Supplementary Material (ESI) for Chemical Communications

Cyclopentadienyl titanium hydroxylaminato complexes as highly active catalysts for the polymerization of propylene

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Supplementary Information

Experimental

General Considerations: All reactions were performed under a nitrogen atmosphere, using either standard Schlenk techniques or a dinitrogen filled glove-box. All solvents and reagents were purchased from Aldrich Chemical Co. unless otherwise stated. Pentane and toluene were passed through purification columns packed with activated Alumina and copper catalyst, diethyl ether was passed through a purification column packed with activated Alumina. 2-Methyl-2-nitrosopropane and nitrosobenzene were sublimed and then recrystallised from dry diethyl ether prior to use. Diethylhydroxylamine was distilled from potassium hydride. Propylene was purchased from Matheson TriGas (Research Purity) and passed through a purification column packed with activated alumina and copper catalyst. Cp*$TiMe_3$ and nitroso compounds were prepared by literature procedures. Trityl borate was kindly donated by Albemarle Corporation.

Physical Methods: NMR spectra were recorded using a Varian UI-500 or UI-300 Spectrometer and referenced the residual proton peaks (C_6D_6 = δ 7.15 ppm). ^{13}C NMR spectra were obtained at 75.4 MHz using a 10 mm broad-band probe operating at 100 ^oC. Samples were prepared as solutions of ca. 80 mg polymer in 2.5 mL of 90:10 (v/v) 1,2-dichlorobenzene/benzene-d6 containing ca 2 mg chromium(III) acetylacetonate as a spin relaxation agent. An inverse-gated decoupled pulse sequence was used. GPC measurements were taken. Elemental Analyses were performed at Atlantic Microlabs Ltd. Variable temperature ^1H NMR was performed using a Varian UI-300 spectrometer. A temperature calibration was performed prior to each experiment using ethylene glycol. Activation parameters were derived by line shape analysis using G-NMR. (Budzelaar, P. H. M., gNMR, version 4.1; Adept Scientific: Herts, (www.adeptscience.com). Cherwell Scientific Publishing, 1999.)

General Polymerization Procedure: In a 300 mL stainless steel Parr reactor a solution of 60 mg TIBA in 8 mL toluene was equilibrated for 30 minutes at 20 ^oC with 90 mL liquid propylene. A 1 mL toluene solution of the titanium complex (0.25 μmol) was injected into the reactor followed by a 1 mL toluene solution of trityl borate (0.25 μmol) via argon pressure. The polymerisation was run for 20 minutes and quenched by addition

of methanol (10 mL). The polymer was precipitated from acidified methanol, filtered, washed with methanol and dried under vacuum at 60 ^{o}C.

Synthesis of Cp*Ti(Me)$_2$(ONEt$_2$), 2. HONEt$_2$ (0.35 mL, 3.4 mmol) was added dropwise to a stirred solution of Cp*TiMe$_3$ (0.78 g, 3.4 mmol) in pentane (70 mL) at 0 ^{o}C. The solution was stirred for 4 hours before being reduced under vacuum to yield a yellow oil. The oil was washed in 10 mL pentane at -78 ^{o}C and yielded a yellow solid (0.78 g, 2.6 mmol, 76 %). Crystals were grown from a saturated pentane solution at -30 ^{o}C.
^{1}H NMR (C$_6$D$_6$, 500MHz): δ 3.08 (ddq, ONC*H*$_2$CH$_3$, $^{3}J_{H\text{-}H}$ = 6.8, 7.0 Hz, $^{2}J_{H\text{-}H}$ = 55.5 Hz, 4H), 1.87 (s, C$_5$(C*H*$_3$)$_5$, 15H), 1.04 (t, ONCH$_2$C*H*$_3$, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 6H), 0.13 (s, TiMe, 6H).
^{13}C {^{1}H} NMR (C$_6$D$_6$, 500MHz): δ 120.2 (*C*$_5$(CH$_3$)$_5$), 51.4 (ON*C*H$_2$CH$_3$), 46.6 (Ti*C*H$_3$), 11.3 (C$_5$(*C*H$_3$)$_5$), 9.8 (ONCH$_2$*C*H$_3$).
Elemental Analysis for C$_{16}$H$_{26}$ONTi (found): C, 63.78 (63.72); H, 10.37 (10.34); N, 4.65 (4.61).

Synthesis of Cp*Ti(Me)$_2$(ONMe(^{t}Bu)), 3. A solution of 2-nitroso-2-methylpropane (0.39 g, 4.5 mmol) in pentane (20 mL) was added slowly to a stirred solution of Cp*TiMe$_3$ (1.00 g, 4.4 mmol) in pentane (70 mL) at 0 ^{o}C. The solution was stirred for 4 hours before being reduced under vacuum to yield a pale yellow solid (0.97 g, 3.1 mmol, 70 %). X-ray quality crystals were grown from a saturated pentane solution at -30 ^{o}C.
^{1}H NMR (C$_6$D$_6$, 500MHz): δ 2.88 (s, ONC*H*$_3$, 3H), 1.87 (s, C$_5$(C*H*$_3$)$_5$, 15H), 1.06 (s, ONC(C*H*$_3$)$_3$, 9H), 0.47, -0.03 (s, TiC*H*$_3$, 3H).
^{13}C {^{1}H} NMR (C$_6$D$_6$, 500MHz): δ 120.5 (*C*$_5$(CH$_3$)$_5$), 62.9 (ONC(*C*H$_3$)$_3$), 52.4, 44.3 (Ti*C*H$_3$), 43.7 (ON*C*H$_3$), 26.4 (ONC(*C*H$_3$)$_3$), 11.5 (C$_5$(*C*H$_3$)$_5$).
Elemental Analysis for C$_{17}$H$_{33}$ONTi (found): C, 64.75 (64.56); H, 10.55 (10.58); N, 4.44 (4.49).

