	2570(3)	59(1)
B(3)	4746(4)	3133(2)	1392(3)	41(1)
B(4)	2844(4)	3626(2)	1494(3)	42(1)
B(5)	2355(3)	3235(2)	2974(3)	38(1)
B(6)	5665(3)	3148(2)	4060(3)	40(1)
B(7)	6240(4)	3477(2)	2648(3)	43(1)
B(8)	4724(4)	4083(2)	1901(3)	44(1)
B(9)	3196(4)	4142(2)	2915(3)	43(1)
B(10)	3838(4)	3575(2)	4241(3)	40(1)
B(11)	5302(4)	4094(2)	3597(3)	46(1)

Table 3. Bond lengths [Å] for.

N(1)-C(4)	1.482(3)	N(1)-C(5)	1.492(3)
N(1)-C(3)	1.493(3)	N(1)-H(101)	1.18(5)
N(2)-C(7)	1.474(3)	N(2)-C(6)	1.484(3)
N(2)-C(8)	1.486(3)	N(2)-H(101)	1.51(5)
C(1)-C(3)	1.518(3)	C(1)-C(2)	1.592(3)
C(1)-B(5)	1.622(4)	C(1)-B(6)	1.729(4)
C(1)-B(10)	1.731(3)	C(2)-C(6)	1.531(3)
C(2)-B(3)	1.615(3)	C(2)-B(7)	1.729(4)
C(2)-B(6)	1.732(4)	C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700	C(4)-H(4A)	0.9600
C(4)-H(4B)	0.9600	C(4)-H(4C)	0.9600
C(5)-H(5A)	0.9600	C(5)-H(5B)	0.9600
C(5)-H(5C)	0.9600	C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700	C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600	C(7)-H(7C)	0.9600
C(8)-H(8A)	0.9600	C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600	B(3)-B(8)	1.766(4)
B(3)-B(7)	1.783(4)	B(3)-B(4)	1.836(4)
B(3)-H(3)	1.1000	B(4)-B(9)	1.753(4)
B(4)-B(8)	1.762(4)	B(4)-B(5)	1.831(4)
B(4)-H(4)	1.1000	B(4)-H(100)	1.10(3)
B(5)-B(9)	1.758(4)	B(5)-B(10)	1.783(4)
B(5)-H(5)	1.1000	B(6)-B(10)	1.747(4)
B(6)-B(7)	1.755(4)	B(6)-B(11)	1.756(4)
B(6)-H(6)	1.1000	B(7)-B(8)	1.751(4)
B(7)-B(11)	1.759(4)	B(7)-H(7)	1.1000
B(8)-B(11)	1.793(5)	B(8)-B(9)	1.811(4)
B(8)-H(8)	1.1000	B(9)-B(10)	1.745(4)
B(9)-B(11)	1.797(4)	B(9)-H(9)	1.1000
B(10)-B(11)	1.760(4)	B(10)-H(10)	1.1000
B(11)-H(11)	1.1000		

Table 4. Angles [deg] for **2**.

C(4)-N(1)-C(5)	110.9(2)	C(4)-N(1)-C(3)	114.0(2)
C(5)-N(1)-C(3)	108.79(19)	C(4)-N(1)-H(101)	111(2)
C(5)-N(1)-H(101)	107(2)	C(3)-N(1)-H(101)	104(2)
C(7)-N(2)-C(6)	112.9(2)	C(7)-N(2)-C(8)	109.3(2)
C(6)-N(2)-C(8)	109.7(2)	C(7)-N(2)-H(101)	111.7(17)
C(6)-N(2)-H(101)	103.4(16)	C(8)-N(2)-H(101)	109.7(16)
C(3)-C(1)-C(2)	119.78(19)	C(3)-C(1)-B(5)	120.2(2)
C(2)-C(1)-B(5)	113.28(18)	C(3)-C(1)-B(6)	112.21(19)
C(2)-C(1)-B(6)	62.70(15)	B(5)-C(1)-B(6)	115.2(2)
C(3)-C(1)-B(10)	115.17(18)	C(2)-C(1)-B(10)	111.39(18)
B(5)-C(1)-B(10)	64.17(16)	B(6)-C(1)-B(10)	60.66(16)
C(6)-C(2)-C(1)	120.27(19)	C(6)-C(2)-B(3)	121.2(2)
C(1)-C(2)-B(3)	111.75(19)	C(6)-C(2)-B(7)	115.14(19)
C(1)-C(2)-B(7)	111.12(18)	B(3)-C(2)-B(7)	64.34(17)
C(6)-C(2)-B(6)	112.1(2)	C(1)-C(2)-B(6)	62.52(15)
B(3)-C(2)-B(6)	115.0(2)	B(7)-C(2)-B(6)	60.94(16)
N(1)-C(3)-C(1)	114.18(19)	N(1)-C(3)-H(3A)	108.7
C(1)-C(3)-H(3A)	108.7	N(1)-C(3)-H(3B)	108.7
C(1)-C(3)-H(3B)	108.7	H(3A)-C(3)-H(3B)	107.6
N(1)-C(4)-H(4A)	109.5	N(1)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5	N(1)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5	H(4B)-C(4)-H(4C)	109.5
N(1)-C(5)-H(5A)	109.5	N(1)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5	N(1)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5	H(5B)-C(5)-H(5C)	109.5
N(2)-C(6)-C(2)	115.5(2)	N(2)-C(6)-H(6A)	108.4
C(2)-C(6)-H(6A)	108.4	N(2)-C(6)-H(6B)	108.4
C(2)-C(6)-H(6B)	108.4	H(6A)-C(6)-H(6B)	107.5
N(2)-C(7)-H(7A)	109.5	N(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5	N(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5	H(7B)-C(7)-H(7C)	109.5
N(2)-C(8)-H(8A)	109.5	N(2)-C(8)-H(8B)	109.5

H(8A)-C(8)-H(8B)	109.5	N(2)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5	H(8B)-C(8)-H(8C)	109.5
C(2)-B(3)-B(8)	106.0(2)	C(2)-B(3)-B(7)	60.94(16)
B(8)-B(3)-B(7)	59.11(17)	C(2)-B(3)-B(4)	107.34(19)
B(8)-B(3)-B(4)	58.53(16)	B(7)-B(3)-B(4)	107.7(2)
C(2)-B(3)-H(3)	113.4	B(8)-B(3)-H(3)	139.9
B(7)-B(3)-H(3)	137.5	B(4)-B(3)-H(3)	113.6
B(9)-B(4)-B(8)	62.01(18)	B(9)-B(4)-B(5)	58.72(16)
B(8)-B(4)-B(5)	106.2(2)	B(9)-B(4)-B(3)	105.9(2)
B(8)-B(4)-B(3)	58.75(17)	B(5)-B(4)-B(3)	101.08(19)
B(9)-B(4)-H(4)	136.8	B(8)-B(4)-H(4)	136.6
B(5)-B(4)-H(4)	116.5	B(3)-B(4)-H(4)	116.6
B(9)-B(4)-H(100)	120.5(16)	B(8)-B(4)-H(100)	119.2(17)
B(5)-B(4)-H(100)	66.1(16)	B(3)-B(4)-H(100)	64.0(16)
H(4)-B(4)-H(100)	86.3	C(1)-B(5)-B(9)	105.4(2)
C(1)-B(5)-B(10)	60.90(15)	B(9)-B(5)-B(10)	59.04(16)
C(1)-B(5)-B(4)	106.39(19)	B(9)-B(5)-B(4)	58.42(16)
B(10)-B(5)-B(4)	107.4(2)	C(1)-B(5)-H(5)	113.9
B(9)-B(5)-H(5)	140.0	B(10)-B(5)-H(5)	137.3
B(4)-B(5)-H(5)	114.0	C(1)-B(6)-C(2)	54.78(13)
C(1)-B(6)-B(10)	59.74(15)	C(2)-B(6)-B(10)	104.3(2)
C(1)-B(6)-B(7)	103.72(19)	C(2)-B(6)-B(7)	59.46(15)
B(10)-B(6)-B(7)	108.7(2)	C(1)-B(6)-B(11)	104.8(2)
C(2)-B(6)-B(11)	104.80(19)	B(10)-B(6)-B(11)	60.32(17)
B(7)-B(6)-B(11)	60.13(17)	C(1)-B(6)-H(6)	125.4
C(2)-B(6)-H(6)	125.2	B(10)-B(6)-H(6)	121.4
B(7)-B(6)-H(6)	121.8	B(11)-B(6)-H(6)	122.7
C(2)-B(7)-B(8)	101.9(2)	C(2)-B(7)-B(6)	59.60(15)
B(8)-B(7)-B(6)	108.2(2)	C(2)-B(7)-B(11)	104.79(19)
B(8)-B(7)-B(11)	61.45(18)	B(6)-B(7)-B(11)	59.97(17)
C(2)-B(7)-B(3)	54.72(15)	B(8)-B(7)-B(3)	59.97(17)
B(6)-B(7)-B(3)	105.87(19)	B(11)-B(7)-B(3)	108.5(2)
C(2)-B(7)-H(7)	126.6	B(8)-B(7)-H(7)	122.5

B(6)-B(7)-H(7)	121.5	B(11)-B(7)-H(7)	121.1
B(3)-B(7)-H(7)	123.1	B(7)-B(8)-B(4)	112.6(2)
B(7)-B(8)-B(3)	60.92(17)	B(4)-B(8)-B(3)	62.72(17)
B(7)-B(8)-B(11)	59.50(18)	B(4)-B(8)-B(11)	109.6(2)
B(3)-B(8)-B(11)	107.8(2)	B(7)-B(8)-B(9)	107.2(2)
B(4)-B(8)-B(9)	58.73(17)	B(3)-B(8)-B(9)	106.4(2)
B(11)-B(8)-B(9)	59.84(17)	B(7)-B(8)-H(8)	120.4
B(4)-B(8)-H(8)	119.0	B(3)-B(8)-H(8)	121.5
B(11)-B(8)-H(8)	121.8	B(9)-B(8)-H(8)	123.8
B(10)-B(9)-B(4)	112.8(2)	B(10)-B(9)-B(5)	61.20(16)
B(4)-B(9)-B(5)	62.86(17)	B(10)-B(9)-B(11)	59.57(17)
B(4)-B(9)-B(11)	109.8(2)	B(5)-B(9)-B(11)	108.4(2)
B(10)-B(9)-B(8)	107.3(2)	B(4)-B(9)-B(8)	59.26(17)
B(5)-B(9)-B(8)	107.3(2)	B(11)-B(9)-B(8)	59.61(17)
B(10)-B(9)-H(9)	120.4	B(4)-B(9)-H(9)	118.8
B(5)-B(9)-H(9)	120.9	B(11)-B(9)-H(9)	121.8
B(8)-B(9)-H(9)	123.5	C(1)-B(10)-B(9)	101.41(19)
C(1)-B(10)-B(6)	59.60(15)	B(9)-B(10)-B(6)	108.5(2)
C(1)-B(10)-B(11)	104.51(19)	B(9)-B(10)-B(11)	61.70(17)
B(6)-B(10)-B(11)	60.09(17)	C(1)-B(10)-B(5)	54.93(14)
B(9)-B(10)-B(5)	59.76(17)	B(6)-B(10)-B(5)	106.6(2)
B(11)-B(10)-B(5)	108.9(2)	C(1)-B(10)-H(10)	127.0
B(9)-B(10)-H(10)	122.6	B(6)-B(10)-H(10)	121.1
B(11)-B(10)-H(10)	121.0	B(5)-B(10)-H(10)	122.8
B(6)-B(11)-B(7)	59.90(17)	B(6)-B(11)-B(10)	59.59(16)
B(7)-B(11)-B(10)	108.0(2)	B(6)-B(11)-B(8)	106.2(2)
B(7)-B(11)-B(8)	59.05(17)	B(10)-B(11)-B(8)	107.4(2)
B(6)-B(11)-B(9)	105.8(2)	B(7)-B(11)-B(9)	107.4(2)
B(10)-B(11)-B(9)	58.74(17)	B(8)-B(11)-B(9)	60.56(17)
B(6)-B(11)-H(11)	123.0	B(7)-B(11)-H(11)	121.8
B(10)-B(11)-H(11)	122.0	B(8)-B(11)-H(11)	122.3
B(9)-B(11)-H(11)	122.5		

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters ($Å^2$ x 10^3) for **2**.
isotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	42(1)	32(1)	39(1)	0(1)	13(1)	-3(1)
N(2)	44(1)	36(1)	44(1)	4(1)	15(1)	10(1)
C(1)	34(1)	33(1)	32(1)	-1(1)	9(1)	-1(1)
C(2)	32(1)	34(1)	35(1)	4(1)	9(1)	2(1)
C(3)	41(1)	35(1)	32(1)	-1(1)	8(1)	-3(1)
C(4)	47(2)	50(2)	53(2)	-8(1)	3(1)	-6(1)
C(5)	63(2)	35(1)	52(2)	7(1)	18(1)	-4(1)
C(6)	37(1)	41(2)	45(1)	7(1)	11(1)	8(1)
C(7)	64(2)	59(2)	45(2)	-2(1)	9(1)	6(2)
C(8)	69(2)	44(2)	66(2)	6(1)	17(2)	22(1)
B(3)	48(2)	41(2)	35(1)	6(1)	14(1)	9(1)
B(4)	43(2)	37(2)	44(2)	3(1)	2(1)	5(1)
B(5)	35(1)	35(2)	44(2)	-1(1)	7(1)	1(1)
B(6)	39(2)	41(2)	38(2)	1(1)	3(1)	-6(1)
B(7)	38(2)	40(2)	53(2)	9(1)	13(1)	-5(1)
B(8)	48(2)	36(2)	49(2)	10(1)	15(1)	2(1)
B(9)	47(2)	33(2)	50(2)	0(1)	13(1)	5(1)
B(10)	51(2)	34(2)	38(2)	-5(1)	11(1)	-2(1)
B(11)	48(2)	36(2)	53(2)	-2(1)	6(2)	-10(1)

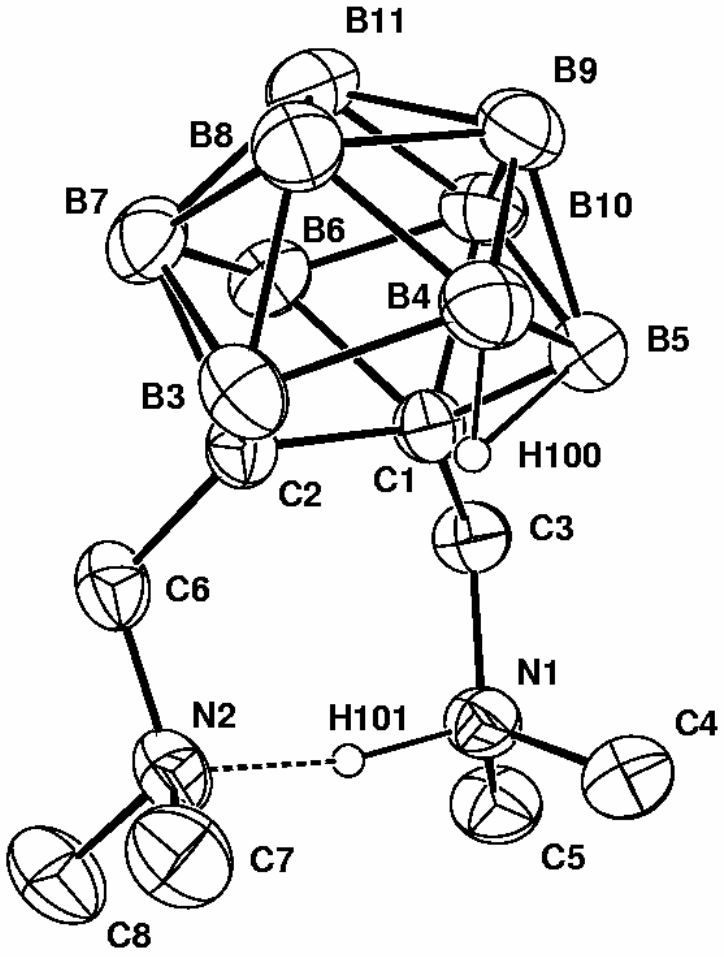

Figure 1. ORTEP diagram of *nido*-dicarbollyl-diamino Ligand (**2**), with atom labeling; ellipsoids show 40% probability levels.

Table 1. Crystal data and structure refinement for **3**

Identification code	kor
Empirical formula	$C_{12}\ B_9\ H_{37}\ N_4\ Ti$
Formula weight	382.65
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 9.2029(13) Å
	b = 15.714(2) Å β = 92.438(3) º.
	c = 14.790(2) Å
Volume	2137.0(5) $Å^3$
Z, Calculated density	4, 1.189 g/cm^3
μ	0.404 mm^{-1}
F(000)	816
Crystal size	0.10 x 0.22 x 0.34 mm
θ range for data collection	1.89 to 25.54 º
Index ranges	-10<=h<=11, -18<=k<=19, -13<=l<=17
Reflections collected / unique	11211 / 3982 [R(int) = 0.1002]
Completeness to 2θ = 51.08	96.0%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3982 / 0 / 252
Goodness-of-fit on F^2	0.955
Final R indices [I>2σ(I)]	[a]R_1 = 0.0740, [b]wR_2 = 0.1422
R indices (all data)	[a]R_1 = 0.1617, [b]wR_2 = 0.1710
Largest diff. peak and hole	0.432 and -0.263 e.$Å^{-3}$

[a]$R_1 = \sum||F_o|-|F_c||$ (based on reflections with $F_o^2>2\sigma F^2$)

[b]$wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(0.095P)^2]$;

$P = [\max(F_o^2, 0)+2F_c^2]/3$(also with $F_o^2>2\sigma F^2$)

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^{2} x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ti(1)	6249(1)	8586(1)	8511(1)	35(1)
N(1)	7842(4)	8410(2)	9338(2)	40(1)
N(2)	6274(4)	9794(2)	8443(2)	43(1)
N(3)	6945(4)	8197(2)	7138(2)	34(1)
N(4)	2881(4)	9067(2)	6273(2)	38(1)
C(1)	4618(5)	7688(2)	7626(3)	32(1)
C(2)	3670(4)	8506(3)	7844(3)	30(1)
C(3)	8491(6)	7595(3)	9587(3)	57(2)
C(4)	8314(6)	9016(4)	10032(4)	73(2)
C(5)	7743(6)	10121(3)	8282(4)	66(2)
C(6)	5318(6)	10519(3)	8529(3)	54(1)
C(7)	5571(5)	7757(3)	6818(3)	34(1)
C(8)	7322(5)	8888(3)	6508(3)	49(1)
C(9)	8187(5)	7598(3)	7170(3)	44(1)
C(10)	3517(5)	9256(3)	7174(3)	38(1)
C(11)	3493(5)	9608(3)	5581(3)	51(1)
C(12)	1290(5)	9143(3)	6232(3)	53(1)
B(3)	3711(5)	8631(3)	8967(3)	36(1)
B(4)	4691(6)	7790(3)	9480(4)	36(1)
B(5)	5293(6)	7205(3)	8551(3)	36(1)
B(6)	2767(6)	7596(3)	7467(4)	37(1)
B(7)	2136(6)	8218(4)	8385(3)	39(1)
B(8)	2785(6)	7745(3)	9401(3)	38(1)
B(9)	3809(6)	6832(4)	9137(4)	41(1)
B(10)	3807(6)	6756(3)	7933(4)	38(1)
B(11)	2209(6)	7088(4)	8455(4)	42(2)

Table 3. Bond lengths [Å] for **3**.