Synthesis of Cp*Ti(Me)$_2$(ONMe(2,4,6-Me$_3$C$_6$H$_2$)), 7. A solution of 2,4,6-trimethylnitrosbenzene (0.37 g, 2.5 mmol) in toluene (50 mL) was added slowly to a stirred solution of Cp*TiMe$_3$ (0.57 g, 2.5 mmol) in toluene (30 mL) at 0 ^{o}C. The solution was stirred for 4 hours before being reduced under vacuum to yield an orange solid (0.82 g, 2.2 mmol, 88.0 %).
^{1}H NMR (C$_6$D$_6$, 500MHz): δ 6.70 (s, Ar, 2H), 3.01 (s, ONC*H*$_3$, 3H), 2.62 (s, Ar-*o*-C*H*$_3$, 6H), 2.05 (s, Ar-*p*-C*H*$_3$, 3H), 1.83 (s, C$_5$(C*H*$_3$)$_5$, 15H), 0.12 (br s, TiC*H*$_3$, 6H).
^{13}C {^{1}H} NMR (C$_6$D$_6$, 500MHz): δ 146.9, 135.1, 132.4, 131.1 (Ar), 120.2 (*C*$_5$(CH$_3$)$_5$), 50.9 (ON*C*H$_3$), 48.7 (Ti*C*H$_3$), 21.1 (Ar-*o*-*C*H$_3$), 20.5 (Ar-*p*-*C*H$_3$), 11.4 (C$_5$(*C*H$_3$)$_5$).
Elemental Analysis for C$_{22}$H$_{35}$ONTi (found): C, 70.02 (69.02); H, 9.35 (9.24); N, 3.71 (3.71).

Table S1. Microstructure analysis of poly(propylene)s.

	mmmm	mmmr	rmmr	mmrr	mmrm/rmmr	mrmr	rrrr	rrmm	mrrm
1	0.92	4.9	4.47	8.42	23.06	11.44	16.27	20.07	10.46
2	2.61	6.3	6.14	10.82	22.65	10.39	17.33	17.91	5.84
3	1.4	5.43	5.07	9.88	23.53	11.03	17.1	19.52	7.04
4	0.91	4.61	4.54	9.01	23	12.54	16.07	19.2	10.11
5	3.73	9.79	5.99	11.37	24.49	13.84	7.94	14.12	8.73
6	2.42	6.80	5.64	10.36	22.11	11.86	11.12	17.05	12.63
6 + ^{t}BuNO	0.87	5.21	4.43	8.7	23.27	11.88	17.39	19.75	8.49
6 + 2,4,6-$Me_3C_6H_2NO$	2.00	6.01	5.10	10.34	23.21	11.46	15.06	18.77	8.05
6 +PhNO	1.65	5.47	5.36	10.40	23.55	10.48	18.17	19.26	5.68
6 + 2,6-$Br_2C_6H_3N$	4.51	7.99	4.99	10.75	22.78	9.25	14.82	17.14	7.77
6 + 3,5-$^{t}Bu_2C_6H_3$	2.13	5.88	5.65	10.29	23.12	11.74	15.54	17.99	7.67

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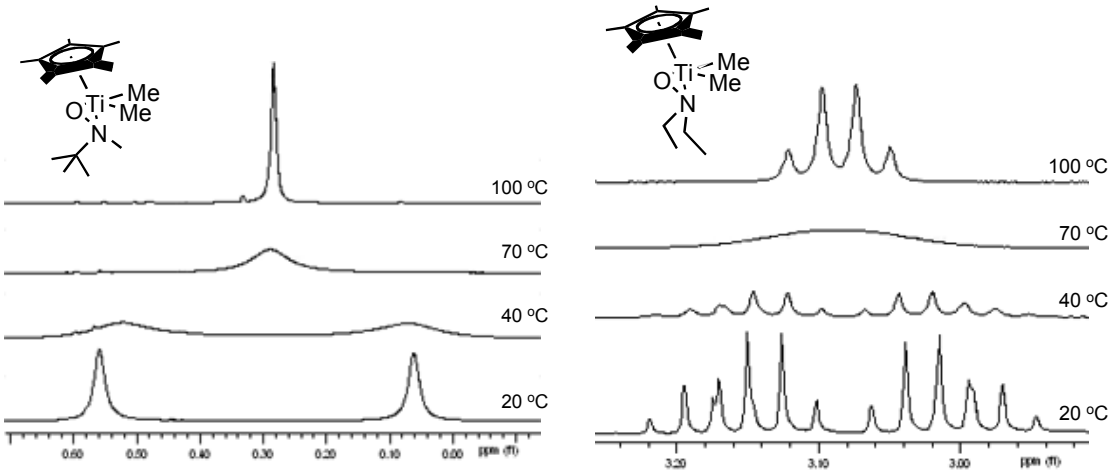
Figure S1 – Variable temperature ^{1}H NMR of complexes **2** and **3** between 20 and 100 ^{o}C.