Ti(1)-N(1)	1.889(4)	Ti(1)-N(2)	1.901(4)
Ti(1)-N(3)	2.240(3)	Ti(1)-B(5)	2.344(5)
Ti(1)-C(1)	2.406(4)	Ti(1)-B(4)	2.418(5)
Ti(1)-B(3)	2.458(5)	Ti(1)-C(2)	2.534(4)
N(1)-C(4)	1.453(6)	N(1)-C(3)	1.454(5)
N(2)-C(6)	1.448(5)	N(2)-C(5)	1.476(6)
N(3)-C(9)	1.480(5)	N(3)-C(8)	1.482(5)
N(3)-C(7)	1.500(5)	N(4)-C(11)	1.461(5)
N(4)-C(10)	1.463(5)	N(4)-C(12)	1.467(5)
C(1)-C(7)	1.516(5)	C(1)-C(2)	1.594(5)
C(1)-B(5)	1.663(7)	C(1)-B(10)	1.715(6)
C(1)-B(6)	1.716(6)	C(2)-C(10)	1.542(5)
C(2)-B(3)	1.671(6)	C(2)-B(7)	1.713(6)
C(2)-B(6)	1.735(6)	B(3)-B(4)	1.754(7)
B(3)-B(8)	1.767(7)	B(3)-B(7)	1.777(7)
B(4)-B(8)	1.755(7)	B(4)-B(5)	1.763(7)
B(4)-B(9)	1.775(7)	B(5)-B(9)	1.750(7)
B(5)-B(10)	1.760(7)	B(6)-B(10)	1.754(8)
B(6)-B(11)	1.760(7)	B(6)-B(7)	1.790(7)
B(7)-B(8)	1.758(7)	B(7)-B(11)	1.781(8)
B(8)-B(9)	1.769(7)	B(8)-B(11)	1.799(8)
B(9)-B(10)	1.785(8)	B(9)-B(11)	1.794(8)
B(10)-B(11)	1.768(7)		

Table 4. Angles [deg] for **3**.

N(1)-Ti(1)-N(2)	99.79(17)	N(1)-Ti(1)-N(3)	107.59(15)
N(2)-Ti(1)-N(3)	102.69(14)	N(1)-Ti(1)-B(5)	97.43(18)
N(2)-Ti(1)-B(5)	158.69(19)	N(3)-Ti(1)-B(5)	83.81(15)
N(1)-Ti(1)-C(1)	135.63(15)	N(2)-Ti(1)-C(1)	124.43(16)
N(3)-Ti(1)-C(1)	62.78(13)	B(5)-Ti(1)-C(1)	40.95(16)
N(1)-Ti(1)-B(4)	90.23(17)	N(2)-Ti(1)-B(4)	123.83(17)
N(3)-Ti(1)-B(4)	126.58(16)	B(5)-Ti(1)-B(4)	43.42(17)
C(1)-Ti(1)-B(4)	69.37(16)	N(1)-Ti(1)-B(3)	123.17(16)
N(2)-Ti(1)-B(3)	90.00(17)	N(3)-Ti(1)-B(3)	124.60(15)
B(5)-Ti(1)-B(3)	70.00(19)	C(1)-Ti(1)-B(3)	65.68(16)
B(4)-Ti(1)-B(3)	42.15(17)	N(1)-Ti(1)-C(2)	158.90(14)
N(2)-Ti(1)-C(2)	92.42(16)	N(3)-Ti(1)-C(2)	86.14(13)
B(5)-Ti(1)-C(2)	67.54(17)	C(1)-Ti(1)-C(2)	37.54(13)
B(4)-Ti(1)-C(2)	68.68(16)	B(3)-Ti(1)-C(2)	39.06(15)
C(4)-N(1)-C(3)	106.9(4)	C(4)-N(1)-Ti(1)	124.1(3)
C(3)-N(1)-Ti(1)	126.3(3)	C(6)-N(2)-C(5)	107.7(4)
C(6)-N(2)-Ti(1)	140.5(3)	C(5)-N(2)-Ti(1)	111.7(3)
C(9)-N(3)-C(8)	106.5(3)	C(9)-N(3)-C(7)	110.8(3)
C(8)-N(3)-C(7)	110.8(3)	C(9)-N(3)-Ti(1)	113.3(3)
C(8)-N(3)-Ti(1)	117.0(3)	C(7)-N(3)-Ti(1)	98.2(2)
C(11)-N(4)-C(10)	111.6(4)	C(11)-N(4)-C(12)	109.7(3)
C(10)-N(4)-C(12)	112.4(3)	C(7)-C(1)-C(2)	116.2(3)
C(7)-C(1)-B(5)	118.2(4)	C(2)-C(1)-B(5)	113.0(3)
C(7)-C(1)-B(10)	122.9(3)	C(2)-C(1)-B(10)	112.8(3)
B(5)-C(1)-B(10)	62.8(3)	C(7)-C(1)-B(6)	120.2(4)
C(2)-C(1)-B(6)	63.1(3)	B(5)-C(1)-B(6)	114.1(3)
B(10)-C(1)-B(6)	61.5(3)	C(7)-C(1)-Ti(1)	91.1(2)
C(2)-C(1)-Ti(1)	75.6(2)	B(5)-C(1)-Ti(1)	67.5(2)
B(10)-C(1)-Ti(1)	128.7(3)	B(6)-C(1)-Ti(1)	135.8(3)
C(10)-C(2)-C(1)	121.5(3)	C(10)-C(2)-B(3)	123.1(4)
C(1)-C(2)-B(3)	107.8(3)	C(10)-C(2)-B(7)	116.6(4)
C(1)-C(2)-B(7)	110.5(3)	B(3)-C(2)-B(7)	63.3(3)

C(10)-C(2)-B(6)	113.2(3)	C(1)-C(2)-B(6)	61.9(3)
B(3)-C(2)-B(6)	114.0(3)	B(7)-C(2)-B(6)	62.5(3)
C(10)-C(2)-Ti(1)	105.7(3)	C(1)-C(2)-Ti(1)	66.9(2)
B(3)-C(2)-Ti(1)	68.0(2)	B(7)-C(2)-Ti(1)	127.5(3)
B(6)-C(2)-Ti(1)	126.4(3)	N(3)-C(7)-C(1)	107.0(3)
N(4)-C(10)-C(2)	116.9(3)	C(2)-B(3)-B(4)	109.4(4)
C(2)-B(3)-B(8)	106.1(4)	B(4)-B(3)-B(8)	59.8(3)
C(2)-B(3)-B(7)	59.5(3)	B(4)-B(3)-B(7)	109.2(4)
B(8)-B(3)-B(7)	59.5(3)	C(2)-B(3)-Ti(1)	72.9(2)
B(4)-B(3)-Ti(1)	67.7(2)	B(8)-B(3)-Ti(1)	123.8(3)
B(7)-B(3)-Ti(1)	128.5(3)	B(3)-B(4)-B(8)	60.5(3)
B(3)-B(4)-B(5)	103.2(4)	B(8)-B(4)-B(5)	105.8(4)
B(3)-B(4)-B(9)	107.1(4)	B(8)-B(4)-B(9)	60.2(3)
B(5)-B(4)-B(9)	59.3(3)	B(3)-B(4)-Ti(1)	70.2(2)
B(8)-B(4)-Ti(1)	126.7(3)	B(5)-B(4)-Ti(1)	66.1(2)
B(9)-B(4)-Ti(1)	123.0(3)	C(1)-B(5)-B(9)	106.8(4)
C(1)-B(5)-B(10)	60.0(3)	B(9)-B(5)-B(10)	61.1(3)
C(1)-B(5)-B(4)	106.5(4)	B(9)-B(5)-B(4)	60.7(3)
B(10)-B(5)-B(4)	110.5(4)	C(1)-B(5)-Ti(1)	71.5(2)
B(9)-B(5)-Ti(1)	128.6(3)	B(10)-B(5)-Ti(1)	130.0(3)
B(4)-B(5)-Ti(1)	70.5(2)	C(1)-B(6)-C(2)	55.0(2)
C(1)-B(6)-B(10)	59.2(3)	C(2)-B(6)-B(10)	104.4(4)
C(1)-B(6)-B(11)	104.3(4)	C(2)-B(6)-B(11)	105.1(4)
B(10)-B(6)-B(11)	60.4(3)	C(1)-B(6)-B(7)	101.7(3)
C(2)-B(6)-B(7)	58.1(3)	B(10)-B(6)-B(7)	107.6(4)
B(11)-B(6)-B(7)	60.2(3)	C(2)-B(7)-B(8)	104.7(4)
C(2)-B(7)-B(3)	57.2(3)	B(8)-B(7)-B(3)	60.0(3)
C(2)-B(7)-B(11)	105.1(4)	B(8)-B(7)-B(11)	61.1(3)
B(3)-B(7)-B(11)	107.9(4)	C(2)-B(7)-B(6)	59.3(3)
B(8)-B(7)-B(6)	107.9(4)	B(3)-B(7)-B(6)	106.4(4)
B(11)-B(7)-B(6)	59.1(3)	B(4)-B(8)-B(7)	110.0(4)
B(4)-B(8)-B(3)	59.7(3)	B(7)-B(8)-B(3)	60.5(3)
B(4)-B(8)-B(9)	60.5(3)	B(7)-B(8)-B(9)	108.7(4)

B(3)-B(8)-B(9)	106.8(4)	B(4)-B(8)-B(11)	109.6(4)
B(7)-B(8)-B(11)	60.1(3)	B(3)-B(8)-B(11)	107.5(4)
B(9)-B(8)-B(11)	60.4(3)	B(5)-B(9)-B(8)	105.8(4)
B(5)-B(9)-B(4)	60.0(3)	B(8)-B(9)-B(4)	59.4(3)
B(5)-B(9)-B(10)	59.7(3)	B(8)-B(9)-B(10)	107.2(4)
B(4)-B(9)-B(10)	108.8(4)	B(5)-B(9)-B(11)	106.6(4)
B(8)-B(9)-B(11)	60.6(3)	B(4)-B(9)-B(11)	108.9(4)
B(10)-B(9)-B(11)	59.2(3)	C(1)-B(10)-B(6)	59.3(3)
C(1)-B(10)-B(5)	57.2(3)	B(6)-B(10)-B(5)	107.6(4)
C(1)-B(10)-B(11)	104.1(4)	B(6)-B(10)-B(11)	60.0(3)
B(5)-B(10)-B(11)	107.3(4)	C(1)-B(10)-B(9)	103.0(4)
B(6)-B(10)-B(9)	108.6(4)	B(5)-B(10)-B(9)	59.2(3)
B(11)-B(10)-B(9)	60.7(3)	B(6)-B(11)-B(10)	59.6(3)
B(6)-B(11)-B(7)	60.7(3)	B(10)-B(11)-B(7)	107.4(4)
B(6)-B(11)-B(9)	107.9(4)	B(10)-B(11)-B(9)	60.1(3)
B(7)-B(11)-B(9)	106.6(4)	B(6)-B(11)-B(8)	107.4(4)
B(10)-B(11)-B(8)	106.6(4)	B(7)-B(11)-B(8)	58.8(3)
B(9)-B(11)-B(8)	59.0(3)		

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters ($Å^2$ x 10^3) for **3**.
isotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti(1)	30(1)	41(1)	34(1)	-3(1)	6(1)	-3(1)
N(1)	30(2)	54(3)	37(2)	1(2)	1(2)	-3(2)
N(2)	37(2)	50(2)	41(2)	-3(2)	5(2)	-4(2)
N(3)	25(2)	44(2)	34(2)	5(2)	7(2)	-2(2)
N(4)	33(2)	50(2)	32(2)	6(2)	1(2)	0(2)
C(1)	31(3)	33(3)	32(3)	0(2)	7(2)	2(2)
C(2)	28(3)	33(3)	30(2)	2(2)	6(2)	-1(2)
C(3)	47(3)	74(4)	51(3)	15(3)	-4(3)	4(3)
C(4)	63(4)	86(4)	67(4)	-19(3)	-18(3)	4(3)
C(5)	61(4)	64(4)	73(4)	3(3)	7(3)	-12(3)
C(6)	54(4)	45(3)	64(4)	-10(3)	2(3)	-11(3)
C(7)	35(3)	38(3)	28(3)	-4(2)	3(2)	-1(2)
C(8)	41(3)	60(3)	47(3)	11(3)	17(2)	-3(3)
C(9)	35(3)	56(3)	42(3)	-4(2)	11(2)	8(3)
C(10)	32(3)	42(3)	40(3)	3(2)	1(2)	5(2)
C(11)	54(4)	58(3)	40(3)	14(3)	6(3)	1(3)
C(12)	35(3)	67(4)	56(3)	16(3)	-6(2)	2(3)
B(3)	31(3)	43(3)	33(3)	-9(3)	7(2)	-3(3)
B(4)	27(3)	50(3)	32(3)	1(3)	3(2)	-1(3)
B(5)	29(3)	49(4)	32(3)	3(3)	1(2)	0(3)
B(6)	26(3)	44(3)	39(3)	-1(3)	-4(2)	-9(3)
B(7)	25(3)	59(4)	34(3)	2(3)	13(2)	-3(3)
B(8)	30(3)	56(4)	29(3)	1(3)	10(2)	2(3)
B(9)	37(4)	45(3)	42(3)	8(3)	4(3)	-3(3)
B(10)	44(4)	32(3)	38(3)	2(3)	4(3)	-9(3)
B(11)	28(3)	56(4)	43(3)	8(3)	7(3)	-9(3)

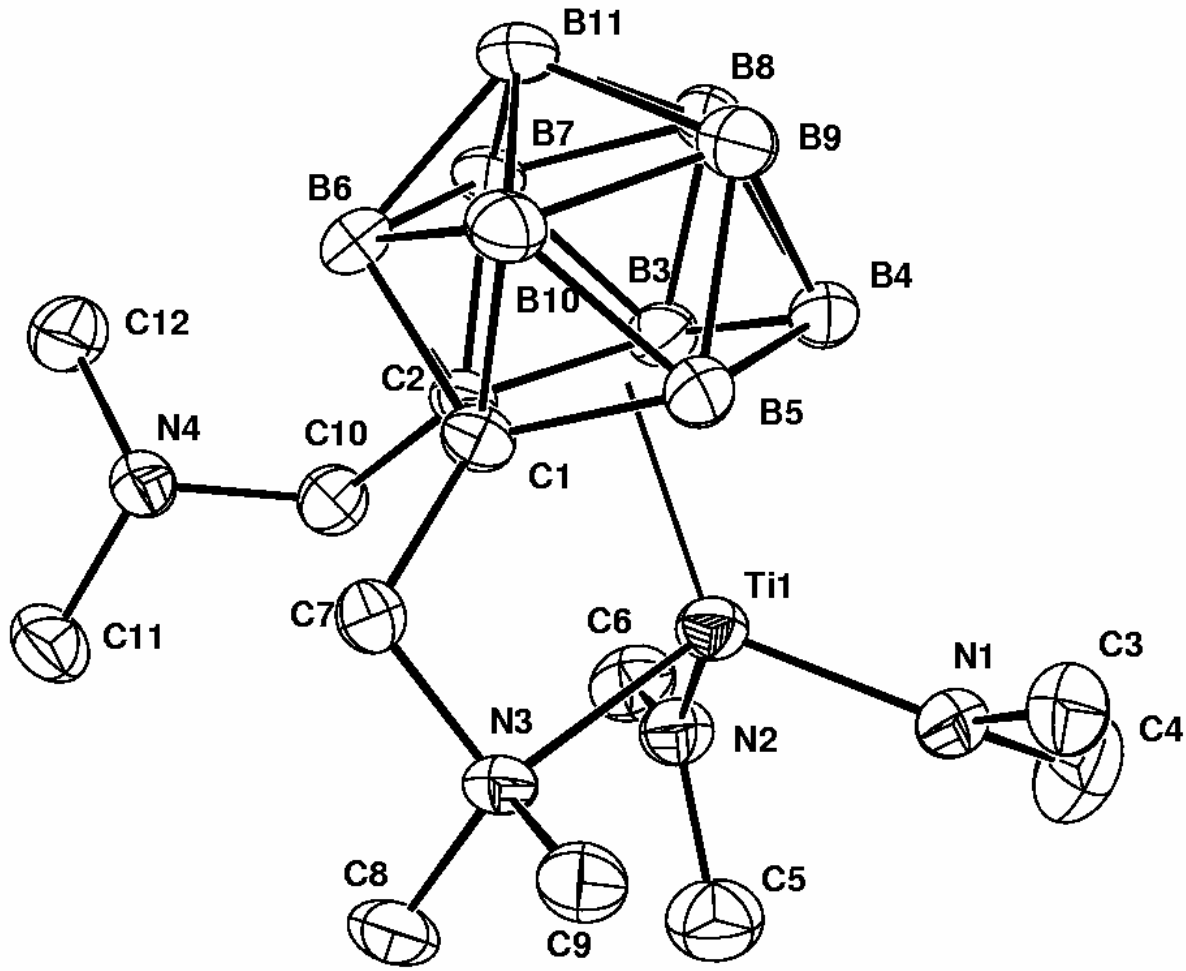

Figure 2. ORTEP diagram of [η^5:η^1-($NMe_2CH_2C_2B_9H_9$-CH_2NMe_2)]Ti(NMe_2)$_2$ (**3**), with atom labeling; ellipsoids show 40% probability levels.

Table 1. Crystal data and structure refinement for **4 · 2.5C_7H_8**.

Identification code	kor294
Empirical formula	$C_{39.50}\,H_{68}\,B_{18}\,N_8\,O\,Ti_3$
Formula weight	1009.30
Temperature	293(2) K
Wavelength	0.71070 Å
Crystal system, space group	Triclinic, Pī
Unit cell dimensions	a = 12.5957(12) A α = 80.984(7) °
	b = 13.0482(14) A β = 82.147(7) °
	c = 18.3677(13) A γ = 80.152(9) °
Volume	2918.8(5) Å^3
Z, Calculated density	2, 1.148 g/cm^3
μ	0.438 mm^{-1}
F(000)	1050
Crystal size	0.3 x 0.3 x 0.45 mm
θ range for data collection	1.13 to 25.97 °
Index ranges	0<=h<=15, -15<=k<=16, -22<=l<=22
Reflections collected / unique	11997 / 11443 [R(int) = 0.1673]
Completeness to 2θ = 51.94	100.0%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11443 / 38 / 573
Goodness-of-fit on F^2	0.965
Final R indices [I>2σ(I)]	[a]R_1 = 0.1233, [b]wR_2 = 0.2339
R indices (all data)	[a]R_1 = 0.4496, [b]wR_2 = 0.3296
Largest diff. peak and hole	0.763 and -0.481 e.Å^{-3}

[a]$R_1 = \sum||F_o|-|F_c||$ (based on reflections with $F_o^2>2\sigma F^2$)

[b]$wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(0.095P)^2]$;

$P = [\max(F_o^2, 0)+2F_c^2]/3$(also with $F_o^2>2\sigma F^2$)

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^{2} x 10^3) for **4 · 2.5C_7H_8**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ti(1)	12163(2)	5515(2)	2708(1)	51(1)
Ti(2)	9889(2)	6349(2)	2521(1)	43(1)
Ti(3)	11446(2)	3561(2)	2552(1)	42(1)
O(1)	10778(6)	4979(6)	2552(4)	36(2)
N(1)	10985(8)	6821(8)	2799(6)	51(3)
N(2)	12754(8)	3925(7)	2605(6)	55(3)
N(3)	13109(10)	6027(11)	1925(8)	91(5)
N(4)	12684(12)	5593(10)	3598(8)	95(5)
N(5)	9945(8)	7220(8)	1369(6)	55(3)
N(6)	7561(10)	5532(10)	1245(8)	81(4)
N(7)	11123(9)	2761(9)	3686(6)	62(3)
N(8)	13520(14)	235(14)	2662(13)	140(7)
C(1)	8245(10)	7329(9)	2171(7)	47(3)
C(2)	8053(9)	6130(9)	2422(6)	42(3)
C(3)	10963(11)	1874(9)	2665(7)	51(4)
C(4)	12159(11)	1734(10)	2207(7)	56(4)
C(5)	11245(11)	7676(12)	3105(9)	96(6)
C(6)	13923(10)	3639(12)	2539(9)	94(6)
C(7)	13348(13)	5640(15)	1227(10)	127(8)
C(8)	13638(16)	6934(14)	1909(13)	184(12)
C(9)	11993(17)	5583(15)	4298(10)	138(9)
C(10)	13794(16)	5690(2)	3697(14)	233(16)
C(11)	8750(10)	7557(10)	1373(7)	61(4)
C(12)	10431(9)	6577(10)	778(7)	64(4)
C(13)	10496(12)	8174(10)	1282(8)	83(5)
C(14)	8235(10)	5325(10)	1882(7)	54(4)
C(15)	8124(13)	5121(12)	590(8)	94(6)
C(16)	6526(14)	5108(13)	1485(10)	116(7)
C(17)	10902(11)	1749(10)	3503(8)	67(4)