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X-ray Crystallographic data for **2**.

Data Collection

A colorless rhombic crystal of C_{17} H_{33} N O Ti having approximate dimensions of 0.18 x 0.18 x 0.10 mm was mounted on a quartz fiber using Paratone N hydrocarbon oil. All measurements were made on a Bruker-Siemens SMART[1] CCD area detector with monochromatic radiation of wavelength 0.71073 Å.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the measured positions of 918 centered reflections with $I > 10\sigma(I)$ in the range $2.51^\circ < \theta < 19.43^\circ$, corresponded to a primitive monoclinic cell with dimensions:

a = 9.060(2) Å	$\alpha = 90^\circ$
b = 16.210(3) Å	$\beta = 100.767(3)^\circ$
c = 12.450(2) Å	$\gamma = 90^\circ$
V = 8876(1) Å^3	

For Z = 4 and $F.W.$ = 315.34, the calculated density is 1.166 g/cm^3.

Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P21/n

The data were collected at a temperature of 143 K. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3º counted for a total of 10 seconds per frame.

Data Reduction

Data were integrated by the program SAINT[2] with box parameters of 1.0 x 1.0 x 0.6º to a maximum θ value of 24.73º. The data were corrected for Lorentz and polarization effects. The linear absorption coefficient, μ, for 0.71073 Å radiation is 0.474 mm^{-1}. Data were analyzed for agreement and possible absorption using SADABS[3]. A semi-empirical absorption correction based on 6.79 reflections with $I > 5\sigma(I)$ was applied that resulted in normalized transmission factors ranging from 0.36 to 0.95. Of the 8041 reflections that were collected, 3002 were unique (R_{int} = 0.1111); equivalent reflections were merged. No decay correction was deemed necessary.

Structure Solution and Refinement

The structure was solved by direct methods (SHELXS-97)[4] and expanded using Fourier techniques[5]. Hydrogen atoms were located by geometrical criteria using HFIX instruction. A single torsional parameter about the H-C the case of methyl groups. The final cycle of full-matrix least-squares refinement[6] was based on 3002 reflections (all data) and 192 variable parameters and converged (largest parameter shift was 0.000 times its esd) with conventional unweighted and weighted agreement factors of:

$$R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o| = 0.0637 \text{ for 1556 data with } F_o > 4\sigma(F_o)$$

$$wR_2 = [(\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w |F_o|^2)]^{1/2} = 0.1501$$

The standard deviation of an observation of unit weight (S)[7] was 0.924. Sheldrick weights[6] were used; weights were refined to convergence. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.32 and -0.97 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[8]. Anomalous dispersion effects were included in Fcalc[9]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[10]. The values for the mass attenuation coefficients were those of Creagh and Hubbel[11]. All calculations were performed using the SHELX97[12] crystallographic software package.

References

(1) SMART: Area-Detector Software Package, Siemens Industrial Automation, Inc.: Madison, WI (1995).

(2) SAINT: SAX Area-Dectector Integration Program, V5.04; Siemens Industrial Automation, Inc.: Madison, WI, (1995)

(3) SADABS: Siemens Area Detector ABSorption correction program, George Sheldrick, (1996). Advance copy, private communication.

(4)SHELXS-97: Sheldrick, G.M. (1997).
SIR97: a new tool for crystal structure determination and refinement.: A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna. J. Appl. Cryst., (1999). 32, 115-119.

(5) DIRDIF99: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M. (1999). The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(6) Least-Squares:

Function minimized: $\Sigma w (|F_o|^2 - |F_c|^2)^2$

$w=1/[\sigma^2(F_o^2)+(0.0660P)^2]$ where $P=(F_o^2+2F_c^2)/3$

Sheldrick weights: G. M. Sheldrick (1997)

(7) Standard deviation of an observation of unit weight:

$$S = [\Sigma w (|F_o|^2 - |F_c|^2)^2/(N_o - N_v)]^{1/2}$$

where: N_o = number of observations

N_v = number of variables

(8) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(9) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(10) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(11) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(12) SHELXL-97: G. M. Sheldrick (1997)

Supplementary Material (ESI) for Chemical Communications

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	C17 H33 N O Ti
Formula Weight	315.34
Crystal Color, Habit	colorless, rhombic
Crystal Dimensions	0.18 x 0.18 x 0.10 mm
Crystal System	monoclinic
Lattice Type	primitive
Lattice Parameters	a = 9.060(2) Å b = 16.210(3) Å c = 12.450(2) Å α = 90º β = 100.767(3)º γ = 90º V = 1796.2(6) Å^3
Space Group	P21/n
Z value	4
d_{calc}	1.166 g/cm^3
F_{000}	688
μ(0.71073 Å radiation)	0.47 cm^{-1}