C(18)	11977(11)	2631(11)	4188(7)	77(5)
C(19)	10121(11)	3318(11)	4091(7)	83(5)
C(20)	13188(11)	1338(12)	2584(8)	83(5)
C(21)	14340(2)	-190(2)	2257(16)	310(3)
C(22)	13720(2)	-200(2)	3358(16)	290(2)
B(3)	8304(12)	5790(13)	3293(9)	62(5)
B(4)	8703(12)	6848(13)	3573(9)	59(5)
B(5)	8654(13)	7812(12)	2836(8)	53(4)
B(6)	6930(12)	7113(12)	2328(9)	60(5)
B(7)	6964(13)	6093(13)	3100(9)	70(5)
B(8)	7364(12)	6528(14)	3850(10)	71(5)
B(9)	7579(13)	7853(13)	3529(9)	67(5)
B(10)	7330(12)	8167(13)	2604(9)	66(5)
B(11)	6504(13)	7395(14)	3217(9)	73(6)
B(12)	12137(12)	2680(12)	1463(8)	57(5)
B(13)	10817(11)	3364(11)	1428(8)	49(4)
B(14)	10068(12)	2790(10)	2264(9)	50(4)
B(15)	11362(14)	831(14)	2200(9)	67(5)
B(16)	12102(15)	1322(13)	1365(9)	73(6)
B(17)	11256(14)	2339(12)	893(9)	68(5)
B(18)	9935(13)	2401(12)	1415(9)	59(5)
B(19)	10036(15)	1460(12)	2213(10)	78(6)
B(20)	10797(14)	1161(12)	1365(9)	66(5)
C(100)	15682(13)	7918(19)	286(14)	245(13)
C(101)	14635(11)	8193(13)	-57(11)	227(12)
C(102)	13880(12)	9042(11)	139(9)	136(7)
C(103)	12920(13)	9308(14)	-189(13)	225(12)
C(104)	12702(14)	8702(17)	-694(13)	252(14)
C(105)	13397(15)	7780(14)	-818(10)	178(9)
C(106)	14379(14)	7540(12)	-517(11)	189(10)
C(107)	16373(15)	1982(12)	3525(8)	184(10)
C(108)	15675(16)	1460(11)	4049(10)	200(11)
C(109)	15170(14)	1927(14)	4663(9)	173(9)

C(110)	15400(14)	2895(13)	4768(8)	150(8)
C(111)	16152(16)	3384(11)	4269(10)	178(10)
C(112)	16634(13)	2931(11)	3644(8)	137(7)
C(113)	16860(2)	1509(18)	2837(10)	234(13)
C(114)	7822(10)	450(3)	4578(18)	360(2)
C(115)	8962(5)	239(13)	4782(9)	40(6)
C(116)	9714(10)	-533(11)	4477(7)	118(6)
C(117)	10753(8)	-771(10)	4692(8)	120(6)

Table 3. Bond lengths [Å] for **4 · 2.5C_7H_8**.

Ti(1)-N(3)	1.854(12)	Ti(1)-N(4)	1.866(12)
Ti(1)-O(1)	2.057(8)	Ti(1)-N(1)	2.071(9)
Ti(1)-N(2)	2.110(10)	Ti(1)-Ti(3)	2.914(3)
Ti(1)-Ti(2)	2.931(3)	Ti(2)-N(1)	1.770(11)
Ti(2)-O(1)	1.937(7)	Ti(2)-N(5)	2.238(10)
Ti(2)-B(5)	2.342(14)	Ti(2)-C(1)	2.353(12)
Ti(2)-B(4)	2.380(15)	Ti(2)-C(2)	2.412(12)
Ti(2)-B(3)	2.435(15)	Ti(3)-N(2)	1.809(10)
Ti(3)-O(1)	1.897(7)	Ti(3)-N(7)	2.196(10)
Ti(3)-B(14)	2.306(15)	Ti(3)-C(3)	2.353(13)
Ti(3)-B(13)	2.374(15)	Ti(3)-B(12)	2.445(14)
Ti(3)-C(4)	2.544(13)	N(1)-C(5)	1.428(15)
N(2)-C(6)	1.449(14)	N(3)-C(7)	1.425(19)
N(3)-C(8)	1.449(19)	N(4)-C(9)	1.45(2)
N(4)-C(10)	1.46(2)	N(5)-C(12)	1.478(13)
N(5)-C(11)	1.495(14)	N(5)-C(13)	1.502(15)
N(6)-C(15)	1.442(16)	N(6)-C(16)	1.488(18)
N(6)-C(14)	1.502(14)	N(7)-C(18)	1.482(14)
N(7)-C(17)	1.492(15)	N(7)-C(19)	1.508(14)
N(8)-C(21)	1.28(3)	N(8)-C(22)	1.36(3)
N(8)-C(20)	1.418(18)	C(1)-C(11)	1.521(15)
C(1)-C(2)	1.609(16)	C(1)-B(5)	1.637(18)
C(1)-B(10)	1.658(17)	C(1)-B(6)	1.705(19)
C(2)-C(14)	1.524(15)	C(2)-B(3)	1.650(18)
C(2)-B(7)	1.724(19)	C(2)-B(6)	1.746(17)
C(3)-C(17)	1.515(16)	C(3)-C(4)	1.618(17)
C(3)-B(14)	1.653(17)	C(3)-B(15)	1.69(2)
C(3)-B(19)	1.72(2)	C(4)-C(20)	1.527(16)
C(4)-B(15)	1.68(2)	C(4)-B(12)	1.692(18)
C(4)-B(16)	1.729(19)	B(3)-B(4)	1.72(2)
B(3)-B(8)	1.72(2)	B(3)-B(7)	1.74(2)
B(4)-B(5)	1.70(2)	B(4)-B(9)	1.76(2)

B(4)-B(8)	1.79(2)	B(5)-B(9)	1.73(2)
B(5)-B(10)	1.75(2)	B(6)-B(10)	1.71(2)
B(6)-B(11)	1.72(2)	B(6)-B(7)	1.79(2)
B(7)-B(8)	1.74(2)	B(7)-B(11)	1.74(2)
B(8)-B(9)	1.79(2)	B(8)-B(11)	1.82(2)
B(9)-B(10)	1.74(2)	B(9)-B(11)	1.76(2)
B(10)-B(11)	1.75(2)	B(12)-B(13)	1.751(19)
B(12)-B(17)	1.78(2)	B(12)-B(16)	1.82(2)
B(13)-B(17)	1.753(19)	B(13)-B(14)	1.81(2)
B(13)-B(18)	1.82(2)	B(14)-B(18)	1.75(2)
B(14)-B(19)	1.76(2)	B(15)-B(19)	1.73(2)
B(15)-B(20)	1.74(2)	B(15)-B(16)	1.77(2)
B(16)-B(20)	1.69(2)	B(16)-B(17)	1.75(2)
B(17)-B(20)	1.79(2)	B(17)-B(18)	1.80(2)
B(18)-B(19)	1.76(2)	B(18)-B(20)	1.80(2)
B(19)-B(20)	1.78(2)	C(100)-C(101)	1.5031(17)
C(101)-C(102)	1.3904(18)	C(101)-C(106)	1.3914(18)
C(102)-C(103)	1.3909(17)	C(103)-C(104)	1.3908(18)
C(104)-C(105)	1.3911(19)	C(105)-C(106)	1.3906(17)
C(107)-C(112)	1.3900(17)	C(107)-C(108)	1.3903(17)
C(107)-C(113)	1.5032(16)	C(108)-C(109)	1.3908(17)
C(109)-C(110)	1.3901(17)	C(110)-C(111)	1.3904(18)
C(111)-C(112)	1.3907(17)	C(114)-C(115)	1.5033(18)
C(115)-C(116)	1.3896(18)	C(115)-C(117)#1	1.3899(18)
C(116)-C(117)	1.389(2)	C(117)-C(115)#1	1.3899(18)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+1

Table 4. Angles [deg] for **4 · 2.5C_7H_8**.

N(3)-Ti(1)-N(4)	108.9(8)	N(3)-Ti(1)-O(1)	122.6(6)
N(4)-Ti(1)-O(1)	128.5(6)	N(3)-Ti(1)-N(1)	101.1(5)
N(4)-Ti(1)-N(1)	93.6(5)	O(1)-Ti(1)-N(1)	77.3(4)
N(3)-Ti(1)-N(2)	94.3(5)	N(4)-Ti(1)-N(2)	99.3(5)
O(1)-Ti(1)-N(2)	78.5(3)	N(1)-Ti(1)-N(2)	155.5(4)
N(3)-Ti(1)-Ti(3)	115.4(5)	N(4)-Ti(1)-Ti(3)	117.4(5)
O(1)-Ti(1)-Ti(3)	40.5(2)	N(1)-Ti(1)-Ti(3)	117.4(3)
N(2)-Ti(1)-Ti(3)	38.2(3)	N(3)-Ti(1)-Ti(2)	112.4(4)
N(4)-Ti(1)-Ti(2)	119.1(5)	O(1)-Ti(1)-Ti(2)	41.2(2)
N(1)-Ti(1)-Ti(2)	36.6(3)	N(2)-Ti(1)-Ti(2)	119.5(3)
Ti(3)-Ti(1)-Ti(2)	81.67(8)	N(1)-Ti(2)-O(1)	87.9(4)
N(1)-Ti(2)-N(5)	97.4(5)	O(1)-Ti(2)-N(5)	111.7(3)
N(1)-Ti(2)-B(5)	92.5(5)	O(1)-Ti(2)-B(5)	163.4(5)
N(5)-Ti(2)-B(5)	84.7(5)	N(1)-Ti(2)-C(1)	127.6(4)
O(1)-Ti(2)-C(1)	144.0(4)	N(5)-Ti(2)-C(1)	63.7(4)
B(5)-Ti(2)-C(1)	40.8(4)	N(1)-Ti(2)-B(4)	92.4(5)
O(1)-Ti(2)-B(4)	121.3(4)	N(5)-Ti(2)-B(4)	126.4(5)
B(5)-Ti(2)-B(4)	42.1(5)	C(1)-Ti(2)-B(4)	68.7(5)
N(1)-Ti(2)-C(2)	159.9(4)	O(1)-Ti(2)-C(2)	107.9(4)
N(5)-Ti(2)-C(2)	88.2(4)	B(5)-Ti(2)-C(2)	68.8(5)
C(1)-Ti(2)-C(2)	39.5(4)	B(4)-Ti(2)-C(2)	69.0(5)
N(1)-Ti(2)-B(3)	128.1(5)	O(1)-Ti(2)-B(3)	97.1(4)
N(5)-Ti(2)-B(3)	127.1(5)	B(5)-Ti(2)-B(3)	69.7(6)
C(1)-Ti(2)-B(3)	66.9(5)	B(4)-Ti(2)-B(3)	41.8(5)
C(2)-Ti(2)-B(3)	39.8(4)	N(1)-Ti(2)-Ti(1)	44.2(3)
O(1)-Ti(2)-Ti(1)	44.4(2)	N(5)-Ti(2)-Ti(1)	104.3(3)
B(5)-Ti(2)-Ti(1)	136.1(4)	C(1)-Ti(2)-Ti(1)	166.3(3)
B(4)-Ti(2)-Ti(1)	118.6(4)	C(2)-Ti(2)-Ti(1)	152.1(3)
B(3)-Ti(2)-Ti(1)	126.5(4)	N(2)-Ti(3)-O(1)	90.6(4)
N(2)-Ti(3)-N(7)	100.0(5)	O(1)-Ti(3)-N(7)	106.8(4)
N(2)-Ti(3)-B(14)	163.9(5)	O(1)-Ti(3)-B(14)	101.9(4)
N(7)-Ti(3)-B(14)	86.3(5)	N(2)-Ti(3)-C(3)	129.0(4)

O(1)-Ti(3)-C(3)	139.6(4)	N(7)-Ti(3)-C(3)	63.6(4)
B(14)-Ti(3)-C(3)	41.5(4)	N(2)-Ti(3)-B(13)	123.9(5)
O(1)-Ti(3)-B(13)	94.9(4)	N(7)-Ti(3)-B(13)	130.8(5)
B(14)-Ti(3)-B(13)	45.6(5)	C(3)-Ti(3)-B(13)	71.3(5)
N(2)-Ti(3)-B(12)	92.1(5)	O(1)-Ti(3)-B(12)	126.6(4)
N(7)-Ti(3)-B(12)	125.1(5)	B(14)-Ti(3)-B(12)	72.3(6)
C(3)-Ti(3)-B(12)	67.3(5)	B(13)-Ti(3)-B(12)	42.6(5)
N(2)-Ti(3)-C(4)	96.6(4)	O(1)-Ti(3)-C(4)	164.4(4)
N(7)-Ti(3)-C(4)	85.6(4)	B(14)-Ti(3)-C(4)	68.9(5)
C(3)-Ti(3)-C(4)	38.3(4)	B(13)-Ti(3)-C(4)	69.6(4)
B(12)-Ti(3)-C(4)	39.6(4)	N(2)-Ti(3)-Ti(1)	46.1(3)
O(1)-Ti(3)-Ti(1)	44.7(2)	N(7)-Ti(3)-Ti(1)	105.8(3)
B(14)-Ti(3)-Ti(1)	146.2(4)	C(3)-Ti(3)-Ti(1)	168.7(3)
B(13)-Ti(3)-Ti(1)	120.1(4)	B(12)-Ti(3)-Ti(1)	120.1(4)
C(4)-Ti(3)-Ti(1)	141.8(3)	Ti(3)-O(1)-Ti(2)	170.8(4)
Ti(3)-O(1)-Ti(1)	94.8(3)	Ti(2)-O(1)-Ti(1)	94.4(3)
C(5)-N(1)-Ti(2)	142.2(9)	C(5)-N(1)-Ti(1)	118.1(8)
Ti(2)-N(1)-Ti(1)	99.2(5)	C(6)-N(2)-Ti(3)	148.2(9)
C(6)-N(2)-Ti(1)	115.6(8)	Ti(3)-N(2)-Ti(1)	95.7(4)
C(7)-N(3)-C(8)	110.1(14)	C(7)-N(3)-Ti(1)	124.8(13)
C(8)-N(3)-Ti(1)	124.9(14)	C(9)-N(4)-C(10)	111.0(15)
C(9)-N(4)-Ti(1)	122.4(12)	C(10)-N(4)-Ti(1)	126.6(15)
C(12)-N(5)-C(11)	113.7(10)	C(12)-N(5)-C(13)	109.0(10)
C(11)-N(5)-C(13)	109.3(10)	C(12)-N(5)-Ti(2)	114.9(7)
C(11)-N(5)-Ti(2)	96.5(7)	C(13)-N(5)-Ti(2)	112.9(8)
C(15)-N(6)-C(16)	111.4(13)	C(15)-N(6)-C(14)	113.0(11)
C(16)-N(6)-C(14)	109.3(12)	C(18)-N(7)-C(17)	113.6(10)
C(18)-N(7)-C(19)	105.3(10)	C(17)-N(7)-C(19)	110.0(11)
C(18)-N(7)-Ti(3)	118.0(8)	C(17)-N(7)-Ti(3)	98.7(8)
C(19)-N(7)-Ti(3)	111.2(8)	C(21)-N(8)-C(22)	102.9(18)
C(21)-N(8)-C(20)	122(3)	C(22)-N(8)-C(20)	114(2)
C(11)-C(1)-C(2)	114.3(10)	C(11)-C(1)-B(5)	120.5(11)
C(2)-C(1)-B(5)	111.7(10)	C(11)-C(1)-B(10)	124.5(10)

C(2)-C(1)-B(10)	112.4(10)	B(5)-C(1)-B(10)	64.0(9)
C(11)-C(1)-B(6)	118.6(11)	C(2)-C(1)-B(6)	63.5(8)
B(5)-C(1)-B(6)	114.7(11)	B(10)-C(1)-B(6)	61.2(9)
C(11)-C(1)-Ti(2)	91.2(7)	C(2)-C(1)-Ti(2)	72.2(6)
B(5)-C(1)-Ti(2)	69.2(7)	B(10)-C(1)-Ti(2)	131.0(9)
B(6)-C(1)-Ti(2)	133.7(8)	C(14)-C(2)-C(1)	122.8(10)
C(14)-C(2)-B(3)	121.4(11)	C(1)-C(2)-B(3)	108.2(10)
C(14)-C(2)-B(7)	117.8(11)	C(1)-C(2)-B(7)	109.2(10)
B(3)-C(2)-B(7)	62.0(8)	C(14)-C(2)-B(6)	116.3(10)
C(1)-C(2)-B(6)	60.9(8)	B(3)-C(2)-B(6)	112.4(10)
B(7)-C(2)-B(6)	61.9(8)	C(14)-C(2)-Ti(2)	101.6(7)
C(1)-C(2)-Ti(2)	68.3(6)	B(3)-C(2)-Ti(2)	70.8(7)
B(7)-C(2)-Ti(2)	129.3(9)	B(6)-C(2)-Ti(2)	127.4(9)
C(17)-C(3)-C(4)	117.1(11)	C(17)-C(3)-B(14)	117.3(11)
C(4)-C(3)-B(14)	114.6(10)	C(17)-C(3)-B(15)	121.1(10)
C(4)-C(3)-B(15)	60.9(8)	B(14)-C(3)-B(15)	113.7(11)
C(17)-C(3)-B(19)	122.7(12)	C(4)-C(3)-B(19)	111.2(11)
B(14)-C(3)-B(19)	62.8(8)	B(15)-C(3)-B(19)	61.0(9)
C(17)-C(3)-Ti(3)	91.7(8)	C(4)-C(3)-Ti(3)	77.2(7)
B(14)-C(3)-Ti(3)	67.7(6)	B(15)-C(3)-Ti(3)	134.8(9)
B(19)-C(3)-Ti(3)	128.6(8)	C(20)-C(4)-C(3)	122.7(11)
C(20)-C(4)-B(15)	115.4(11)	C(3)-C(4)-B(15)	61.6(9)
C(20)-C(4)-B(12)	121.4(12)	C(3)-C(4)-B(12)	107.0(9)
B(15)-C(4)-B(12)	114.6(11)	C(20)-C(4)-B(16)	117.3(11)
C(3)-C(4)-B(16)	110.1(11)	B(15)-C(4)-B(16)	62.7(9)
B(12)-C(4)-B(16)	64.2(9)	C(20)-C(4)-Ti(3)	106.7(9)
C(3)-C(4)-Ti(3)	64.4(6)	B(15)-C(4)-Ti(3)	123.5(9)
B(12)-C(4)-Ti(3)	67.1(6)	B(16)-C(4)-Ti(3)	126.1(8)
N(5)-C(11)-C(1)	107.0(10)	N(6)-C(14)-C(2)	118.0(10)
N(7)-C(17)-C(3)	105.9(10)	N(8)-C(20)-C(4)	115.3(13)
C(2)-B(3)-B(4)	107.4(11)	C(2)-B(3)-B(8)	109.2(11)
B(4)-B(3)-B(8)	62.9(10)	C(2)-B(3)-B(7)	61.1(8)
B(4)-B(3)-B(7)	110.3(12)	B(8)-B(3)-B(7)	60.2(9)