B. Intensity Measurements

Diffractometer	Bruker-Siemens SMART CCD
Radiation	λ = 0.71073 Å graphite monochromated
Exposure Time	10 seconds per frame.
Scan Type	ω (0.3 degrees per frame)
θ_{max}	24.73º
Data Collection Temperature	143 K
No. of Reflections Measured	Total: 8041 Unique: 3002 (R_{int} = 0.1111)
Corrections	Lorentz-polarization Absorption: T_{max} = 0.99 T_{min} = 0.78

C. Structure Solution and Refinement

Structure Solution	Direct (SHELXS-97)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\|F_o\|^2 - \|F_c\|^2)^2$
Least Squares Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0660P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($F_o > 4\sigma(F_o)$)	1556
No. Variables	192
Reflection/Parameter Ratio	15.64
Residuals: R_1; wR_2	0.0637; 0.1501
Goodness of Fit Indicator (S)	0.924
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.32 $e^-/Å^3$
Minimum peak	

Table S2. Atomic coordinates, U_{iso}/U_{eq}, and occupancy for **3**

atom	*x*	*y*	*z*	U_{eq}	occ
Ti1	0.5270(1)	0.1718(1)	0.3017(1)	0.018(1)	1
O1	0.4003(3)	0.1553(2)	0.1640(2)	0.023(1)	1
N1	0.2912(4)	0.1498(2)	0.2326(3)	0.021(1)	1
C1	0.7854(5)	0.1446(3)	0.3845(4)	0.020(1)	1
C2	0.7866(5)	0.2171(3)	0.3234(4)	0.020(1)	1
C3	0.7320(5)	0.1970(3)	0.2113(4)	0.018(1)	1
C4	0.7038(5)	0.1112(3)	0.2051(4)	0.020(1)	1
C5	0.7334(5)	0.0791(3)	0.3129(4)	0.018(1)	1
C6	0.8489(6)	0.1345(3)	0.5039(4)	0.029(1)	1
C7	0.8489(6)	0.2995(3)	0.3655(4)	0.029(1)	1
C8	0.7204(6)	0.2551(3)	0.1162(4)	0.033(1)	1
C9	0.6583(6)	0.0639(3)	0.1000(4)	0.028(1)	1
C10	0.7304(5)	-0.0097(3)	0.3440(4)	0.029(1)	1
C11	0.4985(6)	0.2977(3)	0.3370(4)	0.036(2)	1
C12	0.4913(6)	0.1306(3)	0.4584(4)	0.029(1)	1
C13	0.1824(6)	0.2180(3)	0.2031(4)	0.037(2)	1
C14	0.2155(5)	0.0669(3)	0.2206(4)	0.023(1)	1
C15	0.3357(5)	0.0007(3)	0.2436(4)	0.032(1)	1
C16	0.1227(6)	0.0540(3)	0.1068(4)	0.035(2)	1
C17	0.1151(6)	0.0611(3)	0.3050(4)	0.037(2)	1
H6A	0.7901	0.0949	0.5349	0.044	1
H6B	0.8463	0.1866	0.5403	0.044	1
H6C	0.9509	0.1156	0.5129	0.044	1
H7A	0.8469	0.3037	0.4422	0.044	1
H7B	0.7891	0.3428	0.3268	0.044	1
H7C	0.9506	0.3045	0.3545	0.044	1
H8A	0.8148	0.2569	0.0918	0.050	1
H8B	0.6956	0.3093	0.1384	0.050	1
H8C	0.6434	0.2363	0.0576	0.050	1
H9A	0.6498	0.0064	0.1161	0.042	1
H9B	0.7329	0.0712	0.0553	0.042	1
H9C	0.5633	0.0840	0.0617	0.042	1
H10A	0.8286	-0.0331	0.3481	0.043	1
H10B	0.6597	-0.0387	0.2901	0.043	1
H10C	0.7009	-0.0144	0.4140	0.043	1
H11A	0.5044	0.3304	0.2736	0.054	1
H11B	0.5761	0.3145	0.3965	0.054	1
H11C	0.4021	0.3055	0.3570	0.054	1
H12A	0.3862	0.1336	0.4609	0.043	1
H12B	0.5466	0.1652	0.5144	0.043	1
H12C	0.5252	0.0747	0.4700	0.043	1
H13A	0.2350	0.2696	0.2093	0.055	1
H13B	0.1116	0.2177	0.2516	0.055	1
H13C	0.1299	0.2107	0.1292	0.055	1
H15A	0.3941	0.0009	0.1867	0.048	1
H15B	0.2889	-0.0523	0.2459	0.048	1
H15C	0.4000	0.0115	0.3126	0.048	1
H16A	0.0398	0.0918	0.0951	0.053	1
H16B	0.0854	-0.0016	0.1002	0.053	1
H16C	0.1844	0.0635	0.0532	0.053	1
H17A	0.1728	0.0727	0.3762	0.056	1
H17B	0.0739	0.0065	0.3043	0.056	1
H17C	0.0349	0.1004	0.2880	0.056	1

U_{eq} is defined as one third of the orthogonalized U_{ij} tensor

Table S3. Anisotropic Displacement Parameters for **3**

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti1	0.014(1)	0.019(1)	0.023(1)	-0.001(1)	0.004(1)	0.001(1)
O1	0.016(2)	0.034(2)	0.020(2)	0.001(2)	0.005(2)	-0.002(2)
N1	0.020(2)	0.025(3)	0.022(2)	0.003(2)	0.013(2)	0.008(2)
C1	0.010(3)	0.028(3)	0.021(3)	0.003(2)	-0.003(2)	0.003(2)
C2	0.013(3)	0.022(3)	0.024(3)	-0.002(2)	-0.001(2)	-0.004(2)
C3	0.016(3)	0.024(3)	0.016(3)	0.004(2)	0.007(2)	0.001(2)
C4	0.011(3)	0.020(3)	0.028(3)	-0.002(3)	0.002(2)	-0.002(2)
C5	0.006(2)	0.016(3)	0.033(3)	-0.004(2)	0.005(2)	0.000(2)
C6	0.023(3)	0.032(3)	0.031(3)	0.000(3)	0.000(3)	0.003(3)
C7	0.026(3)	0.021(3)	0.040(3)	-0.003(3)	0.004(3)	-0.009(2)
C8	0.032(3)	0.037(4)	0.032(3)	0.007(3)	0.008(3)	-0.003(3)
C9	0.024(3)	0.030(3)	0.031(3)	-0.006(3)	0.009(3)	-0.003(3)
C10	0.021(3)	0.021(3)	0.045(4)	0.002(3)	0.009(3)	0.004(3)
C11	0.029(3)	0.035(3)	0.042(4)	-0.002(3)	0.001(3)	0.004(3)
C12	0.024(3)	0.034(3)	0.028(3)	-0.003(3)	0.004(3)	0.001(3)
C13	0.021(3)	0.035(4)	0.055(4)	0.011(3)	0.008(3)	0.011(3)
C14	0.019(3)	0.025(3)	0.021(3)	0.003(2)	-0.006(2)	0.001(3)
C15	0.021(3)	0.028(3)	0.044(4)	-0.001(3)	0.001(3)	-0.005(3)
C16	0.021(3)	0.046(4)	0.036(4)	0.000(3)	-0.004(3)	-0.001(3)
C17	0.021(3)	0.055(4)	0.038(4)	0.013(3)	0.010(3)	-0.002(3)

The general temperature factor expression:
$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S4. Bond Lengths (Å) for **3**

atom	atom	distance	atom	atom	distance
Ti1	O1	1.895(3)	Ti1	C11	2.114(5)
Ti1	C12	2.142(5)	Ti1	N1	2.178(4)
Ti1	C3	2.380(5)	Ti1	C5	2.383(5)
Ti1	C4	2.387(5)	Ti1	C1	2.416(5)
Ti1	C2	2.430(5)	O1	N1	1.424(5)
N1	C13	1.481(6)	N1	C14	1.502(6)
C1	C2	1.400(6)	C1	C5	1.410(6)
C1	C6	1.500(6)	C2	C3	1.430(6)
C2	C7	1.506(6)	C3	C4	1.414(6)
C3	C8	1.501(6)	C4	C5	1.418(6)
C4	C9	1.506(6)	C5	C10	1.492(6)
C6	H6A	0.9600	C6	H6B	0.9600 C6
H6C	0.9600	C7	H7A	0.9600	C7 H7B
0.9600	C7	H7C	0.9600	C8	H8A 0.9600
C8	H8B	0.9600	C8	H8C	0.9600 C9
H9A	0.9600	C9	H9B	0.9600	C9 H9C
0.9600	C10	H10A	0.9600	C10	H10B 0.9600
C10	H10C	0.9600	C11	H11A	0.9600 C11
H11B	0.9600	C11	H11C	0.9600	C12 H12A
0.9600	C12	H12B	0.9600	C12	H12C 0.9600
C13	H13A	0.9600	C13	H13B	0.9600 C13
H13C	0.9600	C14	C17	1.516(7)	C14 C15
1.518(6)	C14	C16	1.521(6)	C15	H15A 0.9600
C15	H15B	0.9600	C15	H15C	0.9600 C16
H16A	0.9600	C16	H16B	0.9600	C16 H16C
0.9600	C17	H17A	0.9600	C17	H17B 0.9600
C17	H17C	0.9600			

Symmetry transformations used to generate equivalent atoms:

Table S5. Bond Angles (º) for **3**

atom	atom	atom	angle	atom	atom	atom	angle
O1	Ti1	C11	104.31(17)	O1	Ti1	C12	127.66(17)
C11	Ti1	C12	93.8(2)	O1	Ti1	N1	40.19(13)
C11	Ti1	N1	95.26(17)	C12	Ti1	N1	90.30(17)
O1	Ti1	C3	89.47(15)	C11	Ti1	C3	93.94(19)
C12	Ti1	C3	138.39(18)	N1	Ti1	C3	129.48(15)
O1	Ti1	C5	107.49(15)	C11	Ti1	C5	136.19(18)
C12	Ti1	C5	90.02(18)	N1	Ti1	C5	128.39(15)
C3	Ti1	C5	57.50(16)	O1	Ti1	C4	80.60(15)
C11	Ti1	C4	128.42(19)	C12	Ti1	C4	124.06(18)
N1	Ti1	C4	115.77(15)	C3	Ti1	C4	34.49(15)
C5	Ti1	C4	34.58(15)	O1	Ti1	C1	137.33(16)
C11	Ti1	C1	103.48(18)	C12	Ti1	C1	81.58(18)
N1	Ti1	C1	159.97(15)	C3	Ti1	C1	56.87(16)
C5	Ti1	C1	34.18(14)	C4	Ti1	C1	56.75(16)
O1	Ti1	C2	123.60(15)	C11	Ti1	C2	80.67(18)
C12	Ti1	C2	107.45(18)	N1	Ti1	C2	161.96(15)
C3	Ti1	C2	34.55(15)	C5	Ti1	C2	56.74(16)
C4	Ti1	C2	56.89(16)	C1	Ti1	C2	33.58(14)
N1	O1	Ti1	80.7(2)	O1	N1	C13	108.0(3)
O1	N1	C14	110.6(3)	C13	N1	C14	111.9(4)
O1	N1	Ti1	59.16(19)	C13	N1	Ti1	122.3(3)
C14	N1	Ti1	125.5(3)	C2	C1	C5	109.0(4)
C2	C1	C6	126.1(4)	C5	C1	C6	124.4(4)
C2	C1	Ti1	73.8(3)	C5	C1	Ti1	71.7(3)
C6	C1	Ti1	127.2(3)	C1	C2	C3	107.6(4)
C1	C2	C7	126.6(4)	C3	C2	C7	125.5(4)
C1	C2	Ti1	72.6(3)	C3	C2	Ti1	70.8(3)
C7	C2	Ti1	126.8(3)	C4	C3	C2	107.7(4)
C4	C3	C8	126.1(4)	C2	C3	C8	126.0(4)
C4	C3	Ti1	73.0(3)	C2	C3	Ti1	74.6(3)
C8	C3	Ti1	122.3(3)	C3	C4	C5	108.0(4)
C3	C4	C9	124.4(4)	C5	C4	C9	127.4(4)
C3	C4	Ti1	72.5(3)	C5	C4	Ti1	72.6(3)
C9	C4	Ti1	123.1(3)	C1	C5	C4	107.6(4)
C1	C5	C10	125.7(4)	C4	C5	C10	126.2(4)
C1	C5	Ti1	74.2(3)	C4	C5	Ti1	72.9(3)
C10	C5	Ti1	124.8(3)	C1	C6	H6A	109.5
C1	C6	H6B	109.5	H6A	C6	H6B	109.5
C1	C6	H6C	109.5	H6A	C6	H6C	109.5
H6B	C6	H6C	109.5	C2	C7	H7A	109.5

C2	C7	H7B	109.5	H7A	C7	H7B	109.5
C2	C7	H7C	109.5	H7A	C7	H7C	109.5
H7B	C7	H7C	109.5	C3	C8	H8A	109.5
C3	C8	H8B	109.5	H8A	C8	H8B	109.5
C3	C8	H8C	109.5	H8A	C8	H8C	109.5
H8B	C8	H8C	109.5	C4	C9	H9A	109.5
C4	C9	H9B	109.5	H9A	C9	H9B	109.5
C4	C9	H9C	109.5	H9A	C9	H9C	109.5
H9B	C9	H9C	109.5	C5	C10	H10A	109.5
C5	C10	H10B	109.5	H10A	C10	H10B	109.5
C5	C10	H10C	109.5	H10A	C10	H10C	109.5
H10B	C10	H10C	109.5	Ti1	C11	H11A	109.5
Ti1	C11	H11B	109.5	H11A	C11	H11B	109.5
Ti1	C11	H11C	109.5	H11A	C11	H11C	109.5
H11B	C11	H11C	109.5	Ti1	C12	H12A	109.5
Ti1	C12	H12B	109.5	H12A	C12	H12B	109.5
Ti1	C12	H12C	109.5	H12A	C12	H12C	109.5
H12B	C12	H12C	109.5	N1	C13	H13A	109.5
N1	C13	H13B	109.5	H13A	C13	H13B	109.5
N1	C13	H13C	109.5	H13A	C13	H13C	109.5
H13B	C13	H13C	109.5	N1	C14	C17	108.0(4)
N1	C14	C15	108.4(4)	C17	C14	C15	109.1(4)
N1	C14	C16	112.2(4)	C17	C14	C16	109.8(4)
C15	C14	C16	109.2(4)	C14	C15	H15A	109.5
C14	C15	H15B	109.5	H15A	C15	H15B	109.5
C14	C15	H15C	109.5	H15A	C15	H15C	109.5
H15B	C15	H15C	109.5	C14	C16	H16A	109.5
C14	C16	H16B	109.5	H16A	C16	H16B	109.5
C14	C16	H16C	109.5	H16A	C16	H16C	109.5
H16B	C16	H16C	109.5	C14	C17	H17A	109.5
C14	C17	H17B	109.5	H17A	C17	H17B	109.5
C14	C17	H17C	109.5	H17A	C17	H17C	109.5
H17B	C17	H17C	109.5				