C(2)-B(3)-Ti(2)	69.3(7)	B(4)-B(3)-Ti(2)	67.4(7)
B(8)-B(3)-Ti(2)	127.0(11)	B(7)-B(3)-Ti(2)	127.1(9)
B(5)-B(4)-B(3)	106.2(11)	B(5)-B(4)-B(9)	60.0(9)
B(3)-B(4)-B(9)	105.7(11)	B(5)-B(4)-B(8)	108.7(11)
B(3)-B(4)-B(8)	58.7(9)	B(9)-B(4)-B(8)	60.5(9)
B(5)-B(4)-Ti(2)	67.7(7)	B(3)-B(4)-Ti(2)	70.8(7)
B(9)-B(4)-Ti(2)	124.2(10)	B(8)-B(4)-Ti(2)	126.3(10)
C(1)-B(5)-B(4)	106.4(11)	C(1)-B(5)-B(9)	105.3(11)
B(4)-B(5)-B(9)	61.8(9)	C(1)-B(5)-B(10)	58.6(8)
B(4)-B(5)-B(10)	110.3(12)	B(9)-B(5)-B(10)	60.2(9)
C(1)-B(5)-Ti(2)	70.0(6)	B(4)-B(5)-Ti(2)	70.1(7)
B(9)-B(5)-Ti(2)	128.1(10)	B(10)-B(5)-Ti(2)	126.6(10)
C(1)-B(6)-B(10)	58.1(8)	C(1)-B(6)-B(11)	104.4(12)
B(10)-B(6)-B(11)	61.1(10)	C(1)-B(6)-C(2)	55.6(7)
B(10)-B(6)-C(2)	103.5(10)	B(11)-B(6)-C(2)	104.6(10)
C(1)-B(6)-B(7)	102.3(10)	B(10)-B(6)-B(7)	107.0(12)
B(11)-B(6)-B(7)	59.3(9)	C(2)-B(6)-B(7)	58.4(7)
C(2)-B(7)-B(8)	105.3(12)	C(2)-B(7)-B(11)	105.0(12)
B(8)-B(7)-B(11)	63.3(10)	C(2)-B(7)-B(3)	56.9(8)
B(8)-B(7)-B(3)	59.4(9)	B(11)-B(7)-B(3)	108.1(14)
C(2)-B(7)-B(6)	59.7(8)	B(8)-B(7)-B(6)	109.9(13)
B(11)-B(7)-B(6)	58.6(9)	B(3)-B(7)-B(6)	106.5(12)
B(3)-B(8)-B(7)	60.4(9)	B(3)-B(8)-B(9)	104.2(12)
B(7)-B(8)-B(9)	105.2(12)	B(3)-B(8)-B(4)	58.5(9)
B(7)-B(8)-B(4)	107.0(11)	B(9)-B(8)-B(4)	58.8(9)
B(3)-B(8)-B(11)	105.0(11)	B(7)-B(8)-B(11)	58.4(9)
B(9)-B(8)-B(11)	58.5(9)	B(4)-B(8)-B(11)	105.4(12)
B(5)-B(9)-B(10)	60.4(9)	B(5)-B(9)-B(4)	58.3(8)
B(10)-B(9)-B(4)	107.6(11)	B(5)-B(9)-B(11)	108.0(11)
B(10)-B(9)-B(11)	59.7(9)	B(4)-B(9)-B(11)	109.5(12)
B(5)-B(9)-B(8)	107.5(11)	B(10)-B(9)-B(8)	109.0(12)
B(4)-B(9)-B(8)	60.7(9)	B(11)-B(9)-B(8)	61.6(9)
C(1)-B(10)-B(6)	60.8(8)	C(1)-B(10)-B(9)	103.8(10)

B(6)-B(10)-B(9)	108.9(12)	C(1)-B(10)-B(11)	105.5(11)
B(6)-B(10)-B(11)	59.8(10)	B(9)-B(10)-B(11)	60.8(9)
C(1)-B(10)-B(5)	57.4(7)	B(6)-B(10)-B(5)	109.0(10)
B(9)-B(10)-B(5)	59.4(9)	B(11)-B(10)-B(5)	108.1(11)
B(6)-B(11)-B(7)	62.1(9)	B(6)-B(11)-B(10)	59.1(9)
B(7)-B(11)-B(10)	107.8(11)	B(6)-B(11)-B(9)	107.4(12)
B(7)-B(11)-B(9)	106.3(11)	B(10)-B(11)-B(9)	59.5(10)
B(6)-B(11)-B(8)	108.7(10)	B(7)-B(11)-B(8)	58.3(9)
B(10)-B(11)-B(8)	107.5(12)	B(9)-B(11)-B(8)	59.9(9)
C(4)-B(12)-B(13)	109.5(11)	C(4)-B(12)-B(17)	105.1(11)
B(13)-B(12)-B(17)	59.6(8)	C(4)-B(12)-B(16)	58.9(8)
B(13)-B(12)-B(16)	107.7(12)	B(17)-B(12)-B(16)	58.2(9)
C(4)-B(12)-Ti(3)	73.4(7)	B(13)-B(12)-Ti(3)	66.5(6)
B(17)-B(12)-Ti(3)	122.0(9)	B(16)-B(12)-Ti(3)	127.1(9)
B(12)-B(13)-B(17)	61.0(8)	B(12)-B(13)-B(14)	103.7(10)
B(17)-B(13)-B(14)	105.5(11)	B(12)-B(13)-B(18)	107.1(10)
B(17)-B(13)-B(18)	60.5(9)	B(14)-B(13)-B(18)	57.6(8)
B(12)-B(13)-Ti(3)	70.9(7)	B(17)-B(13)-Ti(3)	127.2(8)
B(14)-B(13)-Ti(3)	65.2(6)	B(18)-B(13)-Ti(3)	120.5(9)
C(3)-B(14)-B(18)	106.4(10)	C(3)-B(14)-B(19)	60.5(8)
B(18)-B(14)-B(19)	60.2(9)	C(3)-B(14)-B(13)	105.0(10)
B(18)-B(14)-B(13)	61.3(8)	B(19)-B(14)-B(13)	109.7(11)
C(3)-B(14)-Ti(3)	70.8(7)	B(18)-B(14)-Ti(3)	127.8(10)
B(19)-B(14)-Ti(3)	129.3(9)	B(13)-B(14)-Ti(3)	69.2(7)
C(4)-B(15)-C(3)	57.5(8)	C(4)-B(15)-B(19)	108.0(12)
C(3)-B(15)-B(19)	60.5(9)	C(4)-B(15)-B(20)	105.7(12)
C(3)-B(15)-B(20)	106.1(11)	B(19)-B(15)-B(20)	61.5(10)
C(4)-B(15)-B(16)	60.1(9)	C(3)-B(15)-B(16)	105.0(12)
B(19)-B(15)-B(16)	108.3(12)	B(20)-B(15)-B(16)	57.6(9)
B(20)-B(16)-C(4)	105.5(12)	B(20)-B(16)-B(17)	62.6(10)
C(4)-B(16)-B(17)	104.8(10)	B(20)-B(16)-B(15)	60.3(10)
C(4)-B(16)-B(15)	57.2(8)	B(17)-B(16)-B(15)	108.6(12)
B(20)-B(16)-B(12)	108.8(11)	C(4)-B(16)-B(12)	56.9(8)

B(17)-B(16)-B(12)	59.8(8)	B(15)-B(16)-B(12)	104.3(11)
B(16)-B(17)-B(13)	110.7(10)	B(16)-B(17)-B(12)	62.0(9)
B(13)-B(17)-B(12)	59.5(8)	B(16)-B(17)-B(20)	57.2(9)
B(13)-B(17)-B(20)	109.9(12)	B(12)-B(17)-B(20)	106.4(11)
B(16)-B(17)-B(18)	106.6(12)	B(13)-B(17)-B(18)	61.6(9)
B(12)-B(17)-B(18)	106.8(11)	B(20)-B(17)-B(18)	60.1(9)
B(14)-B(18)-B(19)	60.1(9)	B(14)-B(18)-B(20)	106.8(11)
B(19)-B(18)-B(20)	59.9(9)	B(14)-B(18)-B(17)	106.2(10)
B(19)-B(18)-B(17)	107.7(11)	B(20)-B(18)-B(17)	59.7(9)
B(14)-B(18)-B(13)	61.1(8)	B(19)-B(18)-B(13)	109.4(11)
B(20)-B(18)-B(13)	106.7(11)	B(17)-B(18)-B(13)	57.9(8)
C(3)-B(19)-B(15)	58.5(9)	C(3)-B(19)-B(14)	56.7(8)
B(15)-B(19)-B(14)	106.5(12)	C(3)-B(19)-B(18)	103.0(11)
B(15)-B(19)-B(18)	108.5(13)	B(14)-B(19)-B(18)	59.6(8)
C(3)-B(19)-B(20)	103.2(12)	B(15)-B(19)-B(20)	59.6(10)
B(14)-B(19)-B(20)	107.3(12)	B(18)-B(19)-B(20)	61.0(10)
B(16)-B(20)-B(15)	62.1(10)	B(16)-B(20)-B(19)	109.7(12)
B(15)-B(20)-B(19)	58.9(9)	B(16)-B(20)-B(17)	60.2(9)
B(15)-B(20)-B(17)	108.2(11)	B(19)-B(20)-B(17)	107.6(11)
B(16)-B(20)-B(18)	109.3(11)	B(15)-B(20)-B(18)	106.4(11)
B(19)-B(20)-B(18)	59.1(9)	B(17)-B(20)-B(18)	60.3(9)
C(102)-C(101)-C(106)	119.91(19)	C(102)-C(101)-C(100)	120.0(2)
C(106)-C(101)-C(100)	119.88(19)	C(101)-C(102)-C(103)	119.96(17)
C(104)-C(103)-C(102)	119.84(17)	C(103)-C(104)-C(105)	119.8(2)
C(106)-C(105)-C(104)	119.9(2)	C(105)-C(106)-C(101)	119.81(16)
C(112)-C(107)-C(108)	120.01(15)	C(112)-C(107)-C(113)	120.00(16)
C(108)-C(107)-C(113)	119.98(16)	C(107)-C(108)-C(109)	119.92(17)
C(110)-C(109)-C(108)	119.94(15)	C(109)-C(110)-C(111)	120.02(16)
C(110)-C(111)-C(112)	119.96(16)	C(107)-C(112)-C(111)	119.93(15)
C(116)-C(115)-C(117)#1	120.01(19)	C(116)-C(115)-C(114)	119.97(19)
C(117)#1-C(115)-C(114)	119.93(19)	C(117)-C(116)-C(115)	120.2(3)
C(116)-C(117)-C(115)#1	119.8(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+1

Table 5. Anisotropic displacement parameters (Å ^{2} x 10^3) for **4 · 2.5C_7H_8**.
isotropic displacement factor exponent takes the form:
□2 pi^2 [h^2 a*^{2} U11 + ... + 2 h k a* b* U12]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti(1)	41(2)	47(2)	65(2)	-5(1)	-7(1)	-8(1)
Ti(2)	45(2)	37(2)	44(2)	-1(1)	-8(1)	1(1)
Ti(3)	43(2)	35(2)	43(2)	1(1)	-2(1)	-3(1)
O(1)	37(5)	38(5)	31(4)	0(4)	-4(4)	-2(4)
N(1)	53(7)	32(6)	74(8)	-23(6)	-17(6)	-3(5)
N(2)	41(7)	42(7)	84(9)	-6(6)	-12(6)	-11(6)
N(3)	57(9)	76(10)	112(12)	15(9)	35(9)	2(7)
N(4)	111(12)	82(10)	111(12)	-45(9)	-77(10)	16(9)
N(5)	47(7)	49(7)	62(8)	5(6)	-6(6)	5(6)
N(6)	65(9)	93(10)	96(11)	-36(8)	-52(8)	15(8)
N(7)	67(8)	72(9)	41(7)	2(6)	-2(6)	-5(7)
N(8)	104(13)	90(13)	210(2)	20(14)	-76(14)	38(11)
C(1)	64(9)	33(8)	42(8)	-1(6)	-9(7)	-1(7)
C(2)	40(8)	46(8)	36(8)	-5(7)	-9(6)	8(6)
C(3)	68(10)	31(8)	47(9)	10(7)	-5(7)	2(7)
C(4)	55(9)	43(9)	63(10)	8(7)	-14(8)	1(7)
C(5)	68(11)	87(13)	134(16)	-30(12)	-22(10)	8(10)
C(6)	33(9)	112(14)	136(15)	-12(12)	-16(9)	-12(9)
C(7)	75(13)	180(2)	122(17)	42(16)	-11(13)	-54(13)
C(8)	150(2)	80(15)	300(3)	-6(18)	70(2)	-59(15)
C(9)	220(3)	127(18)	94(16)	8(14)	-93(17)	-56(17)
C(10)	122(18)	340(4)	300(3)	-220(3)	-140(2)	60(2)
C(11)	74(11)	47(9)	47(9)	21(7)	2(8)	2(8)
C(12)	49(9)	79(10)	49(9)	-3(8)	16(7)	14(8)
C(13)	102(13)	49(10)	91(12)	20(9)	-7(10)	-27(9)
C(14)	46(8)	65(10)	55(9)	-18(8)	-3(7)	-16(7)
C(15)	109(14)	109(14)	78(12)	-35(11)	-48(11)	0(11)
C(16)	91(14)	125(16)	144(18)	-20(13)	-58(13)	-13(12)
C(17)	76(11)	43(9)	77(12)	13(8)	-16(9)	-5(8)
C(18)	82(11)	113(13)	38(9)	-7(9)	-25(8)	-2(9)

C(19)	77(11)	99(12)	52(10)	0(9)	8(8)	24(9)
C(20)	61(11)	85(13)	90(13)	2(10)	-22(9)	24(10)
C(21)	290(4)	360(5)	270(4)	-210(4)	-150(3)	250(4)
C(22)	240(3)	210(3)	280(4)	130(3)	60(3)	160(3)
B(3)	40(10)	68(12)	57(11)	24(9)	9(8)	8(9)
B(4)	45(10)	76(13)	51(11)	3(9)	-11(8)	0(9)
B(5)	67(12)	41(10)	59(11)	-19(9)	-10(9)	-14(9)
B(6)	38(10)	57(11)	79(13)	-4(10)	-20(9)	22(9)
B(7)	46(11)	65(12)	82(14)	15(10)	-7(10)	15(9)
B(8)	41(10)	100(15)	62(12)	-12(11)	-4(9)	16(10)
B(9)	63(12)	71(13)	67(13)	-35(10)	-4(10)	10(10)
B(10)	49(11)	57(12)	70(13)	-6(10)	17(9)	34(9)
B(11)	49(11)	90(14)	57(12)	1(10)	11(9)	32(10)
B(12)	53(10)	57(11)	48(10)	-3(9)	14(8)	11(9)
B(13)	51(10)	39(9)	48(10)	-8(8)	4(8)	10(8)
B(14)	60(11)	20(8)	67(12)	-9(8)	-13(9)	3(8)
B(15)	78(13)	59(12)	65(13)	-2(10)	-17(10)	-13(11)
B(16)	98(15)	60(12)	57(12)	-27(10)	-11(11)	22(11)
B(17)	106(15)	54(11)	56(11)	-20(9)	-59(11)	7(10)
B(18)	66(12)	46(11)	73(12)	7(9)	-38(10)	-22(9)
B(19)	97(15)	29(10)	112(17)	9(10)	-36(13)	-19(10)
B(20)	81(14)	48(11)	82(14)	-35(10)	-21(11)	-16(10)

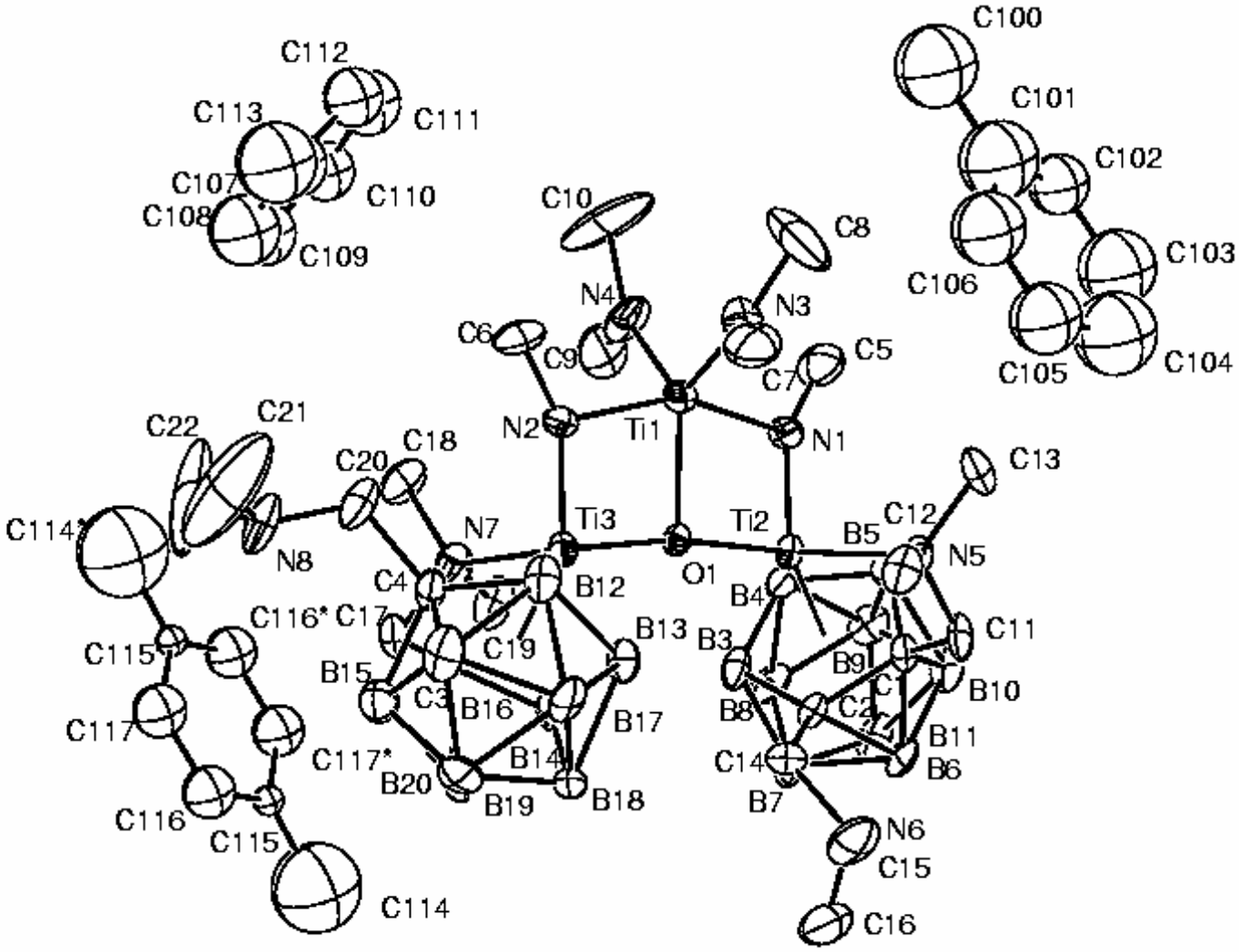

Figure 3. ORTEP diagram of {[η^5:η^1-($NMe_2CH_2C_2B_9H_9$-CH_2NMe_2)]Ti(NMe_2)}$_2$-η^3-O-Ti (**4**)·**2.5C$_7$H$_8$**, with atom labeling; ellipsoids show 25% probability levels.