Symmetry transformations used to generate equivalent atoms:

Table S6. Torsion Angles (º) for **3**

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
C11	Ti1	O1	N1	-81.1(3)	C12	Ti1	O1	N1	25.4(3)
C3	Ti1	O1	N1	-175.0(2)	C5	Ti1	O1	N1	129.5(2)
C4	Ti1	O1	N1	151.5(2)	C1	Ti1	O1	N1	149.8(2)
C2	Ti1	O1	N1	-169.3(2)	Ti1	O1	N1	C13	117.4(3)
Ti1	O1	N1	C14	-119.9(3)	C11	Ti1	N1	O1	106.0(2)
C12	Ti1	N1	O1	-160.2(2)	C3	Ti1	N1	O1	6.5(3)
C5	Ti1	N1	O1	-69.9(3)	C4	Ti1	N1	O1	-31.5(3)
C1	Ti1	N1	O1	-94.6(5)	C2	Ti1	N1	O1	30.1(6)
O1	Ti1	N1	C13	-92.7(4)	C11	Ti1	N1	C13	13.3(4)
C12	Ti1	N1	C13	107.1(4)	C3	Ti1	N1	C13	-86.3(4)
C5	Ti1	N1	C13	-162.6(3)	C4	Ti1	N1	C13	-124.3(4)
C1	Ti1	N1	C13	172.7(4)	C2	Ti1	N1	C13	-62.7(6)
O1	Ti1	N1	C14	94.5(4)	C11	Ti1	N1	C14	-159.5(4)
C12	Ti1	N1	C14	-65.7(4)	C3	Ti1	N1	C14	100.9(4)
C5	Ti1	N1	C14	24.6(4)	C4	Ti1	N1	C14	62.9(4)
C1	Ti1	N1	C14	-0.1(7)	C2	Ti1	N1	C14	124.5(5)
O1	Ti1	C1	C2	80.9(3)	C11	Ti1	C1	C2	-48.5(3)
C12	Ti1	C1	C2	-140.4(3)	N1	Ti1	C1	C2	152.6(4)
C3	Ti1	C1	C2	37.3(3)	C5	Ti1	C1	C2	116.9(4)
C4	Ti1	C1	C2	78.8(3)	O1	Ti1	C1	C5	-36.0(4)
C11	Ti1	C1	C5	-165.5(3)	C12	Ti1	C1	C5	102.6(3)
N1	Ti1	C1	C5	35.6(6)	C3	Ti1	C1	C5	-79.6(3)
C4	Ti1	C1	C5	-38.1(3)	C2	Ti1	C1	C5	-116.9(4)
O1	Ti1	C1	C6	-155.7(3)	C11	Ti1	C1	C6	74.8(4)
C12	Ti1	C1	C6	-17.1(4)	N1	Ti1	C1	C6	-84.1(6)
C3	Ti1	C1	C6	160.7(5)	C5	Ti1	C1	C6	-119.7(5)
C4	Ti1	C1	C6	-157.8(5)	C2	Ti1	C1	C6	123.4(5)
C5	C1	C2	C3	0.9(5)	C6	C1	C2	C3	172.8(5)
Ti1	C1	C2	C3	-62.6(3)	C5	C1	C2	C7	-173.2(4)
C6	C1	C2	C7	-1.2(8)	Ti1	C1	C2	C7	123.4(5)
C5	C1	C2	Ti1	63.5(3)	C6	C1	C2	Ti1	-124.6(5)
O1	Ti1	C2	C1	-126.5(3)	C11	Ti1	C2	C1	132.4(3)
C12	Ti1	C2	C1	41.3(3)	N1	Ti1	C2	C1	-149.4(4)
C3	Ti1	C2	C1	-116.4(4)	C5	Ti1	C2	C1	-36.8(3)
C4	Ti1	C2	C1	-78.4(3)	O1	Ti1	C2	C3	-10.1(3)
C11	Ti1	C2	C3	-111.2(3)	C12	Ti1	C2	C3	157.7(3)
N1	Ti1	C2	C3	-33.0(6)	C5	Ti1	C2	C3	79.6(3)
C4	Ti1	C2	C3	38.0(3)	C1	Ti1	C2	C3	116.4(4)
O1	Ti1	C2	C7	110.4(4)	C11	Ti1	C2	C7	9.3(4)
C12	Ti1	C2	C7	-81.7(4)	N1	Ti1	C2	C7	87.6(6)
C3	Ti1	C2	C7	120.5(5)	C5	Ti1	C2	C7	-159.9(5)

C4	Ti1	C2	C7	158.5(5)	C1	Ti1	C2	C7	-123.1(5)
C1	C2	C3	C4	-2.3(5)	C7	C2	C3	C4	171.8(4)
Ti1	C2	C3	C4	-66.1(3)	C1	C2	C3	C8	-177.2(5)
C7	C2	C3	C8	-3.0(8)	Ti1	C2	C3	C8	119.1(5)
C1	C2	C3	Ti1	63.8(3)	C7	C2	C3	Ti1	-122.1(5)
O1	Ti1	C3	C4	-74.1(3)	C11	Ti1	C3	C4	-178.4(3)
C12	Ti1	C3	C4	81.4(4)	N1	Ti1	C3	C4	-78.2(3)
C5	Ti1	C3	C4	37.2(3)	C1	Ti1	C3	C4	78.1(3)
C2	Ti1	C3	C4	114.4(4)	O1	Ti1	C3	C2	171.6(3)
C11	Ti1	C3	C2	67.3(3)	C12	Ti1	C3	C2	-33.0(4)
N1	Ti1	C3	C2	167.4(2)	C5	Ti1	C3	C2	-77.2(3)
C4	Ti1	C3	C2	-114.4(4)	C1	Ti1	C3	C2	-36.3(3)
O1	Ti1	C3	C8	48.4(4)	C11	Ti1	C3	C8	-55.9(4)
C12	Ti1	C3	C8	-156.2(4)	N1	Ti1	C3	C8	44.2(4)
C5	Ti1	C3	C8	159.6(4)	C4	Ti1	C3	C8	122.4(5)
C1	Ti1	C3	C8	-159.5(4)	C2	Ti1	C3	C8	-123.2(5)
C2	C3	C4	C5	2.9(5)	C8	C3	C4	C5	177.7(5)
Ti1	C3	C4	C5	-64.3(3)	C2	C3	C4	C9	-174.3(4)
C8	C3	C4	C9	0.6(7)	Ti1	C3	C4	C9	118.6(5)
C2	C3	C4	Ti1	67.2(3)	C8	C3	C4	Ti1	-118.0(5)
O1	Ti1	C4	C3	103.0(3)	C11	Ti1	C4	C3	2.1(4)
C12	Ti1	C4	C3	-127.6(3)	N1	Ti1	C4	C3	123.0(3)
C5	Ti1	C4	C3	-116.1(4)	C1	Ti1	C4	C3	-78.5(3)
C2	Ti1	C4	C3	-38.1(3)	O1	Ti1	C4	C5	-141.0(3)
C11	Ti1	C4	C5	118.2(3)	C12	Ti1	C4	C5	-11.5(4)
N1	Ti1	C4	C5	-121.0(3)	C3	Ti1	C4	C5	116.1(4)
C1	Ti1	C4	C5	37.6(3)	C2	Ti1	C4	C5	78.0(3)
O1	Ti1	C4	C9	-17.2(4)	C11	Ti1	C4	C9	-118.1(4)
C12	Ti1	C4	C9	112.3(4)	N1	Ti1	C4	C9	2.8(4)
C3	Ti1	C4	C9	-120.2(5)	C5	Ti1	C4	C9	123.8(5)
C1	Ti1	C4	C9	161.4(5)	C2	Ti1	C4	C9	-158.2(5)
C2	C1	C5	C4	0.9(5)	C6	C1	C5	C4	-171.3(5)
Ti1	C1	C5	C4	65.7(3)	C2	C1	C5	C10	173.3(4)
C6	C1	C5	C10	1.2(8)	Ti1	C1	C5	C10	-121.8(5)
C2	C1	C5	Ti1	-64.8(3)	C6	C1	C5	Ti1	123.0(5)
C3	C4	C5	C1	-2.3(5)	C9	C4	C5	C1	174.7(4)
Ti1	C4	C5	C1	-66.6(3)	C3	C4	C5	C10	-174.7(4)
C9	C4	C5	C10	2.3(8)	Ti1	C4	C5	C10	121.0(5)
C3	C4	C5	Ti1	64.3(3)	C9	C4	C5	Ti1	-118.7(5)
O1	Ti1	C5	C1	155.3(3)	C11	Ti1	C5	C1	20.6(4)
C12	Ti1	C5	C1	-74.9(3)	N1	Ti1	C5	C1	-165.3(3)
C3	Ti1	C5	C1	77.5(3)	C4	Ti1	C5	C1	114.6(4)
C2	Ti1	C5	C1	36.1(3)	O1	Ti1	C5	C4	40.7(3)
C11	Ti1	C5	C4	-94.0(4)	C12	Ti1	C5	C4	170.5(3)
N1	Ti1	C5	C4	80.1(3)	C3	Ti1	C5	C4	-37.1(3)
C1	Ti1	C5	C4	-114.6(4)	C2	Ti1	C5	C4	-78.5(3)

O1	Ti1	C5	C10	-82.0(4)	C11	Ti1	C5	C10	143.4(4)
C12	Ti1	C5	C10	47.9(4)	N1	Ti1	C5	C10	-42.5(5)
C3	Ti1	C5	C10	-159.7(5)	C4	Ti1	C5	C10	-122.6(5)
C1	Ti1	C5	C10	122.8(5)	C2	Ti1	C5	C10	158.9(5)
O1	N1	C14	C17	173.3(3)	C13	N1	C14	C17	-66.3(5)
Ti1	N1	C14	C17	107.2(4)	O1	N1	C14	C15	55.2(5)
C13	N1	C14	C15	175.6(4)	Ti1	N1	C14	C15	-11.0(5)
O1	N1	C14	C16	-65.6(5)	C13	N1	C14	C16	54.8(5)
Ti1	N1	C14	C16	-131.7(4)					

Symmetry transformations used to generate equivalent atoms: