Synthesis and Reactivity of Titanium Cyclopentadienyl Imido Amidinate Complexes

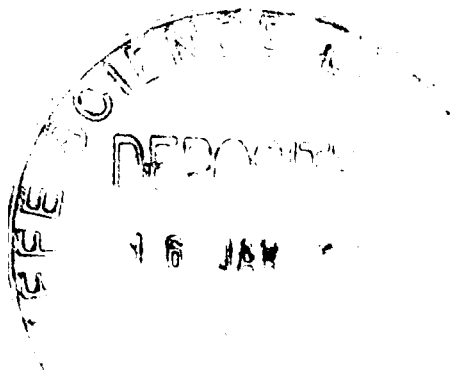
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CHAPTER 7

Experimental

7.1 General Methods and Instrumentation

All manipulations were carried out under an atmosphere of dinitrogen or argon using standard Schlenk-line or dry-box techniques. All solvents used were predried over activated 4Å molecular sieves and refluxed over potassium (benzene, hexane, tetrahydrofuran), sodium-potassium alloy (pentane), sodium (diethyl ether), or calcium hydride (dichloromethane) under an atmosphere of dinitrogen, and collected by distillation. Chloroform-d and dichloromethane-d_2 were dried over freshly ground calcium hydride at room temperature, distilled under vacuum, and stored under dinitrogen in ampoules fitted with J. Young Teflon valves. Benzene-d_6 was dried by refluxing over potassium, distilled under vacuum, and stored under an atmosphere of dinitrogen in ampoules fitted with J. Young Teflon valves. Toluene-d_8 was dried by refluxing over sodium, distilled under vacuum, and stored in ampoules fitted with J. Young Teflon valves.

NMR samples were prepared in the dry-box in 5 mm Wilmad 505-PS tubes equipped with a J. Young NMR / 5 Teflon valve. ^{1}H and ^{13}C-$\{^{1}H\}$ spectra were recorded using either a Varian Unity 500 or Mercury 300 spectrometer. ^{19}F spectra were recorded on a Varian Mercury 300 spectrometer. The ^{1}H and ^{13}C spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). ^{19}F spectra were externally referenced to $CFCl_3$ ($\delta = 0$ ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hertz. Assignments were supported by DEPT-45 and DEPT-90, homo- and hetero-nuclear, one- and two-dimensional experiments

as appropriate.

Infrared spectra were recorded on a Perkin Elmer 1710 spectrometer in the range 4000 – 400 cm^{-1}. Samples were prepared in the dry-box as Nujol mulls, or else as neat thin films, between NaCl, KBr or CsBr discs, and data are quoted in wavenumbers (ν, cm^{-1}).

Elemental analyses were carried out by the analytical department of this laboratory.

Electron Impact and Field Ionisation mass spectra were recorded by Robin Proctor in the Dyson Perrins laboratory, and by Colin Sparrow in this department.

APCI mass spectra were recorded using a Hewlett Packard Series 1050 APCI mass spectrometer. GC-MS measurements were made using a Hewlett Packard 5890 Trio 1 spectrometer. All data are quoted in mass / charge ratio (*m/z*).

Crystal structures were calculated from data collected using an Enraf Nonius DIP2000 or Enraf Nonius KappaCCD Single Crystal X-Ray Diffractometer.

7.2 STARTING MATERIALS

7.2.1 GENERAL REAGENTS

All chemicals used in air / moisture sensitive manipulations were purified by standard techniques.[1]

$Ti(NR)Cl_2(py)_3$ (R = ^{t}Bu, 2,6-$C_6H_3Me_2$, 4-C_6H_4Me),[2,3] $Li(C_5Me_5)$,[4], $Li\{PhC(NSiMe_3)_2\}$,[5] and $Li\{MeC(N^iPr)_2\}$[6] were prepared according to literature procedures. $Li(C_5H_4Me)$ was donated by Dr. P. Mountford.

Carbonyl sulfide (COS) was prepared immediately prior to use. In a typical reaction, 6 ml of a saturated aqueous solution of KSCN was placed in a 250 ml round bottomed flask. To this was added 100 ml of a 30 % sulfuric acid solution. The flask was connected to a vacuum line, and the pressure dropped to 500 mmHg. The flask was then heated to 60 °C for 10 min. All volatiles were trapped in a liquid nitrogen cold finger, and were removed. The pressure in the line was then dropped to 150 mmHg, and the flask heated to 60 °C for a further 30 min. Volatiles were collected in a liquid nitrogen cooled cold finger, and were confirmed to be COS by IR spectroscopy.

7.2.2 Synthesis of Ti(η-C_5H_4Me)(N^{t}Bu)Cl(py)

A solution of 15.73 g (0.037 mol) $Ti(N^tBu)Cl_2(py)_3$ in *ca.* 50 ml THF was cooled to -78 °C, and to this was slowly added 3.17 g (0.037 mol) $Li(C_5H_4Me)$ dissolved in *ca.* 300 ml THF. The resulting red solution was stirred for 16 h, and the volatiles were then removed under reduced pressure. The residue was extracted with *ca.* 250 ml dichloromethane, filtered, and the solvent removed under reduced pressure to leave a red oil. Upon washing with pentane, the product was isolated as a red crystalline solid (10.06 g, 87 %).

7.2.3 Synthesis of Ti(η-C_5Me_5)(N^{t}Bu)Cl(py)

A solution of 25.94 g (0.061 mol) $Ti(N^tBu)Cl_2(py)_3$ in *ca.* 50 ml THF was cooled to -78 °C, and to this was slowly added 8.63 g (0.061 mol) $Li(C_5Me_5)$

slurried in *ca.* 300 ml THF. The resulting dark red solution was stirred for 16 h, and the volatiles were then removed under reduced pressure. The residue was extracted with *ca.* 250 ml dichloromethane, followed by 2 × *ca.* 100 ml dichloromethane, filtered, and the solvent removed under reduced pressure to leave a dark red oil. Upon washing with pentane, the product was isolated as a red-brown waxy solid (20.08 g, 90 %).

7.3 EXPERIMENTAL DETAILS: CHAPTER 2

7.3.1 SYNTHESIS OF Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (1)

To a solution of 714 mg (1.94 mmol) Ti(η-C_5Me_5)(N^{t}Bu)Cl(py) in *ca.* 30 ml benzene was added 532 mg (1.97 mmol) Li{PhC(NSiMe$_3$)$_2$} dissolved in *ca.* 40 ml benzene. After 16 h, the volatiles removed under reduced pressure to yield a dark red waxy solid. This was further purified by tube sublimation (160 °C, 3 × 10^{-6} Torr, 2 h) to give the pure compound (410 mg, 41 %).

7.3.2 SYNTHESIS OF Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (2)

To a solution of 39.48 g (0.026 mol) Ti(η-C_5Me_5)(N^{t}Bu)Cl(py) in *ca.* 200 ml benzene was added 3.81 g (0.026 mol) Li{MeC(N^{i}Pr)$_2$} slurried in *ca.* 30 ml benzene over a period of 30 min. After 16 h the solution was filtered, and volatiles removed under reduced pressure to give the product as a waxy brown solid (10.25 g, 99%).

7.3.3 SYNTHESIS OF Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (3)

To a solution of 6.79 g (0.022 mol) Ti(η-C_5H_4Me)(N^{t}Bu)Cl(py) in *ca.* 70 ml benzene was added 5.88 g (0.022 mol) Li{PhC(NSiMe$_3$)$_2$} dissolved in *ca.*

200 ml benzene. After 16 h the solution was filtered, and the volatiles were then removed under reduced pressure to give a waxy red-brown solid (9.34 g, 93 %).

7.3.4 NMR SCALE REACTION OF $[Ti(\eta\text{-}C_5H_4Me)(N^tBu)Cl]_2$ WITH $Li\{PhC(NSiMe_3)_2\}$

4.9 mg (0.01 mmol) $[Ti(\eta\text{-}C_5H_4Me)(N^tBu)Cl]_2$ and 5.7 mg (0.02 mmol) $Li\{PhC(NSiMe_3)_2\}$ were dissolved in 0.6 ml benzene-d_6. No reaction was observed at room temperature using ^1H NMR spectroscopy. Upon heating to the sample (80 °C, 2 h) peaks corresponding to $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ were observed, along with other, unidentified peaks.

7.3.5 SYNTHESIS OF $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{MeC(N^iPr)_2\}$ (4)

2.50 g (7.96 mmol) $Ti(\eta\text{-}C_5H_4Me)(N^tBu)Cl(py)$ in *ca.* 140 ml benzene was added to 1.18 g (7.96 mmol) $Li\{MeC(N^iPr)_2\}$ slurried in *ca.* 30 ml benzene. After 16 h, the volatiles were removed under reduced pressure, and the residue extracted with *ca.* 100 ml pentane and filtered. Volatiles were then again removed under reduced pressure to afford the product as a red oil (2.59 g, 96 % yield).

7.3.6 NMR SCALE REACTION OF $[Ti(\eta\text{-}C_5H_4Me)(N^tBu)Cl]_2$ WITH $Li\{MeC(N^iPr)_2\}$

20.1 mg (0.04 mmol) $[Ti(\eta\text{-}C_5H_4Me)(N^tBu)Cl]_2$ and 13.1 mg (0.08 mmol) $Li\{MeC(N^iPr)_2\}$ were dissolved in 0.6 ml benzene-d_6. No reaction was observed at room temperature using ^1H NMR spectroscopy, and heating the sample (80 °C, 2 h) resulted in decomposition.

7.3.7 SYNTHESIS OF Ti(η-$C_5H_4{}^iPr$)(N^tBu){PhC($NSiMe_3$)$_2$} (5)

To a solution of 1.074 g (2.51 mmol) Ti(N^tBu)$Cl_2(py)_3$ in *ca.* 40 ml THF was added a slurry of 287 mg (2.51 mmol) Li($C_5H_4{}^iPr$) in *ca.* 50 ml THF. After 16 h, the orange-brown solution was divided into two equal parts. To one of these was added 339 mg (1.25 mmol) Li{PhC($NSiMe_3$)$_2$} dissolved in *ca.* 20 ml THF, to give a darker brown solution. This was stirred for a further 12 h, and the volatiles removed under reduced pressure. The residue was extracted with *ca.* 25 ml pentane, filtered, and volatiles were removed under reduced pressure. The resulting red solid was further purified by sublimation (120 °C, 2×10^{-5} Torr, 3 h) to give a red powder (302 mg, 50 % yield).

7.3.8 SYNTHESIS OF Ti(η-$C_5H_4{}^iPr$)(N^tBu){MeC(N^iPr)$_2$} (6)

To a solution of 1.074 g (2.51 mmol) Ti(N^tBu)$Cl_2(py)_3$ in *ca.* 40 ml THF was added a slurry of 287 mg (2.51 mmol) Li($C_5H_4{}^iPr$) in *ca.* 50 ml THF. After 16 h, the orange-brown solution was divided into two equal parts. To one of these was added 188 mg (1.27 mmol) Li{MeC(N^iPr)$_2$} dissolved in *ca.* 20 ml THF, giving a red solution after a few min. After 12 h, the volatiles were removed under reduced pressure. The residue was extracted with *ca.* 25 ml pentane, filtered, and the volatiles removed under reduced pressure. The resulting red oil was further purified by tube sublimation (80 °C, 2×10^{-5} Torr, 3 h) to give a red oil (416 mg, 55 % yield).

7.3.9 LOW TEMPERATURE ^{1}H NMR STUDIES OF Ti(η-C_5Me_5)(N^tBu){PhC($NSiMe_3$)$_2$} WITH PYRIDINE

15.9 mg (0.03 mmol) Ti(η-C_5Me_5)(N^tBu){PhC($NSiMe_3$)$_2$} was dissolved in 600 μl dichloromethane-d_2. ^{1}H NMR spectra were recorded though the

temperature range 18 °C to -90 °C. 2.0 μl (1.9 mg, 0.03 mmol) pyridine was then added to the sample, and ^{1}H NMR spectra again recorded through the range 18 °C to -90 °C.

7.3.10 Low temperature ^{1}H NMR studies of Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe_3)$_2$} with pyridine

9.5 mg (0.02 mmol) Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe_3)$_2$} was dissolved in 550 μl dichloromethane-d_2. ^{1}H NMR spectra were recorded though the temperature range 18 °C to -90 °C. 1.7 μl (1.7 mg, 0.02 mmol) pyridine was then added to the sample, and ^{1}H NMR spectra again recorded through the range 18 °C to -90 °C.

7.3.11 Synthesis of Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (7)

1.4 ml (1.37 g, 0.011 mol) 2,6-dimethylaniline was added to a solution of 4.53 g (0.011 mol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} in *ca.* 100 ml pentane to give a green solution. After 16 h the volatiles were removed under reduced pressure. The residue was extracted with *ca.* 50 ml dichloromethane, filtered, and the volatiles removed under reduced pressure to leave an oily green solid. Trituration with pentane afforded the product as a green powder (4.62 g, 95 % yield).

7.3.12 Synthesis of Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (8)

676 mg (1.72 mmol) Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} and 186 mg (1.73 mmol) *p*-toluidine were dissolved in *ca.* 40 ml benzene. After 16 h the volatiles were removed under reduced pressure, and the product isolated as a

green solid, which was further purified by tube sublimation (170 °C, 2×10^{-5} Torr, 4 h) to give a green solid (170 mg, 50 % yield).

7.3.13 Synthesis of Ti(η-C_5Me_5)(N-4-$C_6H_4CF_3$){MeC(N^{i}Pr)$_2$} (9)

680 mg (1.73 mmol) Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} was dissolved in *ca.* 15 ml benzene to give a red solution. To this was added dropwise a solution of 217 µl (278 mg, 1.73 mmol) 4-(trifluoromethyl)aniline in *ca.* 5 ml benzene over 5 min to give a green solution. After 18 h all volatiles were removed under reduced pressure. The product was isolated as a brown powder (728 mg, 87 %).

7.3.14 Synthesis of Ti(η-C_5Me_5)(N-4-$C_6H_4NMe_2$){MeC(N^{i}Pr)$_2$} (10)

549 mg (1.40 mmol) Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} was dissolved in *ca.* 15 ml benzene to give a red solution. To this was added 189 mg (1.39 mmol) freshly sublimed *N*,*N*-dimethyl-1,4-phenylenediamine in *ca.* 15 ml benzene to afford a red solution that quickly turned green. After 1 h, all volatiles were removed under reduced pressure to give the product as a green-brown solid (555 mg, 87 %).

7.3.15 Synthesis of Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$){PhC(NSiMe$_3$)$_2$} (11)

1.48 g (3.21 mmol) Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} was dissolved in *ca.* 60 ml pentane, and to this was added 400 µl (394 mg, 3.25 mmol) 2,6-dimethylaniline *via* microlitre syringe. After 16 h, all volatiles were removed under reduced pressure, and the residue taken up in a minimum of pentane and cooled to -30 °C. 576 mg (1.14 mmol, 36 % yield) was obtained from the first batch of crystals. Total yield: 943 mg (1.85 mmol, 58 %).

7.3.16 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} WITH *p*-TOLUIDINE

12.1 mg (0.03 mmol) Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} was dissolved in 0.6 ml chloroform-d, and to this was added 3.8 mg (0.03 mmol) *p*-toluidine. Immediate darkening of the red solution was observed. Peaks consistent with the formation of Ti(η-C_5H_4Me)(N-4-C_6H_4Me){PhC(NSiMe$_3$)$_2$} and *tert*-butylamine, and complete loss of peaks corresponding to the starting materials, were present in the ^{1}H NMR spectrum recorded after 6 h.

7.3.17 SYNTHESIS OF Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$){PhC(NSiMe$_3$)$_2$} (12)

To 600 mg (1.77 mmol) Ti(η-C_5H_4Me)(N^{t}Bu){MeC(N^{i}Pr)$_2$} in 60 ml benzene was added 220 μl (216 mg, 1.79 mmol) 2,6-dimethylaniline *via* microlitre syringe, resulting in an immediate colour change from red to green. After 1 h, all volatiles were removed under reduced pressure to give a dark green oil. This was purified *via* tube sublimation (130 °C, 1 × 10^{-5} Torr, 4 h) to afford the product as a green oil (485 mg, 71 % yield).

7.3.18 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N^{t}Bu){MeC(N^{i}Pr)$_2$} WITH *p*-TOLUIDINE

15 mg (0.04 mmol) Ti(η-C_5H_4Me)(N^{t}Bu){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml benzene-d_6, to which was added 4.7 mg (0.04 mmol) *p*-toluidine. Immediate darkening of the red solution was observed. The ^{1}H NMR spectrum recorded after 16 h was consistent with formation of Ti(η-C_5H_4Me)(NH^{t}Bu)(NH-4-C_6H_4Me) {MeC(N^{i}Pr)$_2$}. Attempts to force the extrusion of *tert*-butylamine by heating to 80 °C and the removal of volatiles under reduced pressure were unsuccessful.

7.3.19 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N^tBu){$MeC(N^iPr)_2$} WITH *p*-TOLUIDINE IN THE PRESENCE OF EXCESS PYRIDINE

10 mg (0.03 mmol) Ti(η-C_5H_4Me)(N^tBu){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 24 μl (23.5 mg, 0.30 mmol) pyridine *via* microlitre syringe, and 3.2 mg (0.03 mmol) *p*-toluidine. Immediate darkening of the red solution was observed. The ^1H NMR spectrum recorded after 14 h was consistent with the formation of Ti(η-C_5H_4Me)(NH^tBu)(NH-4-C_6H_4Me){$MeC(N^iPr)_2$}, and all attempts to force the extrusion of *tert*-butylamine by removal of volatiles under reduced pressure were unsuccessful.

7.3.20 ATTEMPTED SYNTHESIS OF Ti(η-C_5H_4Me)(N-4-C_6H_4Me){$MeC(N^iPr)_2$}

340 mg (1.01 mmol) of Ti(η-C_5H_4Me)(N^tBu){$MeC(N^iPr)_2$} were dissolved in 34 ml benzene. To this was added 108 mg (1.01 mmol) *p*-toluidine, resulting in an immediate darkening of the red solution. After 16 h, the volatiles were removed under reduced pressure, and the waxy brown residue sublimed *via* tube sublimation (100 °C, 1×10^{-5} Torr, 4 h). The product was a mixture of unidentified decomposition compounds.

7.3.21 SYNTHESIS OF Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$)Cl(py) (13)

1.75 g (3.69 mmol) Ti(N-2,6-$C_6H_3Me_2$)$Cl_2(py)_3$ and 524 mg (3.69 mmol) Li(C_5Me_5) were slurried together in *ca.* 70 ml benzene, and refluxed for 48 h. The solution was then filtered, and volatiles removed under reduced pressure to afford the product as a green powder (1.33 g, 87 % yield).

7.3.22 SYNTHESIS OF Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){PhC($NSiMe_3$)$_2$} (14)

409 mg (0.98 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$)Cl(py) and 267 mg (0.99 mmol) Li{PhC($NSiMe_3$)$_2$} were dissolved together in *ca.* 40 ml benzene and heated to 90 °C for 3 h. Volatiles were removed under reduced pressure, and the residue extracted with 25 ml benzene and filtered. The volatiles were again removed under reduced pressure, the residue extracted into a minimum amount of pentane, and the compound further purified by crystallisation to afford the product as a green powder (225 mg, 36 % yield).

7.3.23 ATTEMPTED SYNTHESIS OF Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$)Cl(py) (15)

587 mg (1.24 mmol) Ti(N-2,6-$C_6H_3Me_2$)Cl_2(py)$_3$ was dissolved in *ca.* 50 ml THF. This was cooled to -40 °C. To this was added dropwise 108 mg (1.25 mmol) Li(C_5H_4Me) dissolved in *ca.* 40 ml THF. The solution was allowed to warm to room temperature. After 16 h the solution was refluxed for 3 h, before all volatiles were removed under reduced pressure. The product was extracted using *ca.* 40 ml benzene.

The solution was then split into 2 equal portions. The volatiles from the first portion were removed under reduced pressure, and the residue dissolved in *ca.* 5 ml dichloromethane. To this was added 1 ml pyridine, followed by 10 ml pentane in a layer. Volatiles were removed at -78 °C to afford an oily brown product.

7.3.24 ATTEMPTED SYNTHESIS OF [Ti(η-C_5H_4Me)(μ-N-2,6-$C_6H_3Me_2$)Cl]$_2$ (16)

The volatiles of the second portion of the solution formed in **7.3.14** were removed under reduced pressure, and the product heated to 50 °C for 16 h at a pressure of 2×10^{-2} Torr. Further heating (120 °C, 2×10^{-2} Torr, 1 h) was found to increase the ratio of dimer : monomer present. Product found to be a brown waxy solid, contaminated with Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$)Cl(py) (**15**).

7.3.25 SYNTHESIS OF [Ti(η-C_5Me_5)(μ-N-4-C_6H_4Me)Cl]$_2$ (17)

447 mg (0.97 mmol) Ti(N-4-C_6H_4Me)$Cl_2(py)_3$ and 140 mg (0.98 mmol) Li(C_5Me_5) were slurried together in *ca.* 40 ml THF and refluxed for 22 h. Volatiles were removed from the dark brown solution under reduced pressure, and the residue extracted with *ca.* 40 ml benzene. To this was added *ca.* 5 ml pyridine, and the solution refluxed for 2 h. The solution was filtered, and the volatiles were removed under reduced pressure. Trituration with pentane, and washing with 3 × 3 ml pentane afforded the product as a dark brown powder (252 mg, 80 % yield).

7.3.26 LOW TEMPERATURE ^{1}H NMR STUDIES OF [Ti(η-C_5Me_5)(μ-N-4-C_6H_4Me)Cl]$_2$ WITH PYRIDINE

8.2 mg (0.01 mmol) [Ti(η-C_5Me_5)(μ-N-4-C_6H_4Me)Cl]$_2$ was dissolved in 680 μl dichloromethane-d_2. ^{1}H NMR spectra were recorded though the temperature range 18 °C to -80 °C. 2.0 μl (1.9 mg, 0.03 mmol) pyridine was then added to the sample, and ^{1}H NMR spectra again recorded through the range 18 °C to -80 °C.

7.3.26 SYNTHESIS OF [Ti(η-C_5Me_5)(N-4-C_6H_4Me)(NH-4-C_6H_4Me)]$_2$ (18)

153 mg (0.36 mmol) Ti(η-C_5H_4Me)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} was dissolved in *ca.* 20 ml benzene to give a green solution. To this was added 38 mg (0.36 mmol) *p*-toluidine in *ca.* 15 ml benzene to give a brown solution. This was heated in a sealed ampoule at 80 °C for 16 h. All volatiles were then removed under reduced pressure, and the compound recrystallised from pentane at -30 °C. Product was isolated as a crystalline red powder (70 mg, 50 %).

7.4 EXPERIMENTAL DETAILS: CHAPTER 3

7.4.1 SYNTHESIS OF Ti(η-C_5Me_5){$N(^tBu)C(O)O$}{$PhC(NSiMe_3)_2$} (19)

184 mg (0.36 mmol) Ti(η-C_5Me_5)(N^tBu){$PhC(NSiMe_3)_2$} was dissolved in *ca.* 5 ml benzene, the headspace evacuated, and the solution exposed to CO_2 at a pressure of 1 atm for 20 min. The volatiles were then removed under reduced pressure to afford the product as a red powder (189 mg, 95 % yield).

7.4.2 SYNTHESIS OF Ti(η-C_5Me_5){$N(^tBu)C(O)O$}{$MeC(N^iPr)_2$} (20)

127 mg (0.32 mmol) Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} was dissolved in *ca.* 10 ml pentane and cooled to -78 °C. The headspace was evacuated, and the solution exposed to CO_2 at a pressure of 1 atm for 2 min, during which time the solution was allowed to warm to room temperature. Volatiles were then immediately removed under reduced pressure to give the product as a dark red powder. (92 mg, 65 % yield).

7.4.3 SYNTHESIS OF $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$ (21)

740 mg (1.43 mmol) $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{PhC(NSiMe_3)_2\}$ was dissolved in *ca.* 30 ml pentane. To this was added a slurry of 155 mg (1.45 mmol) PhNO in *ca.* 15 ml pentane, and the resulting mixture stirred vigorously for 16 h. The supernatant was then decanted off, and the residual yellow powder washed with *ca.* 20 ml pentane to afford the product as a fine yellow powder (350 mg, 53 % yield).

7.4.4 SYNTHESIS OF $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ (22)

250 mg (0.64 mmol) $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ was dissolved in *ca.* 5 ml benzene. The headspace was evacuated, and the solution was exposed to CO_2 at a pressure of 1 atm, resulting in an immediate colour change from red to cherry red. The solution was left standing for 72 h, after which time all volatiles were removed under reduced pressure. The residue was washed with 2 × 5 ml pentane, to afford the product as a yellow powder (152 mg, 70 % yield).

7.4.5 REACTION OF $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ WITH H_2O

121 mg (0.31 mmol) $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ was dissolved in *ca.* 30 ml THF. To this was added dropwise 290 μl (0.29 mmol) of a 1 mol dm^{-3} solution of H_2O in THF, resulting in a colour change from red to amber. Removal of volatiles under reduced pressure afforded a yellow solid, which was found to be a mixture of products by ^1H NMR spectroscopy.

7.4.6 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} WITH CO_2

55.9 mg (0.12 mmol) Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} was dissolved in 0.6 ml benzene-d_6, and freeze-pump-thawed (× 3). The solution was then exposed to CO_2 at a pressure of *ca.* 0.5 atm, resulting in an immediate colour change to cherry red. The product, Ti(η-C_5H_4Me){N(^{t}Bu)C(O)O}{PhC(NSiMe$_3$)$_2$}, was identified and characterised by ^{1}H NMR spectroscopy.

7.4.7 SYNTHESIS OF [Ti(η-C_5H_4Me)(μ-O){PhC(NSiMe$_3$)$_2$}]$_2$ (24 / 24a)

242 mg (0.52 mmol) Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} was dissolved in *ca.* 5 ml benzene, the headspace evacuated, and the solution exposed to CO_2 at a pressure of 1 atm for 1 h. Volatiles were then removed under reduced pressure to afford the product (a mixture of *cis* and *trans* isomers) as a very fine beige powder (194 mg, 91% yield).

7.4.8 NMR SCALE REACTION OF *trans*-[Ti(η-C_5H_4Me)(μ-O){PhC(NSiMe$_3$)$_2$}]$_2$ WITH 4-*tert*-BUTYLPYRIDINE

14.7 mg (0.02 mmol) *trans*- [Ti(η-C_5H_4Me)(μ-O){PhC(NSiMe$_3$)$_2$}]$_2$ was dissolved in 0.6 ml benzene-d_6, and to this was added 10.2 μl (9.3 mg, 0.07 mmol) 4-*tert*-butyl pyridine *via* microlitre syringe. The sample was analysed using ^{1}H NMR spectroscopy. No reaction was observed after 16 h at room temperature, or after a further 21 h at 80 °C.

7.4.9 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N^tBu){$MeC(N^iPr)_2$} WITH CO_2

15 mg (0.04 mmol) Ti(η-C_5H_4Me)(N^tBu){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6, and freeze-pump-thawed (× 3). The solution was then exposed to CO_2 at a pressure of 1 atm, resulting in an immediate colour change to cherry red. A further colour change to amber occurred within 2 min. The ^1H NMR spectrum recorded at that time showed the reaction mixture contained only *cis*- and *trans*- isomers of [Ti(η-C_5H_4Me)(μ-O){$MeC(N^iPr)_2$}]$_2$ and *tert*-butyl isocyanate.

7.4.10 SYNTHESIS OF [Ti(η-C_5H_4Me)(μ-O){$MeC(N^iPr)_2$}]$_2$ (25 / 25a)

250 mg (0.74 mmol) Ti(η-C_5H_4Me)(N^tBu){$MeC(N^iPr)_2$} was dissolved in 25 ml benzene, the headspace evacuated, and the solution exposed to CO_2 at 1 atm. Immediate colour change of the solution from red to cherry red occurred, followed by a further colour change to brown over *ca.* 2 min. After 16 h, all volatiles were removed under reduced pressure, and the residue triturated with *ca.* 10 ml pentane. The product (a mixture of *cis* and *trans* isomers) was afforded as a light brown solid (121 mg, 58 % yield).

7.4.11 NMR SCALE REACTION OF [Ti(η-C_5Me_5)(μ-O){$MeC(N^iPr)_2$}]$_2$ WITH *cis*- / *trans*- [Ti(η-C_5H_4Me)(μ-O){$PhC(NSiMe_3)_2$}]$_2$

8.5 mg (0.01 mmol) [Ti(η-C_5Me_5)(μ-O){$MeC(N^iPr)_2$}]$_2$ and 10.2 mg (0.01 mmol) *cis*- / *trans*- [Ti(η-C_5H_4Me)(μ-O){$PhC(NSiMe_3)_2$}]$_2$ were dissolved in 0.6 ml benzene-d_6, and monitored using ^1H NMR spectroscopy. No reaction was observed after 3 h at room temperature. Heating the sample to 80 °C for 1 h resulted in the conversion of *cis*- [Ti(η-C_5H_4Me)(μ-O){$PhC(NSiMe_3)_2$}]$_2$

to *trans*- [Ti(η-C_5H_4Me)(μ-O){$PhC(NSiMe_3)_2$}]$_2$. Heating to 80 °C for a further 14 d had no effect.

7.4.12 SYNTHESIS OF [Ti(η-$C_5H_4{}^iPr$)(μ-O){$PhC(NSiMe_3)_2$}]$_2$ (26 / 26a)

186 mg (0.38 mmol) Ti(η-$C_5H_4{}^iPr$)(N^tBu){$PhC(NSiMe_3)_2$}was dissolved in *ca.* 10 ml benzene, the headspace evacuated, and the solution exposed to CO_2 at 1 atm. Immediate colour change of the solution from red to cherry red occurred, followed by a further colour change to a red-amber colour within 16 h. All volatiles were removed under reduced pressure to afford the product (a mixture of *cis* and *trans* isomers) as an amber powder (139 mg, 84 %).

7.4.13 NMR SCALE REACTION BETWEEN *cis*- / *trans*- [Ti(η-$C_5H_4{}^iPr$)(μ-O){$PhC(NSiMe_3)_2$}]$_2$ AND *cis*- / *trans*- [Ti(η-C_5H_4Me)(μ-O){$PhC(NSiMe_3)_2$}]$_2$

6.2 mg (0.01 mmol) *cis*- / *trans*- [Ti(η-$C_5H_4{}^iPr$)(μ-O){$PhC(NSiMe_3)_2$}]$_2$ and 5.8 mg (0.01 mmol) *cis*- / *trans*- [Ti(η-C_5H_4Me)(μ-O){$PhC(NSiMe_3)_2$}]$_2$ were dissolved in 0.6 ml benzene-d_6, and monitored using ^{1}H NMR spectroscopy. No reaction was observed after 10 min. Upon heating the solution to 80 °C for 1 h, the resonances corresponding to *cis*- [Ti(η-$C_5H_4{}^iPr$)(μ-O){$PhC(NSiMe_3)_2$}]$_2$ and *cis*- [Ti(η-C_5H_4Me)(μ-O){$PhC(NSiMe_3)_2$}]$_2$ disappeared. After a further 3 d at 80 °C, resonances consistent with the formation of the mixed oxo dimer Ti(η-C_5H_4Me){$PhC(NSiMe_3)_2$}(μ-O)$_2$Ti(η-$C_5H_4{}^iPr$){$PhC(NSiMe_3)_2$} were present.

7.4.14 SYNTHESIS OF Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(O)O}{MeC(N^{i}Pr)$_2$} (27)

198 mg (0.45 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} was dissolved in *ca.* 10 ml pentane, the headspace evacuated, and the solution exposed to CO_2 at a pressure of 1 atm for 10 min. Volatiles were then removed under reduced pressure to afford the product as a brown powder (171 mg, 79 % yield).

7.4.15 SYNTHESIS OF Ti(η-C_5H_4Me){N(-2,6-$C_6H_3Me_2$)C(O)O} {PhC(NSiMe$_3$)$_2$} (28)

167 mg (0.33 mmol) Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$){PhC(NSiMe$_3$)$_2$} was dissolved in *ca.* 10 ml benzene to give a brown solution. The headspace was evacuated, and the solution exposed to CO_2 at a pressure of 1 atm. A colour change from brown to red was observed. After 5 min, volatiles were removed under reduced pressure to afford the product as a hard brown solid. This was triturated with *ca.* 5 ml pentane. 90 mg (50 % yield) was recovered, owing to the difficulty of separating the compound from the walls of the vessel.

7.4.16 LOW TEMPERATURE ^{1}H NMR STUDIES OF Ti(η-C_5H_4Me){N(-2,6-$C_6H_3Me_2$)C(O)O}{PhC(NSiMe$_3$)$_2$}

8.8 mg (0.02 mmol) Ti(η-C_5H_4Me){N(-2,6-$C_6H_3Me_2$)C(O)O} {PhC(NSiMe$_3$)$_2$} was dissolved in 0.6 ml dichloromethane-d_2, and the ^{1}H NMR spectrum recorded through the temperature range 18 °C to -50 °C.

7.4.17 SYNTHESIS OF Ti(η-C_5H_4Me){N(-2,6-$C_6H_3Me_2$)C(O)O} {$MeC(N^iPr)_2$} (29)

100 mg (0.26 mmol) Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$){$MeC(N^iPr)_2$} was dissolved in 10 ml benzene to give a green solution. The headspace was evacuated, and the solution exposed to CO_2 at a pressure of 1 atm, resulting in an immediate colour change to deep red. After 5 min, all volatiles were removed under reduced pressure to afford the product as an olive-green powder (82 mg, 74 % yield).

7.4.18 LOW TEMPERATURE ^{1}H NMR STUDIES OF Ti(η-C_5H_4Me){N(-2,6-$C_6H_3Me_2$)C(O)O}{$MeC(N^iPr)_2$}

7.6 mg (0.02 mmol) Ti(η-C_5H_4Me){N(-2,6-$C_6H_3Me_2$)C(O)O}{$MeC(N^iPr)_2$} was dissolved in 0.6 ml dichloromethane-d_2, and the ^{1}H NMR spectrum recorded through the temperature range 18 °C to -60 °C.

7.4.19 SYNTHESIS OF Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(O)O} {$PhC(NSiMe_3)_2$} (30)

57.3 mg (0.10 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){$PhC(NSiMe_3)_2$} was dissolved in *ca.* 5 ml benzene, the headspace evacuated, and the solution exposed to CO_2 at a pressure of 1 atm, which resulted in a colour change from dark green to cherry red within 1 min. After 16 h, all volatiles were removed under reduced pressure, affording the product as a red powder (59.1 mg, 96 % yield).

7.4.20 SYNTHESIS OF

$Ti(\eta\text{-}C_5Me_5)\{OC(O)N(\text{-}2,6\text{-}C_6H_3Me_2)C(O)O\}\{MeC(N^iPr)_2\}$ (31)

125 mg (0.28 mmol) $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ was dissolved in *ca.* 10 ml benzene, the headspace evacuated, and the solution exposed to CO_2 at a pressure of 1 atm for a period of 24 h. Volatiles were then removed under reduced pressure to afford the product as a red powder (122 mg, 82 % yield).

7.4.21 SYNTHESIS OF $Ti(\eta\text{-}C_5H_4Me)$

$\{OC(O)N(\text{-}2,6\text{-}C_6H_3Me_2)C(O)O\}\{PhC(NSiMe_3)_2\}$ (32)

142 mg (0.28 mmol) $Ti(\eta\text{-}C_5H_4Me)(N\text{-}2,6\text{-}C_6H_3Me_2)\{PhC(NSiMe_3)_2\}$ was dissolved in *ca.* 15 ml benzene to give a brown solution. The headspace was evacuated, and the solution exposed to CO_2 at a pressure of 1 atm, resulting in an immediate colour change to red. After 43 h, all volatiles were removed under reduced pressure, and the residue triturated with *ca.* 5 ml pentane. The product was obtained as a brown powder (55 mg, 33 % yield, owing to the difficulty of separating the compound from the walls of the vessel).

7.4.22 SYNTHESIS OF

$Ti(\eta\text{-}C_5H_4Me)\{OC(O)N(\text{-}2,6\text{-}C_6H_3Me_2)C(O)O\}\{MeC(N^iPr)_2\}$ (33)

100 mg (0.26 mmol) $Ti(\eta\text{-}C_5H_4Me)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ was dissolved in 10 ml benzene to give a green solution. The headspace was evacuated, and the solution exposed to CO_2 at a pressure of 1 atm, resulting in an immediate colour change to dark red. After 24 h, all volatiles were removed to afford the product as a red-brown solid (75 mg, 61 % yield).

7.4.23 Synthesis of Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{MeC(N^{i}Pr)$_2$} (34)

371 mg (0.87 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} was dissolved in *ca.* 30 ml benzene. The solution was frozen at -196 °C, and the headspace evacuated. 0.86 mmol CO_2 was condensed onto the frozen solution using a volumetrically calibrated manifold, and the solution warmed to room temperature. Volatiles were removed under reduced pressure after *ca.* 10 min to afford the product as a red powder (225 mg, 55 % yield).

7.4.24 Synthesis of Ti(η-C_5Me_5){N(-4-$C_6H_4CF_3$)C(O)O}{MeC(N^{i}Pr)$_2$} (35)

153 mg (0.31 mmol) Ti(η-C_5Me_5)(N-4-$C_6H_4CF_3$){MeC(N^{i}Pr)$_2$} was dissolved in *ca.* 10 ml benzene to give a dark green solution. The headspace was evacuated, and the solution exposed to CO_2 at a pressure of 1 atm, resulting in an immediate colour change to red. After 25 sec, all volatiles were removed under reduced pressure to afford the product as a brown solid (110 mg, 67 % yield).

7.4.25 Synthesis of Ti(η-C_5Me_5){N(-4-$C_6H_4NMe_2$)C(O)O}{MeC(N^{i}Pr)$_2$} (36)

111 mg (0.24 mmol) Ti(η-C_5Me_5)(N-4-$C_6H_4NMe_2$){MeC(N^{i}Pr)$_2$} was dissolved in *ca.* 10 ml benzene to give a green solution. The headspace was evacuated, and the solution exposed to CO_2 at a pressure of 1 atm, resulting in an immediate colour change to cherry red. After 20 sec, all volatiles were removed under reduced pressure to afford a dark red solid. This was triturated

with *ca.* 5 ml pentane. 60 mg (50 % yield) was obtained, owing to difficulties removing the product from the vessel.

7.4.26 SYNTHESIS OF

Ti(η-C_5Me_5){OC(O)N(-4-C_6H_4Me)C(O)O}{MeC(N^{i}Pr)$_2$} (37)

197 mg (0.46 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} was dissolved in *ca.* 15 ml benzene to give a green solution. The headspace was evacuated, and the solution exposed to CO_2 at a pressure of 1 atm for a period of 16 h. The volatiles were then removed under reduced pressure to afford the product as a brown solid (145 mg, 61 % yield).

7.4.27 SYNTHESIS OF

Ti(η-C_5Me_5){OC(O)N(-4-$C_6H_4CF_3$)C(O)O}{MeC(N^{i}Pr)$_2$} (38)

117 mg (0.24 mmol) Ti(η-C_5Me_5)(N-4-$C_6H_4CF_3$){MeC(N^{i}Pr)$_2$} was dissolved in *ca.* 5 ml benzene to give a dark green solution. The headspace was evacuated, and the solution exposed to CO_2 at a pressure of 1 atm for a period of 4 h. All volatiles were removed under reduced pressure to afford the product as an oily brown solid (85 mg, 62 % yield).

7.4.28 SYNTHESIS OF

Ti(η-C_5Me_5){OC(O)N(-4-$C_6H_4NMe_2$)C(O)O}{MeC(N^{i}Pr)$_2$} (39)

110 mg (0.24 mmol) Ti(η-C_5Me_5)(N-4-$C_6H_4NMe_2$){MeC(N^{i}Pr)$_2$} was dissolved in *ca.* 5 ml benzene to give a green solution. The headspace was evacuated, and the solution exposed to CO_2 at a pressure of 1 atm for a period of 4 h. All volatiles were then removed under reduced pressure to give a dark

red solid. Trituration with *ca.* 2 ml pentane afforded the product as a very fine red-brown powder (71 mg, 54 % yield).

7.4.29 PSEUDO-FIRST ORDER KINETICS EXPERIMENT: REACTION OF Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} WITH > 10 EQUIVALENTS CO_2 (FIRST EXPERIMENT)

5.0 mg (0.01 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} and 1.8 mg (0.01 mmol) 1,4-dimethoxybenzene (internal standard) were dissolved in a 4.0 cm depth of benzene-d_6 in a 5 mm Wilmad NMR tube fitted with a Teflon valve. The solution was freeze-pump-thawed (× 3), and backfilled with 1.6 atm CO_2 (> 10-fold excess). Immediate colour change from green to cherry red was observed. The sample was immediately transferred to the NMR spectrometer, which was held at 18 °C throughout the experiment, and ^{1}H NMR measurements made over the following 90 min.

7.4.30 PSEUDO-FIRST ORDER KINETICS EXPERIMENT: REACTION OF Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} with > 10 EQUIVALENTS CO_2 (SECOND EXPERIMENT)

4.0 mg (0.01 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} and 1.8 mg (0.01 mmol) 1,4-dimethoxybenzene (internal standard) were dissolved in a 4.8 cm depth of benzene-d_6 in a 5 mm Wilmad NMR tube fitted with a Teflon valve. The solution was freeze-pump-thawed (× 3), and backfilled with 1.6 atm CO_2 (> 10-fold excess). Immediate colour change from green to cherry red was observed. The sample was immediately transferred to the NMR spectrometer, which was held at 18 °C throughout the experiment, and ^{1}H NMR measurements made over the following 60 min.

7.4.31 PSEUDO-FIRST ORDER KINETICS EXPERIMENT: REACTION OF $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4CF_3)\{MeC(N^iPr)_2\}$ WITH > 10 EQUIVALENTS CO_2 (FIRST EXPERIMENT)

4.2 mg (0.01 mmol) $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4CF_3)\{MeC(N^iPr)_2\}$ and 1.7 mg (0.01 mmol) 1,4-dimethoxybenzene (internal standard) were dissolved in a 4.0 cm depth of benzene-d_6 in a 5 mm Wilmad NMR tube fitted with a Teflon valve. The solution was freeze-pump-thawed (× 3), and backfilled with 1.6 atm CO_2 (> 10-fold excess). Immediate colour change from brown to cherry red was observed. The sample was immediately transferred to the NMR spectrometer, which was held at 18 °C throughout the experiment, and ^1H NMR measurements made over the following 90 min.

7.4.32 PSEUDO-FIRST ORDER KINETICS EXPERIMENT: REACTION OF $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4CF_3)\{MeC(N^iPr)_2\}$ WITH > 10 EQUIVALENTS CO_2 (SECOND EXPERIMENT)

4.3 mg (0.01 mmol) $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4CF_3)\{MeC(N^iPr)_2\}$ and 1.4 mg (0.01 mmol) 1,4-dimethoxybenzene (internal standard) were dissolved in a 4.0 cm depth of benzene-d_6 in a 5 mm Wilmad NMR tube fitted with a Teflon valve. The solution was freeze-pump-thawed (× 3), and backfilled with 1.6 atm CO_2 (> 10-fold excess). Immediate colour change from brown to cherry red was observed. The sample was immediately transferred to the NMR spectrometer, which was held at 18 °C throughout the experiment, and ^1H NMR measurements made over the following 90 min.

7.4.33 PSEUDO-FIRST ORDER KINETICS EXPERIMENT: REACTION OF $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4NMe_2)\{MeC(N^iPr)_2\}$ WITH > 10 EQUIVALENTS CO_2 (FIRST EXPERIMENT)

4.6 mg (0.01 mmol) $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4NMe_2)\{MeC(N^iPr)_2\}$ and 1.2 mg (0.01 mmol) 1,4-dimethoxybenzene (internal standard) were dissolved in a 4.0 cm depth of benzene-d_6 in a 5 mm Wilmad NMR tube fitted with a Teflon valve. The solution was freeze-pump-thawed (x 3), and backfilled with 1.6 atm CO_2 (> 10-fold excess). Immediate colour change from brown to cherry red was observed. The sample was immediately transferred to the NMR spectrometer, which was held at 18 °C throughout the experiment, and ^1H NMR measurements made over the following 60 min.

7.4.34 PSEUDO-FIRST ORDER KINETICS EXPERIMENT: REACTION OF $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4NMe_2)\{MeC(N^iPr)_2\}$ WITH > 10 EQUIVALENTS CO_2 (SECOND EXPERIMENT)

4.1 mg (0.01 mmol) $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4NMe_2)\{MeC(N^iPr)_2\}$ and 1.4 mg (0.01 mmol) 1,4-dimethoxybenzene (internal standard) were dissolved in a 4.4 cm depth of benzene-d_6 in a 5 mm Wilmad NMR tube fitted with a Teflon valve. The solution was freeze-pump-thawed (× 3), and backfilled with 1.6 atm CO_2 (> 10-fold excess). Immediate colour change from brown to cherry red was observed. The sample was immediately transferred to the NMR spectrometer, which was held at 18 °C throughout the experiment, and ^1H NMR measurements made over the following 45 min.

7.4.35 Low temperature NMR studies of the reaction of Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} with CO_2

7.1 mg (0.02 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} was dissolved in 0.6 ml toluene-d_8, and frozen. The headspace was evacuated, and the solution thawed. The ^1H NMR spectra of the complex at 18 °C and -80 °C were recorded, and the sample was then removed from the instrument and cooled to -78 °C in an *iso*-propyl alcohol / CO_2 slush bath. The headspace was backfilled with 1 atm of CO_2, and the sample immediately transferred to the NMR spectrometer, which had been pre-cooled to -80 °C. ^1H NMR spectra were then acquired over a 60 min period at -80 °C. The temperature was then ramped up 10 °C, held for 10 min, and the ^1H NMR spectrum measured. This process was repeated until -10 °C was reached, at which point reaction was observed to occur. ^1H NMR spectra were acquired over a 30 min period at this temperature, before the temperature was dropped to -80 °C and a spectrum acquired. The sample was then warmed to 30 °C to speed the formation of Ti(η-C_5Me_5){OC(O)ON(-4-C_6H_4Me)C(O)O}{$MeC(N^iPr)_2$}, and again cooled to -80 °C to acquire a ^1H NMR spectrum. The sample was then warmed to room temperature to complete the formation of Ti(η-C_5Me_5){OC(O)ON(-4-C_6H_4Me)C(O)O}{$MeC(N^iPr)_2$}, before being cooled to -80 °C and acquiring a final ^1H NMR spectrum.

7.5 EXPERIMENTAL DETAILS: CHAPTER 4

7.5.1 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N^tBu){$PhC(NSiMe_3)_2$}

WITH *tert*-BUTYL ISOCYANATE

13.9 mg (0.03 mmol) Ti(η-C_5Me_5)(N^tBu){$PhC(NSiMe_3)_2$} was dissolved in 0.6 ml benzene-d_6, and to this was added 3.0 μl (3 mg, 0.03 mmol) *tert*-butyl isocyanate *via* microlitre syringe. The reaction was monitored by ^1H NMR spectroscopy. Formation of 1,3-di-*tert*-butyl carbodiimide (50 % conversion) was observed after 18 d.

7.5.2 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} WITH

tert-BUTYL ISOCYANATE

9.9 mg (0.03 mmol) Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6, and to this was added 3.0 μl (3 mg, 0.03 mmol) *tert*-butyl isocyanate *via* microlitre syringe. The reaction was monitored by ^1H NMR spectroscopy. Complete conversion to *trans*- [Ti(η-C_5Me_5)(μ-O){$MeC(N^iPr)_2$}]$_2$ and 1,3-di-*tert*-butyl carbodiimide was observed after 25 d.

7.5.3 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N^tBu){$PhC(NSiMe_3)_2$}

WITH *tert*-BUTYL ISOCYANATE

11.4 mg (0.03 mmol) Ti(η-C_5H_4Me)(N^tBu){$PhC(NSiMe_3)_2$} was dissolved in 0.6 ml benzene-d_6, and to this was added 2.8 μl (2.8 mg, 0.03 mmol) *tert*-butyl isocyanate *via* microlitre syringe. The reaction was monitored by ^1H NMR spectroscopy. Complete conversion to *cis*- / *trans*- [Ti(η-C_5H_4Me)(μ-O){$PhC(NSiMe_3)_2$}]$_2$ and 1,3-di-*tert*-butyl carbodiimide was observed after 30 d.

7.5.4 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N^tBu){$MeC(N^iPr)_2$}

WITH *tert*-BUTYL ISOCYANATE

19.6 mg (0.06 mmol) Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6, and to this was added 6.6 μl (6.5 mg, 0.06 mmol) *tert*-butyl isocyanate *via* microlitre syringe. The reaction was monitored by ^1H NMR spectroscopy. Complete conversion to *cis*- / *trans*- [Ti(η-C_5H_4Me)(μ-O) {$MeC(N^iPr)_2$}]$_2$ and 1,3-di-*tert*-butyl carbodiimide was observed after 8 d.

7.5.5 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} WITH

2,6-DIMETHYLPHENYL ISOCYANATE

38.2 mg (0.10 mmol) Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} was dissolved in benzene-d_6, and to this was added 13.5 μl (11.6 mg, 0.10 mmol) 2,6-dimethylphenyl isocyanate *via* microlitre syringe. The reaction was monitored by ^1H NMR spectroscopy.

7.5.6 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N^tBu){$PhC(NSiMe_3)_2$}

WITH 2,6-DIMETHYLPHENYL ISOCYANATE

9.9 mg (0.02 mmol) Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} was dissolved in benzene-d_6, and to this was added 3.0 μl (3.2 mg, 0.02 mmol) 2,6-dimethylphenyl isocyanate *via* microlitre syringe. The reaction was monitored by ^1H NMR spectroscopy. Complete conversion to *cis*- / *trans*- [Ti(η-C_5H_4Me)(μ-O) {$MeC(N^iPr)_2$}]$_2$ and *N*-*tert*-butyl-*N'*-2,6-dimethylphenyl carbodiimide was observed after 7 d.

7.5.7 NMR SCALE REACTION OF *trans*-[Ti(η-C_5Me_5)(μ-O){MeC(N^iPr)$_2$}]$_2$ WITH *p*-TOLYL ISOCYANATE

24.5 mg (0.04 mmol) *trans*- [Ti(η-C_5Me_5)(μ-O){MeC(N^iPr)$_2$}]$_2$ was dissolved in 0.6 ml benzene-d_6, and to this was added 12 μl (12.7 mg, 0.10 mmol) *p*-tolyl isocyanate *via* microlitre syringe. The reaction was monitored using ^{1}H NMR spectroscopy. No reaction was observed after 5 d at 80 °C.

7.5.8 NMR SCALE REACTION OF *cis*- / *trans*- [Ti(η-C_5H_4Me)(μ-O){MeC(N^iPr)$_2$}]$_2$ WITH *p*-TOLYL ISOCYANATE

25.5 mg (0.04 mmol) *cis*- / *trans*- [Ti(η-C_5H_4Me)(μ-O){MeC(N^iPr)$_2$}]$_2$ was dissolved in 0.6 ml benzene-d_6, and to this was added 20 μl (21.1 mg, 0.16 mmol) *p*-tolyl isocyanate *via* microlitre syringe. The reaction was monitored using ^{1}H NMR spectroscopy. No reaction was observed after 5 d at 80 °C.

7.5.9 SYNTHESIS OF Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N^tBu)O}{MeC(N^iPr)$_2$} (40)

163 mg (0.37 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^iPr)$_2$}was dissolved in *ca.* 10 ml benzene to give a dark green solution. To this was added 45 μl (39.1 mg, 0.39 mmol) *tert*-butyl isocyanate *via* microlitre syringe. After 4 h, all volatiles were removed under reduced pressure, and the residue triturated with *ca.* 5 ml pentane to afford the product as a sticky brown solid (55 mg, 27 % yield).

7.5.10 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N-4-C_6H_4Me) {$MeC(N^iPr)_2$} WITH *tert*-BUTYL ISOCYANATE

13.2 mg (0.03 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6, and to this was added 3.5 μl (3.0 mg, 0.03 mmol) *tert*-butyl isocyanate *via* microlitre syringe. The reaction was monitored using ^1H NMR spectroscopy. A colour change from green to dark red was observed after *ca.* 10 min. Complete conversion of the starting materials to *trans*-[Ti(η-C_5Me_5)(μ-O){$MeC(N^iPr)_2$}]$_2$ and *N*-*tert*-butyl-*N'*-*p*-tolyl carbodiimide was observed after 16 h.

7.5.11 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N-4-C_6H_4Me) {$MeC(N^iPr)_2$} WITH EXCESS *tert*-BUTYL ISOCYANATE

15.5 mg (0.04 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6, and to this was added 9 μl (7.8 mg, 0.08 mmol) *tert*-butyl isocyanate *via* microlitre syringe. The reaction was monitored using ^1H NMR spectroscopy. Complete conversion of the starting materials to *trans*-[Ti(η-C_5Me_5)(μ-O){$MeC(N^iPr)_2$}]$_2$ and *N*-*tert*-butyl-*N'*-*p*-tolyl carbodiimide was observed after 4 h.

7.5.12 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$) {$PhC(NSiMe_3)_2$} WITH *tert*-BUTYL ISOCYANATE

10.1 mg (0.02 mmol) Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$){$PhC(NSiMe_3)_2$} was dissolved in 0.6 ml benzene-d_6, and to this was added 2.6 μl (2.3 mg, 0.02 mmol) *tert*-butyl isocyanate *via* microlitre syringe. The reaction was monitored using ^1H NMR spectroscopy. A colour change from green to dark brown was observed after *ca.* 40 min. Complete conversion of the starting

materials to *cis-* / *trans-* [Ti(η-C_5H_4Me)(μ-O){PhC($NSiMe_3$)$_2$}]$_2$ and *N-tert*-butyl-*N'*-2,6-dimethylphenyl- carbodiimide was observed after 24 h.

7.5.13 Synthesis of Ti(η-C_5Me_5) {N(-2,6-$C_6H_3Me_2$)C(N-2,6-$C_6H_3Me_2$)O}{MeC(N^{i}Pr)$_2$} (41)

273 mg (0.62 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} was dissolved in *ca.* 15 ml benzene. To this was added 86 μl (84.6 mg, 0.62 mmol) 2,6-dimethylphenyl isocyanate *via* microlitre syringe, and the solution stirred for 21 h. Volatiles were then removed under reduced pressure to afford the product as a brown solid (308 mg, 84 % yield).

7.5.14 Synthesis of Ti(η-C_5Me_5) {N(-2,6-$C_6H_3Me_2$)C(N-4-C_6H_4Me)O}{MeC(N^{i}Pr)$_2$} (42)

565 mg (1.28 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} was dissolved in *ca.* 40 ml pentane, to which was added 161 μl (170 mg, 1.28 mmol) *p*-tolyl isocyanate *via* microlitre syringe, and the resulting solution stirred for 18 h. A crop of dark brown crystals (362 mg, 49 % yield) was isolated from the mother liquor. The remaining solution had all volatiles removed under reduced pressure to afford a further 262 mg (36% yield) of product as a brown powder (total yield: 624 mg, 85 %).

7.5.15 Synthesis of Ti(η-C_5Me_5) {N(-4-C_6H_4Me)C(N-2,6-$C_6H_3Me_2$)O}{MeC(N^{i}Pr)$_2$} (43)

234 mg (0.55 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} was dissolved in *ca.* 20 ml pentane. To this was added 76 μl (75 mg, 0.55 mmol) 2,6-dimethylphenyl isocyanate. The solution was stirred, and then stood for

18 h at -30 °C. The supernatant was then decanted off, and the resulting brown powder desolvated under reduced pressure to afford 210 mg (67 % yield).

7.5.16 SYNTHESIS OF

$Ti(\eta\text{-}C_5Me_5)\{N(\text{-}4\text{-}C_6H_4Me)C(N\text{-}4\text{-}C_6H_4Me)O\}\{MeC(N^iPr)_2\}$ (44)

437 mg (1.02 mmol) $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4Me)\{MeC(N^iPr)_2\}$ was dissolved in *ca.* 25 ml benzene, to which was added 131 µl (138 mg, 1.02 mmol) *p*-tolyl isocyanate. The resulting red solution was stirred for 30 min, after which volatiles were removed under reduced pressure. The residue was extracted with *ca.* 40 ml pentane, and cooled to -30 °C. 235 mg (41 % yield) brown crystals were removed from the supernatant, which then had all volatiles removed under reduced pressure to afford a further 66 mg of product as a brown powder (total yield: 301 mg, 53 %).

7.5.17 SYNTHESIS OF

$Ti(\eta\text{-}C_5Me_5)\{N(\text{-}4\text{-}C_6H_4CF_3)C(N\text{-}4\text{-}C_6H_4Me)O\}\{MeC(N^iPr)_2\}$ (45)

129 mg (0.27 mmol) $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4CF_3)\{MeC(N^iPr)_2\}$ was dissolved in *ca.* 5 ml benzene to afford a green-brown solution. To this was added dropwise a solution of 34.6 mg (0.26 mmol) *p*-tolyl isocyanate in *ca.* 5 ml benzene. An immediate colour change to red-brown occurred. The solution was stirred for 1.5 h before volatiles were removed under reduced pressure. The final 0.5 ml solution was triturated with *ca.* 10 ml pentane to afford the product as a very fine, static sensitive, dark brown powder (yield: 77 mg, 47 %).

7.5.18 SYNTHESIS OF Ti(η-C_5Me_5) {N(-4-$C_6H_4NMe_2$)C(N-4-C_6H_4Me)O}{MeC(N^{i}Pr)$_2$} (46)

104 mg (0.23 mmol) Ti(η-C_5Me_5)(N-4-$C_6H_4NMe_2$){MeC(N^{i}Pr)$_2$} was dissolved in *ca.* 25 ml benzene to afford a green solution. To this was added dropwise a solution of 29.4 mg (0.22 mmol) *p*-tolyl isocyanate in *ca.* 5 ml benzene. An immediate colour change from green to red was observed. The solution was stirred for 10 min before all volatiles were removed under reduced pressure. The residue was triturated with *ca.* 5 ml pentane to afford the product as a brown solid (yield: 97 mg, 71 %).

7.5.19 SYNTHESIS OF Ti(η-C_5Me_5) {N(-2,6-$C_6H_3Me_2$)C(N-2,6-$C_6H_3Me_2$)O}{PhC(N$SiMe_3$)$_2$} (46)

12.1 mg (0.02 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){PhC(N$SiMe_3$)$_2$} was dissolved in 0.6 ml benzene-d_6, and to this was added 3 μl (3.0 mg, 0.02 mmol) 2,6-dimethylphenyl isocyanate *via* microlitre syringe. A colour change from green to brown was observed after *ca.* 10 min. The solution was left standing under dry nitrogen for 16 h, after which all volatiles were removed under reduced pressure to afford the product as a brown powder (yield: 4.6 mg, 31 % due to extraction difficulties).

7.5.20 SYNTHESIS OF Ti(η-C_5Me_5) {OC(N-4-C_6H_4Me) N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O}{MeC(N^{i}Pr)$_2$} (48)

204 mg (0.48 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} was dissolved in *ca.* 20 ml benzene to give a dark green solution. To this was added 120 μl (127 mg, 0.99 mmol) *p*-tolyl isocyanate *via* microlitre syringe. The solution was observed to turn brown, and was stirred for 16 h. Volatiles were then

removed under reduced pressure to afford an oily red product. This was triturated with pentane to yield a very static sensitive, dark brown solid (yield: 171 mg, 51 % yield).

7.5.21 NMR SCALE REACTION OF Ti(η-C_5Me_5){N(-4-C_6H_4Me) C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} WITH *p*-TOLYL ISOCYANATE

22.5 mg (0.04 mmol) Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O} {$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6, and to this was added 5 µl (5.3 mg, 0.04 mmol) *p*-tolyl isocyanate. A colour change from brown to red-brown was observed. The ^1H NMR spectrum recorded after 2 h showed complete conversion of the starting materials to Ti(η-C_5Me_5) {OC(N-4-C_6H_4Me)N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$}.

7.5.22 SYNTHESIS OF Ti(η-C_5Me_5){OC(N-4-C_6H_4Me)N(-4-$C_6H_4CF_3$) C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (49)

105 mg (0.22 mmol) Ti(η-C_5Me_5)(N-4-$C_6H_4CF_3$){$MeC(N^iPr)_2$} was dissolved in *ca.* 10 ml benzene to give a green-brown solution. To this was added 57.9 mg (0.43 mmol) *p*-tolyl isocyanate in *ca.* 5 ml benzene to give a dark red solution. After 15 min, all volatiles were removed under reduced pressure, and the residue triturated with *ca.* 10 ml pentane to afford the product as a very static sensitive, brown powder (yield: 85 mg, 52 %).

7.5.23 SYNTHESIS OF Ti(η-C_5Me_5){OC(N-4-C_6H_4Me)N(-4-$C_6H_4NMe_2$) C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (50)

94 mg (0.21 mmol) Ti(η-C_5Me_5)(N-4-$C_6H_4NMe_2$){$MeC(N^iPr)_2$} was dissolved in *ca.* 10 ml benzene to give a green solution. To this was added

dropwise a solution of 26.6 mg (0.21 mmol) *p*-tolyl isocyanate in *ca.* 5 ml benzene. An immediate colour change from green to red occurred. After 10 min, all volatiles were removed under reduced pressure, to afford the product as a red-brown solid (yield: 85 mg, 71 %).

7.5.24 PSEUDO-FIRST ORDER KINETICS EXPERIMENT: REACTION OF Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} WITH > 10 EQUIVALENTS *p*-TOLYL ISOCYANATE

5.9 mg (0.01 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} and 0.9 mg (0.005 mmol) 1,4-dimethoxybenzene (internal standard) were dissolved in 592 mg benzene-d_6. To this was added 17.3 μl (18.3 mg, 10-fold excess) *p*-tolyl isocyanate. Immediate colour change from green to red was observed. The sample was immediately transferred to the NMR spectrometer, and reaction was determined to have gone to completion after 2 min 15 sec by ^{1}H NMR spectroscopy.

7.5.25 PSEUDO-FIRST ORDER KINETICS EXPERIMENT: REACTION OF Ti(η-C_5Me_5)(N-4-$C_6H_4CF_3$){MeC(N^{i}Pr)$_2$} WITH > 10 EQUIVALENTS *p*-TOLYL ISOCYANATE

4.6 mg (0.01 mmol) Ti(η-C_5Me_5)(N-4-$C_6H_4CF_3$){MeC(N^{i}Pr)$_2$} and 1.0 mg (0.005 mmol) 1,4-dimethoxybenzene (internal standard) were dissolved in 579 mg benzene-d_6. To this was added 12 μl (12.7 mg, 10-fold excess) *p*-tolyl isocyanate. Immediate colour change from brown to red was observed. The sample was immediately transferred to the NMR spectrometer, and reaction was determined to have gone to completion after 2 min 15 sec by ^{1}H NMR spectroscopy.

7.5.26 PSEUDO-FIRST ORDER KINETICS EXPERIMENT: REACTION OF Ti(η-C_5Me_5)(N-4-$C_6H_4NMe_2$){MeC(N^{i}Pr)$_2$} WITH > 10 EQUIVALENTS *p*-TOLYL ISOCYANATE

4.7 mg (0.01 mmol) Ti(η-C_5Me_5)(N-4-$C_6H_4NMe_2$){MeC(N^{i}Pr)$_2$} and 0.8 mg (0.005 mmol) 1,4-dimethoxybenzene (internal standard) were dissolved in 580 mg benzene-d_6. To this was added 13 μl (13.7 mg, 10-fold excess) *p*-tolyl isocyanate. Immediate colour change from green to red was observed. The sample was immediately transferred to the NMR spectrometer, and reaction was determined to have gone to completion after 2 min 20 sec by ^{1}H NMR spectroscopy.

7.5.27 LOW TEMPERATURE PSEUDO-FIRST ORDER KINETICS EXPERIMENT: REACTION OF Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O} {MeC(N^{i}Pr)$_2$} WITH > 10 EQUIVALENTS *p*-TOLYL ISOCYANATE

4.6 mg (0.01 mmol) Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O} {MeC(N^{i}Pr)$_2$} and 1.0 mg (0.005 mmol) 1,4-dimethoxybenzene (internal standard) were dissolved in 656 mg toluene-d_8. This was then cooled to -35 °C for 100 min. To this was added 11 μl (11.6 mg, 10-fold excess) *p*-tolyl isocyanate. The sample was immediately placed into an *iso*-propyl alcohol / CO_2 cold bath at -30 °C, and transferred to the NMR spectrometer, which had been pre-cooled to -30 °C. Reaction was determined to have gone to completion after 2 min 45 sec by ^{1}H NMR spectroscopy.

7.5.28 LOW TEMPERATURE PSEUDO-FIRST ORDER KINETICS EXPERIMENT: REACTION OF $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}4\text{-}C_6H_4CF_3)C(N\text{-}4\text{-}C_6H_4Me)O\}\{MeC(N^iPr)_2\}$ WITH > 10 EQUIVALENTS *p*-TOLYL ISOCYANATE

4.8 mg (0.01 mmol) $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}4\text{-}C_6H_4CF_3)C(N\text{-}4\text{-}C_6H_4Me)O\}\{MeC(N^iPr)_2\}$ and 1.2 mg (0.005 mmol) 1,4-dimethoxybenzene (internal standard) were dissolved in 662 mg toluene-d_8. This was then cooled to -35 °C for 110 min. To this was added 5.2 µl (5.5 mg, 10-fold excess) *p*-tolyl isocyanate. The sample was immediately placed into an *iso*-propyl alcohol / CO_2 cold bath at -30 °C, and transferred to the NMR spectrometer, which had been pre-cooled to -30 °C. Reaction was determined to have gone to completion after 3 min 30 sec by ^1H NMR spectroscopy.

7.5.29 LOW TEMPERATURE PSEUDO-FIRST ORDER KINETICS EXPERIMENT: REACTION OF $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}4\text{-}C_6H_4NMe_2)C(N\text{-}4\text{-}C_6H_4Me)O\}\{MeC(N^iPr)_2\}$ WITH > 10 EQUIVALENTS *p*-TOLYL ISOCYANATE

5.0 mg (0.01 mmol) $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}4\text{-}C_6H_4NMe_2)C(N\text{-}4\text{-}C_6H_4Me)O\}\{MeC(N^iPr)_2\}$ and 0.5 mg (0.005 mmol) 1,4-dimethoxybenzene (internal standard) were dissolved in 636 mg toluene-d_8. This was then cooled to -35 °C for 80 min. To this was added 11 µl (11.6 mg, 10-fold excess) *p*-tolyl isocyanate. The sample was immediately placed into an *iso*-propyl alcohol / CO_2 cold bath at -30 °C, and transferred to the NMR spectrometer, which had been pre-cooled to -30 °C. Reaction was determined to have gone to completion after 3 min 30 sec by ^1H NMR spectroscopy.

7.5.30 NMR SCALE REACTION OF Ti(η-C_5Me_5){N(-4-C_6H_4Me) C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} WITH CO_2

5.7 mg (0.01 mmol) Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O} {$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. The sample was freeze-pump-thawed (× 3), and exposed to CO_2 at a pressure of 1.5 atm. The reaction was monitored using ^1H NMR spectroscopy, and found to be complete after 1 h.

7.5.31 NMR SCALE REACTION OF Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O} {$MeC(N^iPr)_2$} WITH *p*-TOLYL ISOCYANATE

9.6 mg (0.02 mmol) Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 2.6 μl (2.7 mg, 0.02 mmol) *p*-tolyl isocyanate *via* a microlitre syringe. The reaction was monitored using ^1H NMR spectroscopy, and found to be complete within 4 min.

7.5.32 SYNTHESIS OF Ti(η-C_5Me_5) {OC(O)N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (51)

103 mg (0.22 mmol) Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{$MeC(N^iPr)_2$} was dissolved in *ca.* 15 ml benzene to give a deep red solution. To this was added 28.9 mg (0.22 mmol) *p*-tolyl isocyanate in *ca.* 5 ml benzene to give a lighter red solution. After 10 min, all volatiles were removed under reduced pressure, and the resulting dark red oily solid triturated with *ca.* 10 ml pentane. The product was afforded as a red-brown powder (yield: 73 mg, 55 %).

7.5.33 SYNTHESIS OF Ti(η-C_5Me_5){OC(O)N(-4-C_6H_4Me)C(N-2,6-$C_6H_3Me_2$)O}{$MeC(N^iPr)_2$} (52)

44.5 mg (0.09 mmol) Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{$MeC(N^iPr)_2$} was dissolved in *ca.* 5 ml benzene. To this was added a solution of 13.8 mg (0.09 mmol) 2,6-dimethylphenyl isocyanate in *ca.* 1 ml benzene. After 18 h, volatiles were removed under reduced pressure, and the final 0.5 ml benzene triturated with *ca.* 2 ml pentane. All remaining volaties were removed under reduced pressure to afford the product as a dark red solid (yield: 38 mg, 65 %).

7.5.34 NMR SCALE REACTION OF Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} WITH 2,6-DIMETHYLPHENYL ISOCYANATE

8.1 mg (0.01 mmol) Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 2.0 μl (2.0 mg, 0.01 mmol) 2,6-dimethylphenyl isocyanate *via* a microlitre syringe. The reaction was monitored using ^{1}H NMR spectroscopy, and was found to be complete after 2 h.

7.5.35 NMR SCALE REACTION OF Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-2,6-$C_6H_3Me_2$)O}{$MeC(N^iPr)_2$} WITH *p*-TOLYL ISOCYANATE

7.5 mg (0.01 mmol) Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-2,6-$C_6H_3Me_2$)O}{$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 1.7 μl (1.7 mg, 0.01 mmol) *p*-tolyl isocyanate *via* a microlitre syringe. The reaction was monitored using ^{1}H NMR spectroscopy, and was found to be complete after 4 min.

7.5.36 SYNTHESIS OF Ti(η-C_5Me_5){OC(N-4-C_6H_4Me)N(-4-C_6H_4Me)C(N-2,6-$C_6H_3Me_2$)O}{$MeC(N^iPr)_2$} (53)

83.6 mg (0.15 mmol) Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-2,6-$C_6H_3Me_2$)O}{$MeC(N^iPr)_2$} was dissolved in a solution of 19.3 mg (0.15 mmol) *p*-tolyl isocyanate in *ca.* 5 ml benzene to give a ruby solution. After 30 min, volatiles were removed under reduced pressure, and the final 1 ml benzene was triturated with *ca.* 5 ml pentane. All remaining volatiles were removed under reduced pressure to afford the product as a light brown powder (yield: 84.3 mg, 82 %).

7.5.37 PSEUDO-FIRST ORDER KINETICS EXPERIMENT: REACTION OF Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} WITH > 10 EQUIVALENTS 2,6-DIMETHYLPHENYL ISOCYANATE

6.1 mg (0.01 mmol) Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} and 0.8 mg (0.005 mmol) 1,4-dimethoxybenzene (internal standard) were dissolved in 654 mg benzene-d_6. To this was added 15 µl (14.8 mg, 10-fold excess) 2,6-dimethylphenyl isocyanate. The sample was immediately transferred to the NMR spectrometer, and the monitored using ^{1}H NMR spectroscopy. The reaction was complete after 12 min.

7.5.38 PSEUDO-FIRST ORDER KINETICS EXPERIMENT: REACTION OF Ti(η-C_5Me_5)(N-4-$C_6H_4NMe_2$){$MeC(N^iPr)_2$} WITH > 10 EQUIVALENTS 2,6-DIMETHYLPHENYL ISOCYANATE

4.7 mg (0.01 mmol) Ti(η-C_5Me_5){N(-4-$C_6H_4NMe_2$)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} and 0.8 mg (0.005 mmol) 1,4-dimethoxybenzene (internal

standard) were dissolved in 645 mg benzene-d_6. To this was added 11 µl (10.8 mg, 10-fold excess) 2,6-dimethylphenyl isocyanate. The sample was immediately transferred to the NMR spectrometer, and the monitored using ^{1}H NMR spectroscopy. The reaction was complete after 18 min.

7.5.39 Attempted synthesis of $Ti(NMe)Cl_2(py)_3$

30 ml (0.060 mol) methylamine (2.0 mol dm^{-3} solution in THF) was dissolved in *ca.* 100 ml dichloromethane, and cooled to -78 °C using an *iso*-propyl alcohol / CO_2 cold bath. To this was added 1.1 ml (1.90 g, 0.013 mol) titanium(IV) tetrachloride, causing the immediate formation of an orange solution with an orange precipitate. The solution was allowed to warm to room temperature over 2 h, and *ca.* 15 ml (0.19 mol) pyridine was added, causing the solution to darken to red. After 16 h the solution was filtered using Celite. The volatiles were removed under reduced pressure to afford a red oil, which was triturated with *ca.* 10 ml pentane, to afford a red powder. This was found to be insoluble in chloroform-d, and dichloromethane-d_2. Addition of pyridine did not increase solubility.

7.5.40 Synthesis of $[Ti(\mu\text{-}NMe)Cl_2(NHMe_2)_2]_2$ (54)

540 mg (2.61 mmol) $Ti(NMe_2)_2Cl_2$ was dissolved in *ca.* 20 ml benzene to give a light red solution. To this was added 1.6 ml (3.20 mmol) methylamine (2.0 mol dm^{-3} solution in THF), resulting in an immediate colour change to a darker red. Some precipitate was noted. The solution was filtered and volatiles removed under reduced pressure to afford the product as a crusty red solid (370 mg, 60 % yield).

7.5.41 ATTEMPTED SYNTHESIS OF $Ti(N^nPr)Cl_2(py)_3$

15 ml (0.182 mol) *n*-propylamine was dissolved in *ca.* 50 ml dichloromethane, and cooled to -78 °C using an *iso*-propyl alcohol / CO_2 cold bath. To this was added 4.0 ml (6.9 mg, 0.036 mol) titanium(IV) tetrachloride, causing the immediate formation of a red solution with a red precipitate. The solution was allowed to warm to room temperature over 3.5 h, and *ca.* 15 ml (0.19 mol) pyridine was added. After 16 h, the solution was found to be clear, and a sample analysed by ^1H NMR confirmed the presence of dissolved $[H_3N^nPr]^+[Cl]^-$. Further attempts to remove the hydrochloride salts were not pursued.

7.5.42 SYNTHESIS OF $Ti(N^nPr)Cl_2(NHMe_2)_2$ (55)

246 mg (1.19 mmol) $Ti(NMe_2)_2Cl_2$ was dissolved in *ca.* 15 ml benzene to give a light red solution. To this was added 120 µl (2.80 mmol) *n*-propylamine *via* microlitre syringe, causing an immediate darkening of the solution, followed within moments to a lightening to orange. After 2 h, all volatiles were removed under reduced pressure to give the product as a static-sensitive orange powder (203 mg, 64 % yield).

7.5.43 SYNTHESIS OF $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}4\text{-}C_6H_4Me)C(N\text{-}4\text{-}C_6H_4Me)N(\text{-}4\text{-}C_6H_4Me)\}\{MeC(N^iPr)_2\}$ (56)

19.0 mg (0.04 mmol) $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4Me)\{MeC(N^iPr)_2\}$ was dissolved in 0.6 ml benzene-d_6. To this was added 9.8 mg (0.04 mmol) 1,3-di-*p*-tolyl carbodiimide, resulting in an immediate colour change from dark green to dark brown. The reaction was monitored using ^1H NMR spectroscopy, and was found to go to completion after 1 h. Removal of all volatiles under

reduced pressure and trituration with pentane afforded the product as a brown powder (yield: 21 mg, 73 %).

7.5.44 SYNTHESIS OF Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N-4-C_6H_4Me) N(-4-C_6H_4Me)}{MeC(N^{i}Pr)$_2$} (57)

46.5 mg (0.11 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 23.4 mg (0.15 mmol) 1,3-di-*p*-tolyl carbodiimide, and the reaction monitored using ^{1}H NMR spectroscopy. Complete formation of product was observed after 24 h. Removal of all volatiles, and trituration with *ca.* 2 ml pentane afforded the product as a dark brown powder (yield: 50.2 mg, 72 %).

7.6 EXPERIMENTAL DETAILS: CHAPTER 5

7.6.1 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} WITH COS

20.5 mg (0.04 mmol) Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} was dissolved in 0.6 ml benzene-d_6. The solution was freeze-pump-thawed (× 3), and the headspace filled with COS at a pressure of 500 mmHg. The product was an insoluble dark red crystalline solid, and *tert*-butyl isocyanate.

7.6.2 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} WITH COS

9.5 mg (0.02 mmol) Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml benzene-d_6. The solution was freeze-pump-thawed (× 3), and the

headspace filled with COS at a pressure of 500 mmHg. The reaction was monitored using ^{1}H NMR spectroscopy.

7.6.3 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N^tBu){PhC($SiMe_3$)$_2$} WITH COS

22.8 mg (0.05 mmol) Ti(η-C_5H_4Me)(N^tBu){PhC($SiMe_3$)$_2$} was dissolved in 0.6 ml benzene-d_6. The solution was freeze-pump-thawed (× 3), and the headspace filled with COS at a pressure of 500 mmHg. The reaction was monitored using ^{1}H NMR spectroscopy.

7.6.4 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N^tBu){MeC(N^iPr)$_2$} WITH COS

15 mg (0.04 mmol) Ti(η-C_5H_4Me)(N^tBu){MeC(N^iPr)$_2$} was dissolved in 0.6 ml benzene-d_6. The solution was freeze-pump-thawed (× 3), and the headspace filled with COS at a pressure of 500 mmHg. The reaction was monitored using ^{1}H NMR spectroscopy.

7.6.5 SYNTHESIS OF Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(O)S}{MeC(N^iPr)$_2$} (62)

277 mg (0.63 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^iPr)$_2$} was dissolved in *ca.* 20 ml benzene to give a dark green solution. The solution was freeze-pump-thawed (× 3), and the headspace filled with COS at a pressure of 500 mmHg. The solution was shaken for 5 min, after which time a colour change to dark red had occurred. Volatiles were removed under reduced pressure to afford the product as a black-brown solid (yield: 220 mg, 70 %).

7.6.6 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N-4-C_6H_4Me) {$MeC(N^iPr)_2$} WITH COS

22.5 mg (0.05 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. The solution was freeze-pump-thawed (× 3), and the headspace filled with COS at a pressure of 500 mmHg. The reaction was monitored using ^1H NMR spectroscopy.

7.6.7 SYNTHESIS OF [Ti(η-C_5Me_5)(μ-S){$PhC(SiMe_3)_2$}]$_2$ (58)

115 mg (0.22 mmol) Ti(η-C_5Me_5)(N^tBu){$PhC(SiMe_3)_2$} was dissolved in *ca.* 15 ml benzene, and to this was added an excess (several drops) of CS_2. Volatiles were removed under reduced pressure after 26 h, and the residue extracted with *ca.* 30 ml pentane. This was cooled to -30 °C, and the product afforded as red crystals (71 mg, 68% yield).

7.6.8 SYNTHESIS OF [Ti(η-C_5Me_5)(μ-S){$MeC(N^iPr)_2$}]$_2$ (59)

305 mg (0.69 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$)($MeC(N^iPr)_2$} was dissolved in *ca.* 15 ml benzene, the headspace was evacuated, and the solution exposed to COS at a pressure of 500 mmHg. Volatiles were removed under reduced pressure after 18 h, and extracted with *ca.* 10 ml benzene. This was layered with *ca.* 15 ml pentane to afford the product as red-brown crystals (55 mg, 22 % yield).

7.6.9 SYNTHESIS OF [Ti(η-C_5H_4Me)(μ-S){$PhC(SiMe_3)_2$}]$_2$ (60)

103 mg (0.22 mmol) Ti(η-C_5H_4Me)(N^tBu){$PhC(SiMe_3)_2$} was dissolved in *ca.* 10 ml benzene, and to this was added an excess (several drops) of CS_2. Volatiles were removed under reduced pressure after a period of 5 d, the

residue extracted in a minimum amount of pentane, and cooled to -30 °C. The product was afforded as a brown powder (15 mg, 16 % yield). Volatiles were removed from the filtrate under reduced pressure to afford a brown oily solid (20 mg recovered due to extraction problems; total yield *ca.* 30 %).

7.6.10 Synthesis of $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}S)\{MeC(N^iPr)_2\}]_2$ (61)

85 mg (0.25 mmol) $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{MeC(N^iPr)_2\}$ was dissolved in *ca.* 10 ml pentane, and to this was added an excess (several drops) of CS_2. After 18 d, the supernatant was filtered away from brown crystalline needles which had formed (25 mg, 33 % yield). The filtrate was reduced down and cooled to -30 °C, but no further product was extracted from solution.

7.6.11 Synthesis of $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}S)\{N(^iPr)C(Me)N(^iPr)C(S)S\}]_2$ (63)

127.4 mg (0.32 mmol) $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ was dissolved in *ca.* 10 ml benzene, to which was added an excess (several drops) of CS_2. Volatiles were removed under reduced pressure after 27 d, and the residue extracted with *ca.* 40 ml pentane. This was cooled to -30 °C, and the product afforded as an olive-brown powder (14 mg, 10 %). Volatiles were removed from filtrate to afford an olive-brown powder (110 mg, 80 %).

7.6.12 NMR scale reaction of $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}S)\{MeC(N^iPr)_2\}]_2$ with CS_2

7.1 mg (0.01 mmol) $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}S)\{MeC(N^iPr)_2\}]_2$ was dissolved in 0.6 ml benzene-d_6 and treated with 12 µl (15.2 mg, 0.20 mmol) CS_2 *via* microlitre syringe. The reaction was monitored using ^1H NMR spectroscopy. No reaction was observed after 21 d.

7.6.13 REACTION OF Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} WITH CS_2 (ONE EQUIVALENT)

272 mg (0.69 mmol) Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} was dissolved in *ca.* 15 ml benzene to give a dark red solution. To this was added 40 μl (50.2 mg, 0.66 mmol) CS_2 *via* microlitre syringe. The reaction mixture was sampled after 6 d, and ^{1}H NMR spectroscopy confirmed no reaction had occurred. A sample taken after 68 d was found to contain a mixture of Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$}, [Ti(η-C_5Me_5)(μ-S){N(^{i}Pr)C(Me)N(^{i}Pr)C(S)S}, and *tert*-butyl isothiocyanate in a ratio 2 : 1 : 2 by ^{1}H NMR spectroscopy.

7.6.14 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N-4-C_6H_4Me) {MeC(N^{i}Pr)$_2$} WITH CS_2

22.5 mg (0.05 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added a few drops (excess) CS_2. A colour change from green to brown occurred within 5 min. The reaction was monitored by ^{1}H NMR spectroscopy.

7.6.15 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$) {PhC($SiMe_3$)$_2$} WITH CS_2

11.7 mg (0.02 mmol) Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$){PhC($SiMe_3$)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added a few drops (excess) CS_2. An immediate colour change from dark red to dark green was observed. The reaction was monitored by ^{1}H NMR spectroscopy.

7.6.16 SYNTHESIS OF Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(S)S}{MeC(N^{i}Pr)$_2$} (64)

244 mg (0.55 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} was dissolved in *ca.* 20 ml pentane to give a dark green solution, and to this was added an excess of CS_2. After 6 h all volatiles were then removed under reduced pressure to afford the product as a very fine black powder (170 mg, 60 %).

7.6.17 NMR SCALE REACTION OF Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(O)O}{MeC(N^{i}Pr)$_2$} WITH CS_2

26.1 mg (0.05 mmol) Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(O)O}{MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added a drop (excess) of CS_2. The reaction was monitored using ^{1}H NMR spectroscopy, and found to decompose to a mixture of unidentified products within 2 weeks.

7.6.18 NMR SCALE REACTION OF Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(S)S}{MeC(N^{i}Pr)$_2$} WITH CO_2

11.2 mg (0.02 mmol) Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(S)S}{MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml benzene-d_6 to give a dark green solution. This was freeze-pump-thawed (× 3), and the headspace filled with CO_2 at a pressure of 1 atm. The reaction was monitored using ^{1}H NMR spectroscopy, and found to decompose to [Ti(η-C_5Me_5)(μ-S){MeC(N^{i}Pr)$_2$}]$_2$ and *tert*-butyl isothiocyanate within 3 d.

7.6.19 NMR SCALE REACTION OF $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ WITH H_2S

21.5 mg (0.05 mmol) $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ was dissolved in 0.6 ml benzene-d_6. The solution was freeze-pump-thawed (× 3), and the headspace filled with H_2S at a pressure of 1 atm. The reaction was monitored by ^1H NMR spectroscopy, and afforded the products $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}S)\{PhC(NSiMe_3)_2\}]_2$ and *tert*-butylamine within 16 h.

7.6.20 NMR SCALE REACTION OF $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{PhC(NSiMe_3)_2\}$ WITH *TERT*-BUTYL ISOTHIOCYANATE

14.5 mg (0.03 mmol) $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{PhC(NSiMe_3)_2\}$ was dissolved in 0.6 ml benzene-d_6. To this was added 3.5 µl (3.2 mg, 0.03 mmol) *tert*-butyl isothiocyanate *via* microlitre syringe. The sample was heated to 80 °C for 16 d, after which ^1H NMR spectroscopy confirmed the presence of trace 1,3-di-*tert*-butyl carbodiimide in the reaction mixture.

7.6.21 NMR SCALE REACTION OF $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ WITH *TERT*-BUTYL ISOTHIOCYANATE

14.8 mg (0.04 mmol) $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{PhC(NSiMe_3)_2\}$ was dissolved in 0.6 ml benzene-d_6. To this was added 5.0 µl (4.5 mg, 0.04 mmol) *tert*-butyl isothiocyanate *via* microlitre syringe. The sample was heated to 80 °C for 16 d, after which ^1H NMR spectroscopy showed the reaction mixture to contain $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$, $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}S)\{MeC(N^iPr)_2\}]_2$, and 1,3-di-*tert*-butyl carbodiimide in the ratio 3 : 1 : 2.

7.6.22 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N^tBu){$PhC(NSiMe_3)_2$} WITH *TERT*-BUTYL ISOTHIOCYANATE

13.5 mg (0.03 mmol) Ti(η-C_5H_4Me)(N^tBu){$PhC(NSiMe_3)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 3.7 μl (3.4 mg, 0.03 mmol) *tert*-butyl isothiocyanate *via* microlitre syringe. The sample was heated to 80 °C for 13 d, after which ^1H NMR showed the reaction mixture to contain Ti(η-C_5H_4Me)(N^tBu){$PhC(NSiMe_3)_2$}, [Ti(η-C_5H_4Me)(μ-S){$PhC(NSiMe_3)_2$}]$_2$, and 1,3-di-*tert*-butyl carbodiimide in the ratio 10 : 1 : 2.

7.6.23 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} WITH 2,6-DIMETHYLPHENYL ISOTHIOCYANATE

13.8 mg (0.04 mmol) Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 5.3 μl (5.8 mg, 0.04 mmol) 2,6-dimethylphenyl isothiocyanate *via* microlitre syringe. The reaction was monitored using ^1H NMR spectroscopy. No reaction was observed after heating the sample to 80 °C for 4 d.

7.6.24 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N^tBu){$PhC(NSiMe_3)_2$} WITH 2,6-DIMETHYLPHENYL ISOTHIOCYANATE

18.5 mg (0.04 mmol) Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 6.0 μl (6.5 mg, 0.04 mmol) 2,6-dimethylphenyl isothiocyanate *via* microlitre syringe. The reaction was monitored using ^1H NMR spectroscopy. A mixture of compounds was detected after 89 h.

7.6.25 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$) {$MeC(N^iPr)_2$} WITH 2,6-DIMETHYLPHENYL ISOTHIOCYANATE

13.6 mg (0.03 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 4.6 µl (5.0 mg, 0.03 mmol) 2,6-dimethylphenyl isothiocyanate *via* microlitre syringe. The reaction was monitored using ^{1}H NMR spectroscopy. Heating to 80 °C caused complete conversion to [Ti(η-C_5Me_5)(µ-S){$MeC(N^iPr)_2$}]$_2$ and 1,3-di-2,6-dimethylphenyl carbodiimide within 4 d.

7.6.26 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$) {$PhC(NSiMe_3)_2$} WITH 2,6-DIMETHYLPHENYL ISOTHIOCYANATE

15.4 mg (0.04 mmol) Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$){$PhC(NSiMe_3)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 6.0 µl (6.5 mg, 0.04 mmol) 2,6-dimethylphenyl isothiocyanate *via* microlitre syringe. The reaction was monitored using ^{1}H NMR spectroscopy. Complete conversion to [Ti(η-C_5H_4Me)(µ-S){$PhC(NSiMe_3)_2$}]$_2$ and 1,3-di-2,6-dimethylphenyl carbodiimide was observed at room temperature within 42 h.

7.6.27 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$) {$MeC(N^iPr)_2$} WITH *p*-TOLYL ISOTHIOCYANATE

13.0 mg (0.03 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 4.3 mg (0.03 mmol) *p*-tolyl isothiocyanate. The reaction was monitored using ^{1}H NMR spectroscopy. After 18 h, a trace of [Ti(η-C_5Me_5)(µ-S){$MeC(N^iPr)_2$}]$_2$ was detected, along with peaks consistent with 1-2,6-dimethylphenyl-3-*p*-tolyl carbodiimide, and a thioureate of the form Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N-4-C_6H_4Me)S}

{MeC(N^{i}Pr)$_2$}. This compound could not be isolated using available techniques.

7.6.28 NMR SCALE REACTION OF Ti(η-C$_5$Me$_5$)(N-4-C$_6$H$_4$Me) {MeC(N^{i}Pr)$_2$} WITH *p*-TOLYL ISOTHIOCYANATE

20.8 mg (0.05 mmol) Ti(η-C$_5$Me$_5$)(N-4-C$_6$H$_4$Me){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml benzene-d$_6$. To this was added 7.3 mg (0.05 mmol) *p*-tolyl isothiocyanate. The reaction was monitored using ^{1}H NMR spectroscopy. Complete conversion to [Ti(η-C$_5$Me$_5$)(μ-S){MeC(N^{i}Pr)$_2$}]$_2$ and 1,3-di-*p*-tolyl carbodiimide was observed after 18 h. During the reaction, peaks consistent with a thioureate of the form Ti(η-C$_5$Me$_5$){N(-4-C$_6$H$_4$Me) C(N-4-C$_6$H$_4$Me)S}{MeC(N^{i}Pr)$_2$} were observed. This compound could not be isolated using available techniques.

7.6.29 NMR SCALE REACTION OF Ti(η-C$_5$Me$_5$){N(-4-C$_6$H$_4$Me)C(O)O}{MeC(N^{i}Pr)$_2$} WITH CS$_2$

8.4 mg (0.02 mmol) Ti(η-C$_5$Me$_5$){N(-4-C$_6$H$_4$Me)C(O)O}{MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml benzene-d$_6$. To this was added a few drops (excess) CS$_2$, and the reaction monitored using ^{1}H NMR spectroscopy. The reaction afforded an unidentified product after 4 d consistent with insertion of CS$_2$ into the molecule. This decomposed to a mixture of unidentified products within 4 weeks.

7.6.30 NMR SCALE REACTION OF Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O} {$MeC(N^iPr)_2$} WITH 2,6-DIMETHYLPHENYL ISOTHIOCYANATE

8.1 mg (0.02 mmol) Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 6 μl (excess) 2,6-dimethylphenyl isothiocyanate *via* microlitre syringe, and the reaction monitored using ^1H NMR spectroscopy. The reaction afforded a product consistent with insertion of 2,6-dimethylphenyl isothiocyanate into the molecule within 4 d.

7.6.31 NMR SCALE REACTION OF Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O} {$MeC(N^iPr)_2$} WITH *p*-TOLYL ISOTHIOCYANATE

9.1 mg (0.02 mmol) Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 2.9 mg (0.02 mmol) *p*-tolyl isothiocyanate, and the reaction monitored using ^1H NMR spectroscopy. The reaction afforded an unidentified product within 2 d, consistent with an insertion product.

7.7 EXPERIMENTAL DETAILS: CHAPTER 6

7.7.1 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N^tBu){$PhC(NSiMe_3)_2$} WITH ONE EQUIVALENT OF NITROSOBENZENE

12.0 mg (0.02 mmol) Ti(η-C_5Me_5)(N^tBu){$PhC(NSiMe_3)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 2.4 mg (0.02 mmol) nitrosobenzene, resulting in an colour change from orange to amber within 5 min. The reaction was monitored using ^1H NMR spectroscopy.

7.7.2 SYNTHESIS OF $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$

740 mg (1.43 mmol) $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{PhC(NSiMe_3)_2\}$ was dissolved in *ca.* 30 ml pentane, and to this was added a solution of 155 mg (1.45 mmol) nitrosobenzene dissolved in *ca.* 15 ml pentane. The reaction was stirred for 16 h, after which a fine yellow precipitate was observed. The supernatant was decanted off and the residue washed with *ca.* 20 ml pentane, to afford the product as an insoluble, static sensitive, yellow powder (350 mg, 76 % yield).

7.7.3 NMR SCALE REACTION OF $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ WITH TWO EQUIVALENTS OF NITROSOBENZENE

20.4 mg (0.05 mmol) $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ was dissolved in 0.6 ml benzene-d_6. To this was added 11.0 mg (0.10 mmol) nitrosobenzene, resulting in an immediate colour change from red to brown. The reaction was monitored using ^1H NMR spectroscopy.

7.7.4 NMR SCALE REACTION OF $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ WITH ONE EQUIVALENT OF NITROSOBENZENE IN BENZENE-d_6

12.0 mg (0.03 mmol) $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ was dissolved in 0.6 ml benzene-d_6. To this was added 2.7 mg (0.03 mmol) nitrosobenzene, resulting in a colour change from red to light tan over *ca.* 5 min. The reaction was monitored using ^1H NMR spectroscopy.

7.7.5 NMR SCALE REACTION OF $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ WITH ONE EQUIVALENT OF NITROSOBENZENE IN CHLOROFORM-d

11.9 mg (0.03 mmol) $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ was dissolved in 0.6 ml benzene-d_6. To this was added 2.6 mg (0.03 mmol) nitrosobenzene,

resulting in a colour change from red to light tan over *ca.* 5 min. The reaction was monitored using ^{1}H NMR spectroscopy.

7.7.6 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe_3)$_2$} WITH ONE EQUIVALENT OF NITROSOBENZENE IN TETRACHLOROMETHANE

12.0 mg (0.03 mmol) Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe_3)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 3.0 mg (0.03 mmol) nitrosobenzene, resulting in a colour change from red to light tan over *ca.* 5 min. A drop of benzene-d_6 was added to enable deuterium-locking of the NMR spectrometer, and the reaction was monitored using ^{1}H NMR spectroscopy.

7.7.7 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$) {MeC(N^{i}Pr)$_2$} WITH ONE EQUIVALENT OF NITROSOBENZENE

16.0 mg (0.04 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 3.9 mg (0.04 mmol) nitrosobenzene, resulting in an immediate colour change from green to orange. The reaction was monitored using ^{1}H NMR spectroscopy.

7.7.8 LOW TEMPERATURE NMR STUDIES OF THE REACTION OF Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} WITH ONE EQUIVALENT OF NITROSOBENZENE

15.8 mg (0.04 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml toluene-d_8. To this was added 3.8 mg (0.04 mmol) nitrosobenzene, resulting in an immediate colour change from green to

orange. The reaction was monitored using ^{1}H NMR spectroscopy in the temperature range 18 °C to -70 °C.

7.7.9 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N-4-C_6H_4Me) {$MeC(N^iPr)_2$} WITH ONE EQUIVALENT OF NITROSOBENZENE

7.9 mg (0.02 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 2.0 mg (0.02 mmol) nitrosobenzene, resulting in an immediate colour change from green to orange. The reaction was monitored using ^{1}H NMR spectroscopy.

7.7.10 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N-4-C_6H_4Me) {$MeC(N^iPr)_2$} WITH FOUR EQUIVALENTS OF NITROSOBENZENE

9.5 mg (0.02 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 7.0 mg (0.07 mmol) nitrosobenzene, resulting in an immediate colour change from green to orange. The reaction was monitored using ^{1}H NMR spectroscopy.

7.7.11 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N^tBu){$PhC(NSiMe_3)_2$} WITH ONE EQUIVALENT OF ACETONE

13.1 mg (0.03 mmol) Ti(η-C_5Me_5)(N^tBu){$PhC(NSiMe_3)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 1.8 µl (1.4 mg, 0.03 mmol) acetone *via* a microlitre syringe. The reaction was monitored using ^{1}H NMR spectroscopy.

7.7.12 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} WITH ONE EQUIVALENT OF ACETONE

14.5 mg (0.04 mmol) Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 2.7 μl (2.1 mg, 0.04 mmol) acetone *via* a microlitre syringe. The reaction was monitored using ^{1}H NMR spectroscopy.

7.7.13 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} WITH ONE EQUIVALENT OF ACETONE

21.9 mg (0.05 mmol) Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 3.5 μl (2.8 mg, 0.05 mmol) acetone using a microlitre syringe. The reaction was monitored using ^{1}H NMR spectroscopy.

7.7.14 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} WITH ONE EQUIVALENT OF BENZOPHENONE

15.2 mg (0.04 mmol) Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 7.0 mg (0.04 mmol) benzophenone. No reaction was observed after 16 h by ^{1}H NMR spectroscopy.

7.7.15 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N-4-C_6H_4Me) {MeC(N^{i}Pr)$_2$} WITH ONE EQUIVALENT OF BENZOPHENONE

30.4 mg (0.07 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 13.2 mg (0.07 mmol) benzophenone. Reaction was monitored using ^{1}H NMR spectroscopy.

7.7.16 Low temperature ^{1}H NMR studies of the reaction of Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} and benzophenone to afford Ti(η-C_5Me_5){N(-4-C_6H_4Me)$C(Ph)_2O$}{$MeC(N^iPr)_2$} (65)

7.0 mg (0.02 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$}, 3.0 mg (0.02 mmol) benzophenone, and 1.9 mg (0.01 mmol) 1,4-dimethoxybenzene (internal standard) were dissolved in 592 mg toluene-d_8. The reaction was monitored using ^{1}H NMR spectroscopy in the temperature range 16 °C to - 40 °C. Upon cooling of the solution to -40 °C, Ti(η-C_5Me_5) {N(-4-C_6H_4Me)$C(Ph)_2O$}{$MeC(N^iPr)_2$} (**65**) was afforded in *ca.* 100 % yield by ^{1}H NMR spectroscopy.

7.7.17 Low temperature ^{1}H NMR studies of the reaction of Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} and benzophenone in the presence of one equivalent of pyridine

13.9 mg (0.03 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$}, and 7.8 mg (0.06 mmol) 1,4-dimethoxybenzene (internal standard) were dissolved in 810 μl dichloromethane-d_2. ^{1}H NMR spectra were recorded over the temperature range 16 °C to -90 °C. 2.6 μl (2.5 mg, 0.03 mmol) pyridine was then added, and the measurements repeated. Finally, 5.7 mg (0.03 mmol) benzophenone was added, and the measurements repeated again.

7.7.18 NMR scale reaction of Ti(η-C_5Me_5)(N-4-C_6F_4H){$MeC(N^iPr)_2$} with one equivalent of benzophenone

10.4 mg (0.02 mmol) Ti(η-C_5Me_5)(N-4-C_6F_4H){$MeC(N^iPr)_2$} (donated by T. Blundell of this research group) was dissolved in 0.6 ml benzene-d_6. To this

was added 4.0 mg (0.02 mmol) benzophenone. The reaction was monitored using ^{1}H NMR spectroscopy.

7.7.19 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$) {PhC($NSiMe_3$)$_2$} WITH ONE EQUIVALENT OF BENZOPHENONE

10.0 mg (0.02 mmol) Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$){PhC($NSiMe_3$)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 3.6 mg (0.02 mmol) benzophenone. The reaction was monitored using ^{1}H NMR spectroscopy.

7.7.20 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$) {MeC(N^{i}Pr)$_2$} WITH A THREE-FOLD EXCESS OF BENZOPHENONE

7.0 mg (0.02 mmol) Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$ was dissolved in 0.6 ml benzene-d_6. To this was added 10.2 mg (0.06 mmol) benzophenone. The reaction was monitored using ^{1}H NMR spectroscopy.

7.7.21 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} WITH ONE EQUIVALENT OF BENZALDEHYDE TO FORM Ti(η-C_5Me_5){N(^{t}Bu)C(Ph)(H)O}{MeC(N^{i}Pr)$_2$} (66)

20.4 mg (0.05 mmol) Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml benzene-d_6, and loaded into a 5 mm Wilmad NMR tube fitted with a Teflon valve. To this was added 5.0 μl (5.2 mg, 0.05 mmol) benzaldehyde *via* microlitre syringe, and the reaction monitored using ^{1}H NMR spectroscopy. Complete consumption of the starting materials, and formation of the cycloadduct Ti(η-C_5Me_5){N(^{t}Bu)C(Ph)(H)O}{MeC(N^{i}Pr)$_2$} (**66**) was observed after 5 min.

7.7.22 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$) {$MeC(N^iPr)_2$} WITH ONE EQUIVALENT OF BENZALDEHYDE

20.2 mg (0.05 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 4.6 μl (4.8 mg, 0.05 mmol) benzaldehyde *via* microlitre syringe, resulting in an immediate colour change from green to red, followed by a colour change to orange over *ca.* 5 min. The reaction was monitored using ^{1}H NMR spectroscopy.

7.7.23 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N-4-C_6H_4Me) {$MeC(N^iPr)_2$} WITH ONE EQUIVALENT OF BENZALDEHYDE TO GIVE Ti(η-C_5Me_5){N(4-C_6H_4Me)C(Ph)(H)O}{$MeC(N^iPr)_2$} (67A / 67B)

7.5 mg (0.02 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 1.8 μl (1.9 mg, 0.02 mmol) benzaldehyde *via* microlitre syringe, and the reaction monitored using ^{1}H NMR spectroscopy. Complete conversion of the starting materials to form the product, presumed to be **67A,** was observed after 5 min. This compound was found to interconvert to another product, presumed to be **67B**, with a half-life of *ca.* 15 min. Decomposition of this compound to the oxo species [Ti(η-C_5Me_5)(μ-O){$MeC(N^iPr)_2$}]$_2$ **(22)** prevented isolation and full characterisation of the sec species.

7.7.24 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} WITH ONE EQUIVALENT OF ACETOPHENONE

13.8 mg (0.04 mmol) Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 4.0 μl (4.1 mg, 0.04 mmol) acetophenone

via microlitre syringe. No reaction was observed using ^{1}H NMR spectroscopy after 16 h.

7.7.25 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$) {$MeC(N^iPr)_2$} WITH ONE EQUIVALENT OF ACETOPHENONE

14.0 mg (0.03 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 3.7 μl (3.8 mg, 0.03 mmol) acetophenone *via* microlitre syringe. No reaction was observed using ^{1}H NMR spectroscopy after 16 h.

7.7.26 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N-4-C_6H_4Me) {$MeC(N^iPr)_2$} WITH ONE EQUIVALENT OF ACETOPHENONE

13.3 mg (0.03 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 3.6 μl (3.7 mg, 0.03 mmol) acetophenone *via* microlitre syringe. An immediate colour change from green to brown was observed. The reaction was monitored using ^{1}H NMR spectroscopy.

7.7.27 SYNTHESIS OF Ti(η-C_5Me_5){N(4-C_6H_4Me)C(Ph)(Me)O} {$MeC(N^iPr)_2$} (68)

182 mg (0.43 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} was dissolved in *ca.* 5 ml benzene. To this was added a solution of 49.6 μl (51.1 mg, 0.43 mmol) acetophenone in *ca.* 5 ml benzene to afford a dark brown solution. After 15 min all volatiles were removed under reduced pressure, and the residue triturated with *ca.* 5 ml pentane to afford the product as a dark brown tar (132 mg, 57 % yield).

7.7.28 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} WITH ONE EQUIVALENT OF *N*-BENZYLIDENE-*p*-TOLUIDINE

4.7 mg (0.01 mmol) Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 2.1 mg (0.01 mmol) *N*-benzylidene-*p*-toluidine. No reaction was observed using ^{1}H NMR spectroscopy after 5 d at 80 °C.

7.7.29 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$) {MeC(N^{i}Pr)$_2$} WITH ONE EQUIVALENT OF *N*-BENZYLIDENE-*p*-TOLUIDINE

22.1 mg (0.05 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 15.1 mg (0.08 mmol) *N*-benzylidene-*p*-toluidine. No reaction was observed using ^{1}H NMR spectroscopy after 5 d at 80 °C.

7.7.30 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N-4-C_6H_4Me) {MeC(N^{i}Pr)$_2$} WITH ONE EQUIVALENT OF *N*-BENZYLIDENE-*p*-TOLUIDINE

10.6 mg (0.03 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 5.0 mg (0.03 mmol) *N*-benzylidene-*p*-toluidine. No reaction was observed using ^{1}H NMR spectroscopy after 24 h at 80 °C.

7.7.31 NMR SCALE REACTION OF $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4NMe_2)\{MeC(N^iPr)_2\}$ WITH ONE EQUIVALENT OF *N*-BENZYLIDENE-*p*-TOLUIDINE

9.8 mg (0.02 mmol) $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4NMe_2)\{MeC(N^iPr)_2\}$ was dissolved in 0.6 ml benzene-d_6. To this was added 5.8 mg (0.03 mmol) *N*-benzylidene-*p*-toluidine. The reaction was monitored using ^1H NMR spectroscopy.

7.7.32 NMR SCALE REACTION OF $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{PhC(NSiMe_3)_2\}$ WITH TRIMETHYLSILYLACETYLENE

11.1 mg (0.02 mmol) $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{PhC(NSiMe_3)_2\}$ was dissolved in 0.6 ml benzene-d_6. To this was added 3.0 μl (2.1 mg, 0.02 mmol) trimethylsilylacetylene *via* microlitre syringe, and the reaction was monitored using ^1H NMR spectroscopy. A further 27.2 μl (18.9 mg, 0.20 mmol) trimethylsilylacetylene was added, and the reaction again monitored using ^1H NMR spectroscopy.

7.7.33 NMR SCALE REACTION OF $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ WITH TRIMETHYLSILYLACETYLENE

10.7 mg (0.03 mmol) $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ was dissolved in 0.6 ml benzene-d_6. To this was added 3.8 μl (2.6 mg, 0.03 mmol) trimethylsilylacetylene *via* microlitre syringe, and the reaction was monitored using ^1H NMR spectroscopy. A further 34.6 μl (24.3 mg, 0.27 mmol) trimethylsilylacetylene was added, and the reaction again monitored using ^1H NMR spectroscopy.

7.7.34 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N^tBu){$PhC(NSiMe_3)_2$} WITH TRIMETHYLSILYLACETYLENE

16.4 mg (0.04 mmol) Ti(η-C_5H_4Me)(N^tBu){$PhC(NSiMe_3)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 5.0 μl (3.5 mg, 0.04 mmol) trimethylsilylacetylene *via* microlitre syringe, and the reaction was monitored using ^1H NMR spectroscopy. A further 45.2 μl (32.5 mg, 0.32 mmol) trimethylsilylacetylene was added, and the reaction again monitored using ^1H NMR spectroscopy.

7.7.35 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N^tBu){$PhC(NSiMe_3)_2$} WITH PHENYLACETYLENE

9.5 mg (0.02 mmol) Ti(η-C_5Me_5)(N^tBu){$PhC(NSiMe_3)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 2.0 μl (1.9 mg, 0.02 mmol) phenylacetylene *via* microlitre syringe, and the reaction was monitored using ^1H NMR spectroscopy. A further 4 μl (3.8 mg, 0.40 mmol) phenylacetylene was added, and the reaction again monitored using ^1H NMR spectroscopy.

7.7.36 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} WITH PHENYLACETYLENE TO GIVE Ti(η-C_5Me_5)(NH^tBu)(η^1-C_2Ph){$MeC(N^iPr)_2$} (69)

15 mg (0.04 mmol) Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 12.6 μl (11.7 mg, 0.12 mmol) phenylacetylene. The reaction was monitored using ^1H NMR spectroscopy. After 16 h, the solution was found to contain starting materials and the product

Ti(η-C_5Me_5)(NH^{t}Bu)(η^1-C_2Ph){MeC(N^{i}Pr)$_2$} (**69**) in the ratio 22 : 88 by ^{1}H NMR spectroscopy.

7.7.37 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} WITH PHENYLACETYLENE

21.3 mg (0.05 mmol) Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 5.0 µl (4.7 mg, 0.05 mmol) phenylacetylene *via* microlitre syringe, and the reaction was monitored using ^{1}H NMR spectroscopy.

7.7.38 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$) {MeC(N^{i}Pr)$_2$} WITH PHENYLACETYLENE

14.7 mg (0.03 mmol) Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 3.7 µl (3.4 mg, 0.03 mmol) phenylacetylene *via* microlitre syringe, and the reaction was monitored using ^{1}H NMR spectroscopy.

7.7.39 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N-4-C_6H_4Me) {MeC(N^{i}Pr)$_2$} WITH PHENYLACETYLENE

20.5 mg (0.05 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 5.3 µl (4.9 mg, 0.05 mmol) phenylacetylene *via* microlitre syringe, and the reaction was monitored using ^{1}H NMR spectroscopy.

7.7.40 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe_3)$_2$} WITH *p*-TOLYLACETYLENE

17.1 mg (0.03 mmol) Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe_3)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 4.3 μl (3.9 mg, 0.03 mmol) *p*-tolylacetylene *via* microlitre syringe, and the reaction was monitored using ^{1}H NMR spectroscopy.

7.7.41 NMR SCALE REACTION OF Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} WITH *p*-TOLYLACETYLENE TO GIVE Ti(η-C_5Me_5)(NH^{t}Bu)(η^1-C_2-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (70)

17.8 mg (0.05 mmol) Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 5.8 μl (5.4 mg, 0.05 mmol) *p*-tolylacetylene *via* microlitre syringe, and the reaction was monitored using ^{1}H NMR spectroscopy. After 16 h, the solution was found to contain starting materials and a product Ti(η-C_5Me_5)(NH^{t}Bu)(η^1-C_2-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**70**) in a ratio 55 : 45 by ^{1}H NMR spectroscopy.

7.7.42 NMR SCALE REACTION OF Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe_3)$_2$} WITH *p*-TOLYLACETYLENE

21.4 mg (0.05 mmol) Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe_3)$_2$} was dissolved in 0.6 ml benzene-d_6. To this was added 6.0 μl (5.5 mg, 0.05 mmol) *p*-tolylacetylene *via* microlitre syringe, and the reaction was monitored using ^{1}H NMR spectroscopy.

7.8 REFERENCES FOR CHAPTER 7

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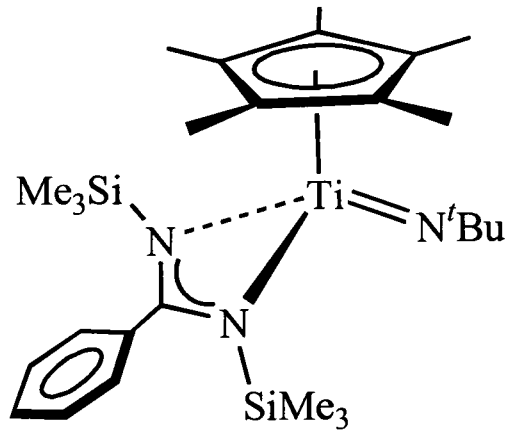
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CHAPTER 8

Characterising Data

8.1 Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe_3)$_2$} (1)



Appearance: Red powder

Molecular formula: $C_{27}H_{47}N_3Si_2Ti$

Elemental analysis for $C_{27}H_{47}N_3Si_2Ti$:

Found (calculated) % : C 61.0 (62.6); H 9.2 (9.2); N 7.6 (8.1)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.25	3 H, m	*o*-, *p*- C_6H_5
7.03	2 H, m	*m*- C_6H_5
2.14	15 H, s	C_5Me_5
1.20	9 H, s	N^t*Bu*
-0.01	18 H, s	Si*Me*$_3$

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

173.3	$C_6H_5CN_2$
139.8	*i*- $C_6H_5CN_2$

128.6	*o*- $C_6H_5CN_2$
128.3	*m*- $C_6H_5CN_2$
127.9	*p*- $C_6H_5CN_2$
119.7	C_5Me_5
67.1	$NCMe_3$
33.0	$NC\mathit{Me_3}$
12.7	$C_5\mathit{Me_5}$
3.2	$Si\mathit{Me_3}$

IR data (NaCl plates, Nujol mull)

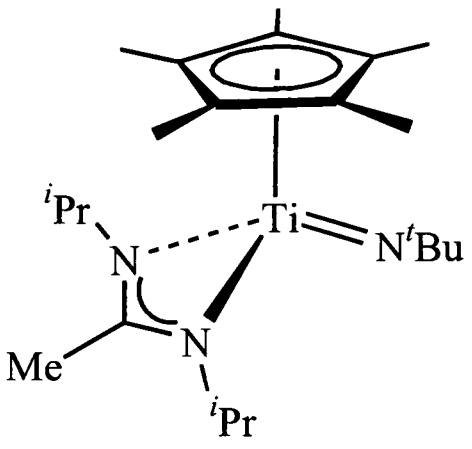
2725 (w), 1732 (w), 1407 (s), 1350 (m), 1246 (s), 1207 (w), 1169 (w), 1122 (w), 1074 (w), 1005 (m), 995 (m), 919 (w), 841 (s), 763 (m), 723 (m), 703 (m), 588 (w), 542 (w), 506 (w), 444 (w), 415 (w) cm^{-1}

Mass Spec. (E.I.)

m/z = 517 $[M]^+$

m/z = 502 $[M\text{-}Me]^+$

8.2 Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} (2)



Appearance: Red/brown powder

Molecular Formula: $C_{22}H_{41}N_3Ti$

Elemental analysis for $C_{22}H_{41}N_3Ti$:

Found (calculated) % : C 67.1 (66.8); H 10.4 (10.5); N 10.2 (10.6)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

3.56	2 H, apparent sept	J = 6.4 Hz	NC*H*MeMe
2.13	15 H, s		C_5Me_5
1.68	3 H, s		$MeCN_2$
1.10	9 H, s		N^tBu
1.04	6 H, d	J = 6.4 Hz	NCH*Me*Me
1.01	6 H, d	J = 6.4 Hz	NCHMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

163.6	Me*C*N_2
118.9	C_5Me_5
66.0	N*C*Me_3
47.9	N*C*HMeMe
31.8	NC*Me*$_3$
25.2	NCHMeMe
24.0	NCHMeMe
11.2	C_5*Me*$_5$
9.8	*Me*CN_2

I.R. data (KBr plates, Nujol mull)

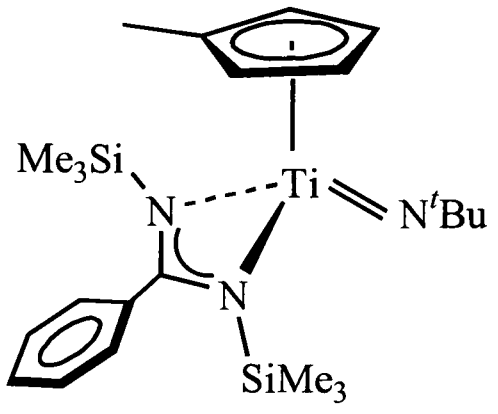
2722 (w), 2041 (w), 1597 (w), 1339 (s, br), 1317 (m), 1244 (s), 1213 (s), 1174 (s), 1143 (w), 1122 (m), 1057 (w), 1018 (m), 812 (m), 754 (w), 723 (m), 700 (w), 623 (m), 591 (m), 554 (s), 534 (s), 507 (w), 419 (s) cm^{-1}

Mass Spec. (E.I.)

m/z = 395 $[M]^+$

m/z = 380 $[M\text{-}Me]^+$

8.3 Ti(η-C_5H_4Me)(N^tBu){$PhC(NSiMe_3)_2$} (3)



Appearance: Red powder

Molecular formula: $C_{23}H_{39}N_3Si_2Ti$

Elemental analysis for $C_{23}H_{39}N_3Si_2Ti$:

Found (calculated) % : C 59.8 (59.8); H 8.2 (8.5); N 9.0 (9.1)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.16	3 H, m	*o*-, *p*- C_6H_5
7.03	2 H, m	*m*- C_6H_5
6.87	2 H, virtual t	C_5H_2(*β*)H_2(α)Me
5.80	2 H, virtual t	C_5H_2(β)H_2(*α*)Me
2.06	3 H, s	C_5H_4*Me*
1.17	9 H, s	N^t*Bu*
-0.10	18 H, s	Si*Me*$_3$

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

170.6	$C_6H_5CN_2$
139.7	*i*- $C_6H_5CN_2$
128.6	*o*- $C_6H_5CN_2$
128.1	*m*- $C_6H_5CN_2$
127.5	*p*- $C_6H_5CN_2$
123.0	$C_2(\beta)C_2(\alpha)CMe$
113.1	$C_2(\beta)C_2(\alpha)CMe$
108.8	$C_2(\beta)C_2(\alpha)CMe$
67.0	$NCMe_3$
32.7	$NCMe_3$
14.8	$C_2(\beta)C_2(\alpha)CMe$
2.0	$SiMe_3$

I.R. data (KBr plates, Nujol mull)

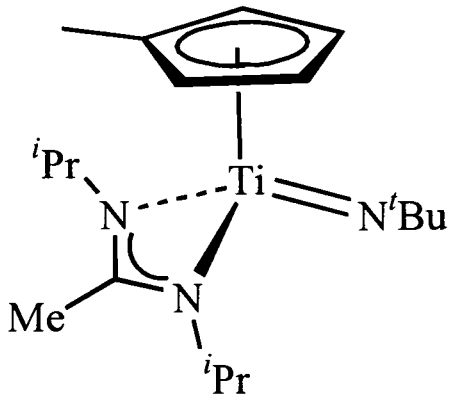
3061 (w), 2728 (w), 2363 (w), 1946 (w), 1614 (w, br), 1578 (w, br), 1350 (s), 1305 (m), 1248 (s), 1209 (m), 1177 (m), 1123 (m), 1073 (m), 1047 (w), 1033 (m), 1007 (s), 996 (s), 935 (w), 918 (m), 839 (s, br), 805 (w), 785 (s), 764 (s), 723 (w), 701 (m), 687 (w), 625 (m, br), 604 (m, br), 548 (s), 507 (s), 446 (m), 402 (m) cm^{-1}

Mass Spec. (E.I.)

m/z = 461 $[M]^+$

m/z = 446 $[M\text{-}Me]^+$

8.4 Ti(η-C_5H_4Me)(N^tBu){$MeC(N^iPr)_2$} (4)



Appearance: Red oil

Molecular Formula: $C_{18}H_{33}N_3Ti$

Elemental analysis for $C_{18}H_{33}N_3Ti$:

Found (calculated) %: C 50.6 (63.7); H 10.6 (9.8); N 7.0 (12.4)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

6.68	2 H, virtual t		C_5H_2(*β*)H_2(α)Me
5.94	2 H, virtual t		C_5H_2(β)H_2(*α*)Me
3.55	2 H, apparent sept	J = 6.4 Hz	NC*H*MeMe
1.98	3 H, s		C_5H_2(β)H_2(α)*Me*
1.54	3 H, s		*Me*CN_2
1.11	9 H, s		N^tBu
1.06	6 H, d	J = 6.4 Hz	NCH*Me*Me
0.87	6 H, d	J = 6.4 Hz	NCHMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

159.3	Me*C*N_2
121.8	$C_2(\beta)C_2(\alpha)$*C*Me
112.6	$C_2(\beta)$*$C_2(\alpha)$*CMe
108.5	*$C_2(\beta)$*$C_2(\alpha)$CMe
66.8	N*C*Me_3
48.2	N*C*HMeMe
32.9	NC*Me*$_3$
25.9	NCH*Me*Me
25.7	NCHMe*Me*
14.2	$C_2(\beta)C_2(\alpha)$C*Me*
10.3	*Me*CN_2

I.R. data (KBr plates, neat thin film)

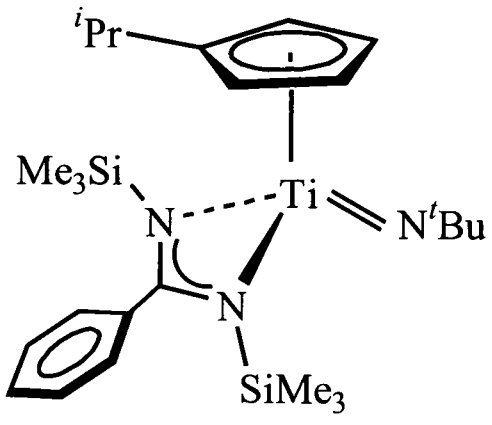
2963 (s), 2931 (s), 2867 (m), 2601 (w), 2362 (w), 1489 (s, br), 1451 (s, br), 1378 (m), 1361 (m), 1336 (s), 1317 (m), 1247 (s), 1225 (s), 1210 (m), 1174 (m), 1145 (w), 1123 (m), 1091 (m), 1059 (w), 1033 (w), 986 (w), 935 (w), 842 (m), 785 (s, br), 721 (m), 621 (w), 590 (m, br), 558 (m), 534 (w), 507 (w), 470 (w) cm^{-1}

Mass Spec. (E.I.)

m/z = 339.2 $[M]^+$ *m/z* = 324.2 $[M\text{-}Me]^+$

m/z = 268.1 $[M\text{-}N^tBu]^+$

8.5 Ti(η-$C_5H_4{}^iPr$)(N^tBu){$PhC(NSiMe_3)_2$} (5)



Appearance: Red powder

Molecular formula: $C_{25}H_{43}N_3Si_2Ti$

Elemental analysis for $C_{25}H_{43}N_3Si_2Ti$:

Found (calculated) % : C 61.7 (61.5); H 7.9 (8.7); N 8.1 (8.6)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.23 – 7.21	2 H, m		*m*- C_6H_5
7.05 – 7.03	3 H, m		*o*- ,*p*- C_6H_5
6.96	2 H, virtual t	J = 2.7 Hz	C_5H_2(*β*)H_2(α)Me
5.84	2 H, virtual t	J = 2.7 Hz	C_5H_2(β)H_2(*α*)Me
2.81	1 H, sept	J = 7.0 Hz	$C_5H_4CHMe_2$
1.21	6 H, d	J = 7.0 Hz	$C_5H_4CHMe_2$
1.17	9 H, s		N^tBu
-0.08	18 H, s		$SiMe_3$

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

170.6	$C_6H_5CN_2$
139.7	*i*- $C_6H_5CN_2$
135.4	*i*- $C_5H_4{}^{i}Pr$
128.6	*o*- $C_6H_5CN_2$
128.3	*m*- $C_6H_5CN_2$
127.4	*p*- $C_6H_5CN_2$
110.3	$C_2(\beta)C_2(\alpha)CHMe_2$
108.6	$C_2(\beta)C_2(\alpha)CHMe_2$
67.0	$NCMe_3$
32.7	$NCMe_3$
28.5	$C_2(\beta)C_2(\alpha)CHMe_2$
23.9	$C_2(\beta)C_2(\alpha)CHMe_2$
2.0	$SiMe_3$

I.R. data (KBr plates, Nujol mull)

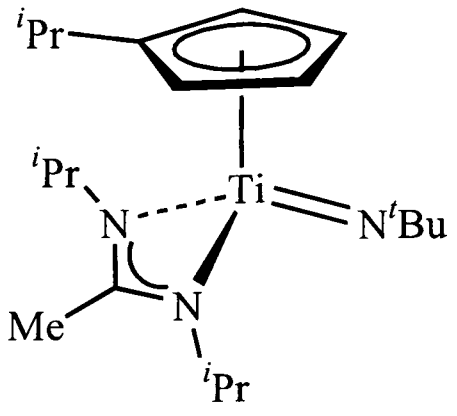
2956 (s), 2726 (w), 2362 (w), 1946 (w), 1616 (w), 1578 (w), 1423 (s), 1412 (s), 1351 (m), 1248 (s), 1209 (m), 1151 (m), 1122 (m), 1074 (m), 1033 (m), 1006 (m), 996 (m), 932 (w), 918 (w), 841 (s), 805 (m), 786 (m), 764 (m), 725 (m), 701 (m), 686 (w), 604 (w), 548 (w), 507 (w), 445 (w) cm^{-1}

Mass Spec. (E.I.)

m/z = 489 $[M]^+$

m/z = 474 $[M\text{-}Me]^+$

8.6 Ti(η-$C_5H_4{}^iPr$)(N^tBu){$MeC(N^iPr)_2$} (6)



Appearance: Red oil

Molecular Formula: $C_{20}H_{37}N_3Ti$

Elemental analysis for $C_{20}H_{37}N_3Ti$:

Found (calculated) %: C 65.4 (65.4); H 10.0 (10.2); N 11.3 (11.4)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

6.70	2 H, virtual t	J = 2.7 Hz	$C_5H_2(\beta)H_2(\alpha)CHMe_2$
6.06	2 H, virtual t	J = 2.7 Hz	$C_5H_2(\beta)H_2(\alpha)CHMe_2$
3.56	2 H, apparent sept	J = 6.4 Hz	NC*H*MeMe
2.77	1 H, sept	J = 6.8 Hz	$C_5H_4CHMe_2$
1.54	3 H, s		$MeCN_2$
1.19	6 H, d	J = 6.8 Hz	$C_5H_4CHMe_2$
1.14	9 H, s		N^tBu
1.08	6 H, d	J = 6.4 Hz	NCH*Me*Me
0.90	6 H, d	J = 6.4 Hz	NCHMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

159.6	Me*C*N_2
134.6	*i*- $C_5H_4{}^{i}Pr$
128.3	$C_2(\beta)C_2(\alpha)$*C*HMe_2
109.6	$C_2(\beta)$*C*$_2$*(*α*)*$CHMe_2$
108.6	*C*$_2$*(*β*)*$C_2(\alpha)CHMe_2$
66.9	N*C*Me_3
48.3	N*C*HMeMe
32.9	NC*Me*$_3$
28.7	C_5H_4CH*Me*$_2$
26.0	NCH*Me*Me
25.7	NCHMe*Me*
10.4	*Me*CN_2

I.R. data (KBr plates, neat thin film)

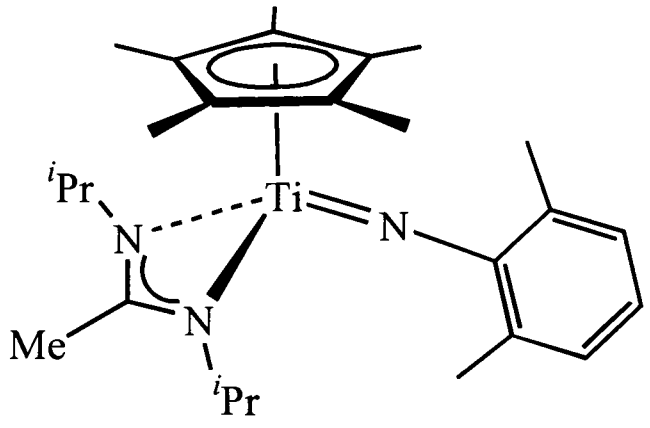
2962 (s), 2932 (s), 2869 (s), 2601 (w), 1618 (w, br), 1494 (s, br), 1378 (m), 1361 (m), 1335 (m, br), 1316 (m), 1246 (s), 1224 (s, br), 1174 (m), 1146 (m), 1122 (m), 1106 (m), 1088 (m), 1060 (m, br), 1019 (m), 931 (w), 844 (m), 787 (s, br), 694 (m), 624 (w), 594 (w), 556 (w), 534 (w), 507 (w), 474 (w) cm^{-1}

Mass Spec. (E.I.)

m/z = 367 $[M]^+$

m/z = 352 $[M\text{-}Me]^+$

8.7 Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (7)



Appearance: Green powder

Molecular Formula: $C_{26}H_{41}N_3Ti$

Elemental analysis for $C_{26}H_{41}N_3Ti$:

Found (calculated) % : C 70.0 (70.4); H 9.3 (9.3); N 9.4 (9.5)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.02	2 H, d	J = 7.3 Hz	*m*- aryl
6.73	1 H, t	J = 7.3 Hz	*p*- aryl
3.56	2 H, apparent sept	J = 6.4 Hz	NC*H*MeMe
2.30	6 H, s		N-2,6-C_6H_3*Me*$_2$
1.98	15 H, s		C_5*Me*$_5$
1.67	3 H, s		*Me*CN_2
1.07	6 H, d	J = 6.4 Hz	NCH*Me*Me
1.00	6 H, d	J = 6.4 Hz	NCHMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

164.1	Me*C*N_2
158.5	*i*-aryl
131.5	*o*-aryl
127.6	*m*-aryl
120.7	*p*-aryl
118.9	C_5Me_5
49.1	N*C*HMeMe
25.9	NCHMe*Me*
25.1	NCH*Me*Me
20.7	N($C_6H_3Me_2$)
12.5	*Me*CN_2
12.3	C_5Me_5

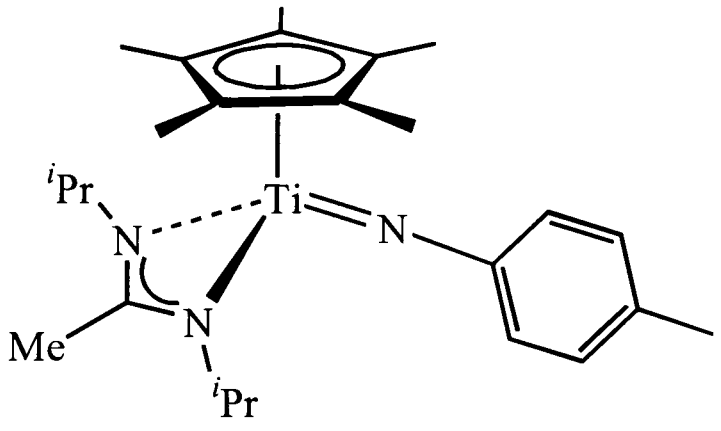
I.R. data (KBr discs, Nujol mull)

2720 (w), 2595 (w), 2046(w), 1892 (w), 1838 (w), 1785 (w), 1653 (w), 1623 (w), 1587 (m), 1407 (s), 1364 (s), 1334 (s), 1310(s), 1295 (s), 1216 (s), 1174 (m), 1157 (w), 1139 (w), 1121 (m), 1096 (m), 1055 (w), 1014 (m, br), 973 (m), 959 (m), 914 (w), 894 (w), 873 (w), 815 (s), 760 (s), 743 (m), 723 (m), 618 (m), 589 (m), 574 (w), 565 (m), 547 (w), 445 (s) cm^{-1}

Mass Spec. (E.I.)

m/z = 443 $[M]^+$

8.8 Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} (8)



Appearance: Green powder

Molecular Formula: $C_{25}H_{39}N_3Ti$

Elemental analysis for $C_{25}H_{39}N_3Ti$:

Found (calculated) % : C 69.9 (69.9) H 9.2 (9.2) N 9.3 (9.8)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

6.93	2 H, d	J = 7.9 Hz	*m*- (N-4-C_6H_4Me)
6.74	2 H, d	J = 7.9 Hz	*o*- (N-4-C_6H_4Me)
3.54	2 H, apparent sept	J = 6.3 Hz	NC*H*MeMe
2.13	3 H, s		N-4-C_6H_4*Me*
2.07	15 H, s		C_5*Me*$_5$
1.51	3 H, s		*Me*CN_2
1.10	6 H, d	J = 6.3 Hz	NCH*Me*Me
0.97	6 H, d	J = 6.3 Hz	NCHMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

163.6	Me*C*N_2
158.9	*i*- N-4-C_6H_4Me
129.0	*m*- N-4-C_6H_4Me
127.9	*p*- N-4-C_6H_4Me
123.2	*o*- N-4-C_6H_4Me
120.6	C_5Me_5
49.3	N*C*HMeMe
26.2	NCHMe*Me*
25.3	NCH*Me*Me
21.1	N-4-C_6H_4*Me*
12.3	C_5*Me*$_5$
11.6	*Me*CN_2

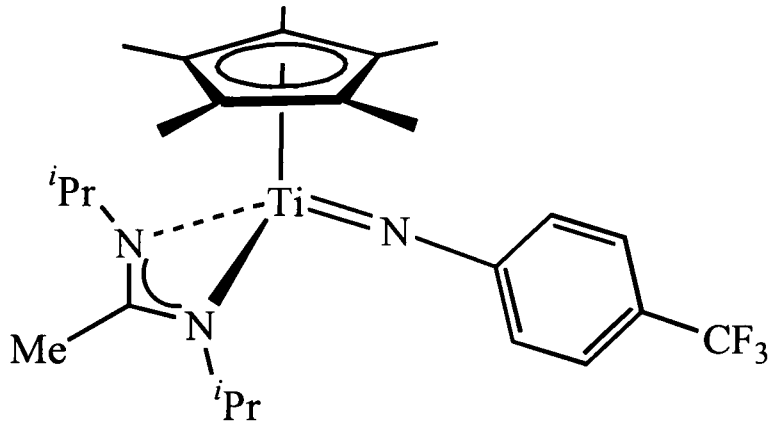
I.R. data (KBr plates, Nujol mull)

2958 (s), 1871 (w), 1655 (w), 1599 (m), 1490 (s), 1315 (s, br), 1261 (s), 1212 (s, br), 1171 (m), 1141 (w), 1120 (w), 1099 (w, br), 1019 (s), 964 (m), 817 (s, br), 723 (w), 656 (m), 625 (w), 607 (w), 557 (w), 526 (w), 589 (m), 440 (m, br) cm^{-1}

Mass Spec. (E.I.)

m/z = 429 $[M]^+$

8.9 Ti(η-C_5Me_5)(N-4-$C_6H_4CF_3$){$MeC(N^iPr)_2$} (9)



Appearance: Brown powder

Molecular Formula: $C_{25}H_{36}F_3N_3Ti$

Elemental analysis for $C_{25}H_{36}F_3N_3Ti$:

Found (calculated) % : C 61.8 (62.1) H 7.5 (7.5) N 8.9 (8.7)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.34	2 H, d	J = 8.0 Hz	*m*- (N-4-$C_6H_4CF_3$)
6.56	2 H, d	J = 8.0 Hz	*o*- (N-4-$C_6H_4CF_3$)
3.46	2 H, apparent sept	J = 6.4 Hz	NC*H*MeMe
1.98	15 H, s		C_5Me_5
1.47	3 H, s		*Me*CN_2
0.96	6 H, d	J = 6.4 Hz	NCH*Me*Me
0.91	6 H, d	J = 6.6 Hz	NCHMe*Me*

^{13}C-{^{1}H} NMR data (75.5 MHz, 298 K, benzene-d_6)

164.2	Me*C*N_2
162.8	*i*- N-4-$C_6H_4CF_3$
126.3	*p*- N-4-$C_6H_4CF_3$
125.9	*m*- N-4-$C_6H_4CF_3$
123.0	*o*- N-4-$C_6H_4CF_3$
121.8	C_5Me_5
49.8	N*C*HMeMe
26.5	NCHMe*Me*
25.4	NCH*Me*Me
12.8	C_5Me_5
12.1	*Me*CN_2

CF_3 resonance not observed

^{19}F NMR data (282.4 MHz, 298 K, benzene-d_6)

-61.0 CF_3

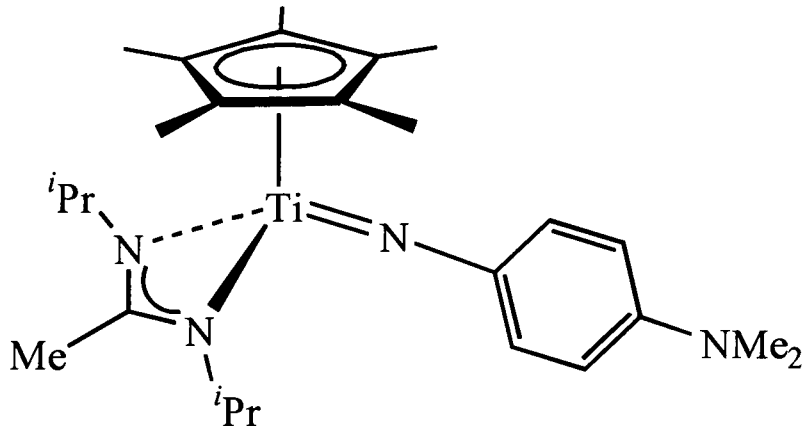
I.R. data (KBr plates, Nujol mull)

2726 (w), 2670 (w), 1892 (w), 1654 (m), 1601 (s), 1499 (s, br), 1412 (m), 1317 (s), 1275 (m, br), 1213 (m), 1159 (s), 1115 (s), 1066 (s), 1020 (w), 964 (m), 890 (w), 849 (m), 838 (m), 812 (w), 793 (w), 772 (w), 723 (m), 687 (m), 664 (w), 644 (w), 633 (w), 581 (w), 473 (w), 440 (w), 402 (w) cm^{-1}

Mass Spec. (E.I.)

m/z	=	483	$[M]^+$
m/z	=	464	$[M-F]^+$
m/z	=	445	$[M-2F]^+$
m/z	=	426	$[M-3F]^+$

8.10 Ti(η-C_5Me_5)(N-4-$C_6H_4NMe_2$){$MeC(N^iPr)_2$} (10)



Appearance: Green powder

Molecular Formula: $C_{26}H_{42}N_4Ti$

Elemental analysis for $C_{26}H_{42}N_4Ti$:

Found (calculated) % : C 67.2 (68.1) H 9.2 (9.2) N 12.2 (12.2)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

6.80	2 H, d	J = 9.0 Hz	*m*- N-4-$C_6H_4NMe_2$
6.56	2 H, d	J = 9.0 Hz	*o*- N-4-$C_6H_4NMe_2$
3.58	2 H, apparent sept	J = 6.4 Hz	NC*H*MeMe
2.51	6 H, s		N*Me*$_2$
2.11	15 H, s		C_5*Me*$_5$
1.55	3 H, s		*Me*CN_2
1.16	6 H, d	J = 6.4 Hz	NCH*Me*Me
1.00	6 H, d	J = 6.4 Hz	NCHMe*Me*

^{13}C-{^{1}H} NMR data (75.5 MHz, 298 K, benzene-d_6)

162.9	Me*C*N_2
153.7	*i*- N-4-$C_6H_4NMe_2$
144.6	*p*- N-4-$C_6H_4NMe_2$
124.1	*m*- N-4-$C_6H_4NMe_2$
120.1	C_5Me_5
113.9	*o*- N-4-$C_6H_4NMe_2$
49.6	N*C*HMeMe
41.7	N*Me*$_2$
26.7	NCHMe*Me*
25.7	NCH*Me*Me
12.8	C_5*Me*$_5$
12.0	*Me*CN_2

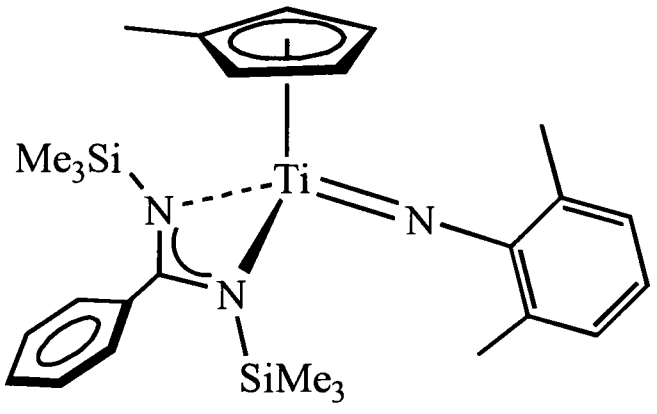
I.R. data (KBr plates, Nujol mull)

2956 (s), 2724 (w), 1655 (w), 1599 (w), 1499 (s), 1337 (w), 1313 (m), 1261 (m), 1218 (m), 1171 (w), 1123 (w), 1060 (w), 1021 (w), 969 (w), 947 (w), 858 (w), 814 (s), 753 (w), 724 (w), 625 (w), 555 (w), 470 (w) cm^{-1}

Mass Spec. (E.I.)

m/z = 458 $[M]^+$

8.11 Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$){$PhC(NSiMe_3)_2$} (11)



Appearance: Reddish-green powder

Molecular formula: $C_{27}H_{39}N_3Si_2Ti$

Elemental analysis for $C_{27}H_{39}N_3Si_2Ti$:

Found (calculated) % : C 63.3 (63.6); H 8.3 (7.7); N 8.2 (8.2)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.14 – 7.09	3 H, m	*aryl-H*
7.00 – 6.95	5 H, m	*aryl-H*
6.74	2 H, virtual t	$C_5H_2(\beta)H_2(\alpha)Me$
5.86	2 H, virtual t	$C_5H_2(\beta)H_2(\alpha)Me$
2.56	6 H, s	N-2,6-$C_6H_3Me_2$
2.10	3 H, s	$C_5H_2(\beta)H_2(\alpha)Me$
-0.15	18 H, s	$SiMe_3$

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

171.0	$C_6H_5CN_2$
159.6	*i*- 2,6-$C_6H_3Me_2$
138.6	*i*- $C_6H_5CN_2$
132.4	*o*- 2,6-$C_6H_3Me_2$
128.9	*o*- $C_6H_5CN_2$
127.6	*m*- 2,6-$C_6H_3Me_2$
127.5	*p*- $C_6H_5CN_2$
125.2	*p*- 2,6-$C_6H_3Me_2$
119.9	$C_2(\beta)C_2(\alpha)CMe$
114.5	$C_2(\beta)C_2(\alpha)CMe$
111.7	$C_2(\beta)C_2(\alpha)CMe$
20.6	N-2,6-$C_6H_3Me_2$
14.9	$C_2(\beta)C_2(\alpha)CMe$
2.2	$SiMe_3$

I.R. data (KBr plates, Nujol mull)

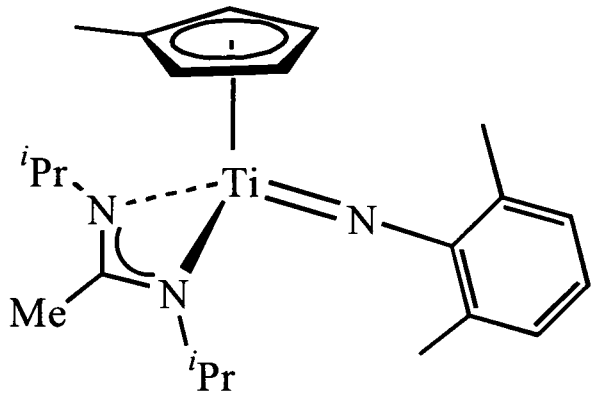
2726 (w), 1589 (w), 1406 (m, br), 1308 (m, br), 1249 (s), 1171 (w, br), 1094 (w), 1033 (w), 1006 (m), 996 (m), 919 (w), 840 (s), 793 (m), 781 (m), 760 (m), 723 (w), 702 (w), 643 (w), 517 (m) cm^{-1}

Mass Spec. (E.I.)

m/z = 509 $[M]^+$

m/z = 495 $[M\text{-}Me]^+$

8.12 Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$){$MeC(N^iPr)_2$} (12)



Appearance: Green Oil

Molecular formula: $C_{22}H_{33}N_3Ti$

Elemental analysis for $C_{22}H_{33}N_3Ti$:

Found (calculated) % : C 66.0 (68.2); H 8.7 (8.6); N 10.8 (10.9)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.01	2 H, d	J = 7.5 Hz	*m*- 2,6-$C_6H_3Me_2$
6.72	1 H, t	J = 7.5 Hz	*p*- 2,6-$C_6H_3Me_2$
6.37	2 H, virtual t	J = 2.7 Hz	$C_2H_2(\beta)C_2H_2(\alpha)CMe$
5.92	2 H, virtual t	J = 2.7 Hz	$C_2H_2(\beta)C_2H_2(\alpha)CMe$
3.50	2 H, apparent sept	J = 6.4 Hz	NC*H*MeMe
2.38	6 H, s		2,6-$C_6H_3Me_2$
2.10	3 H, s		$C_2H_2(\beta)C_2H_2(\alpha)CMe$
1.53	3 H, s		*Me*CN_2
1.01	6 H, d	J = 6.4 Hz	NCH*Me*Me
0.86	6 H, d	J = 6.4 Hz	NCHMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

160.3	Me*C*N_2
131.6	*i*- 2,6-$C_6H_3Me_2$
128.3	*o*- 2,6-$C_6H_3Me_2$
127.6	*m*- 2,6-$C_6H_3Me_2$
125.0	*p*- 2,6-$C_6H_3Me_2$
119.5	$C_2(\beta)C_2(\alpha)$*C*Me
113.6	$C_2(\beta)$*$C_2(\alpha)$*CMe
111.8	*$C_2(\beta)$*$C_2(\alpha)$CMe
48.8	N*C*HMeMe
25.6	NCH*Me*Me
25.4	NCHMe*Me*
20.6	N-2,6-C_6H_3*Me_2*
15.1	$C_2(\beta)C_2(\alpha)$C*Me*
10.6	*Me*CN_2

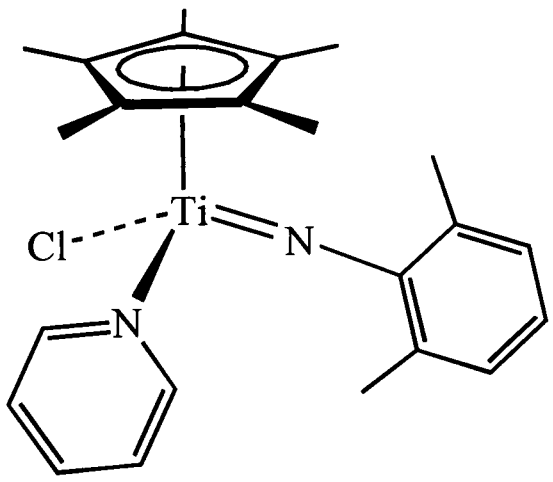
I.R. data (KBr plates, neat thin film)

3170 (w), 3054 (m), 3028 (m), 2965 (s), 2927 (s), 2868 (s), 2720 (w), 2601 (w), 2365 (w), 2053 (w), 1827 (w), 1765 (w), 1640 (w, br), 1587 (m), 1467 (s, br), 1408 (s), 1378 (s), 1361 (s), 1336 (s), 1308 (s, br), 1227 (s), 1173 (m), 1143 (m), 1123 (m), 1094 (m), 1057 (m), 1049 (m), 1032 (m), 1019 (m), 980 (m), 963 (m), 936 (w), 915 (w), 885 (w), 845 (m), 816 (s), 786 (s), 758 (s), 742 (m), 624 (m), 585 (m), 564 (w), 550 (w), 503 (w), 435 (m) cm^{-1}

Mass Spec. (E.I.)

m/z = 387 $[M]^+$

8.13 Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$)Cl(py) (13)



Appearance: Green powder

Molecular formula: $C_{23}H_{29}N_2TiCl$

Elemental analysis for $C_{23}H_{29}N_2TiCl$:

Found (calculated) % : C 62.2 (66.3); H 6.4 (7.0); N 6.6 (6.7)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

9.22	2 H, d	J = 4.8 Hz	*o*- py
7.00	2 H, d	J = 7.3 Hz	*m*- 2,6-$C_6H_3Me_2$
6.74	1 H, t	J = 7.3 Hz	*p*- 2,6-$C_6H_3Me_2$
6.69	1 H, m		*p*- py
6.38	2 H, m		*m*- py
2.54	6 H, s		N-2,6-C_6H_3*Me*$_2$
1.88	15 H, s		C_5*Me*$_5$

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

158.5	*i*- 2,6-$C_6H_3Me_2$
151.2	*o*- py
138.3	*p*- py
132.5	*o*- 2,6-$C_6H_3Me_2$
127.6	*m*- 2,6-$C_6H_3Me_2$
124.2	*m*- py
121.5	C_5Me_5
120.4	*p*- 2,6-$C_6H_3Me_2$
20.8	2,6-C_6H_3*Me*$_2$
11.9	C_5*Me*$_5$

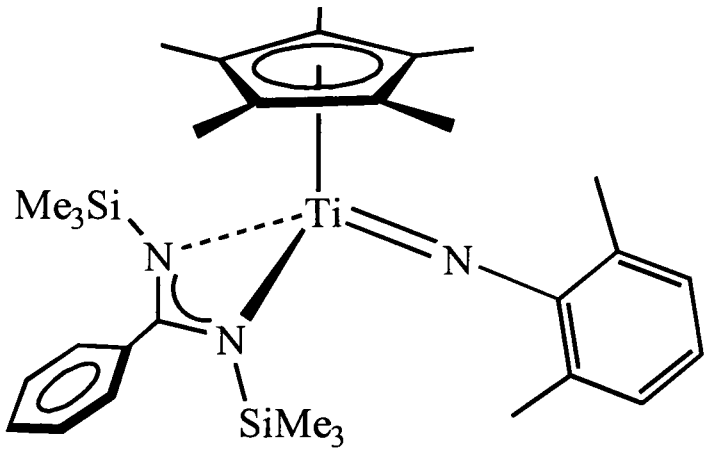
I.R. data (KBr plates, Nujol mull)

2955 (s), 2726 (w), 2477 (w), 2353 (w), 2318 (w), 2037 (w), 1920 (w), 1844 (w), 1732 (w), 1696 (w), 1682 (w), 1659 (w), 1634 (w), 1606 (m), 1586 (m), 1556 (w), 1504 (w), 1486 (m), 1448 (s), 1403 (m), 1312 (m), 1286 (s, br), 1215 (m), 1157 (m), 1096 (m), 1071 (m), 1045 (m), 1026 (w), 1016 (m), 978 (w), 957 (m), 915 (w), 886 (w), 874 (w), 805 (w), 794 (w), 757 (m), 744 (m), 724 (w), 693 (s), 642 (w), 583 (w), 568 (w), 507 (w), 450 (s), 421 (m) cm^{-1}

Mass Spec (E.I.)

m/z = 674 (pyridine-free dimer [Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$)Cl]$_2$)

8.14 Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){PhC($NSiMe_3$)$_2$} (14)



Appearance: Green powder

Molecular Formula: $C_{31}H_{47}N_3Si_2Ti$

Elemental analysis for $C_{31}H_{47}N_3Si_2Ti$:

Found (calculated) % : C 65.6 (65.8); H 8.6 (8.4); N 7.3 (7.4)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.17 - 7.13	3 H, m		*o*-, *p*- C_6H_5
7.03 - 7.00	4 H, m		*m*- C_6H_5,
			m- 2,6-$C_6H_3Me_2$
6.73	1 H, t	J = 7.4 Hz	*p*- 2,6-$C_6H_3Me_2$
2.36	6 H, s		2,6-C_6H_3*Me*$_2$
2.02	15 H, s		C_5*Me*$_5$
-0.08	18 H, s		Si*Me*$_3$

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

174.7	$C_6H_5CN_2$
158.5	*i*- 2,6-$C_6H_3Me_2$
138.9	*i*- $C_6H_5CN_2$
132.0	*o*- 2,6-$C_6H_3Me_2$
128.9	one CH from *o*-, *p*-Ph or *m*-$Me_2C_6H_3$
128.5	*m*- C_6H_5
128.0	one CH from *o*-, *p*-Ph or *m*-$Me_2C_6H_3$
127.4	one CH from *o*-, *p*-Ph or *m*-$Me_2C_6H_3$
121.5	C_5Me_5
119.2	*p*- $C_6H_3Me_2$
20.8	$C_6H_3Me_2$
12.5	C_5Me_5
3.3	$SiMe_3$

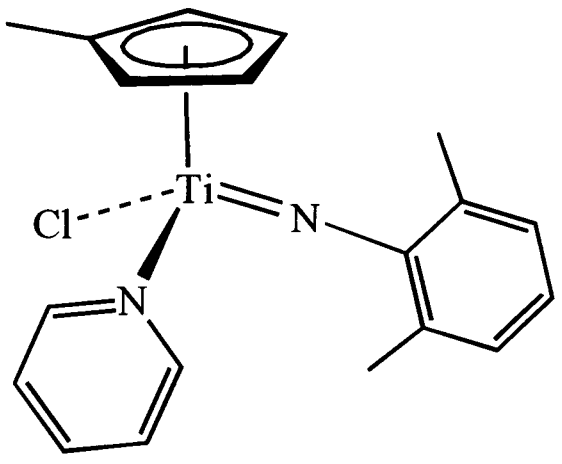
I.R. data (KBr discs, Nujol mull)

2726 (w), 1881 (w), 1651 (w), 1586 (w), 1307 (s), 1293 (s), 1248 (s), 1162 (w), 1093 (m), 1077 (w), 1031 (w), 1005 (m), 996 (m), 961 (w), 932 (w), 839 (s), 781 (m), 756 (s), 743 (s), 706 (m), 623 (w), 581 (w), 563 (w), 511 (m), 438 (m) cm^{-1}

Mass Spec. (E.I.)

m/z = 565 $[M]^+$

8.15 Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$)Cl(py) (15)



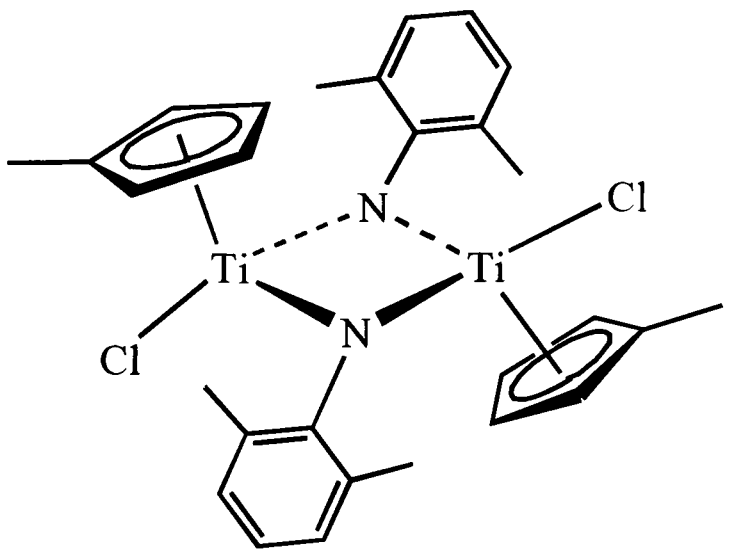
Appearance: Oily brown solid

Molecular formula: $C_{19}H_{21}N_2TiCl$

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

8.51	2 H, d	J = 4.8 Hz	*o*- py
6.96	2 H, d	J = 7.3 Hz	*m*- 2,6-$C_6H_3Me_2$
6.89 – 6.83	4 H, m		*m*-, *p*- py,
			p- 2,6-$C_6H_3Me_2$
6.24	2 H, s, br		$C_5H_2(\beta)H_2(\alpha)Me$
6.04	2 H, s, br		$C_5H_2(\beta)H_2(\alpha)Me$
2.56	6 H, s		2,6-$C_6H_3Me_2$
2.11	3 H, s		C_5H_4Me

8.16 $[Ti(\eta\text{-}C_5H_4Me)(N\text{-}2,6\text{-}C_6H_3Me_2)Cl]_2$ (16)



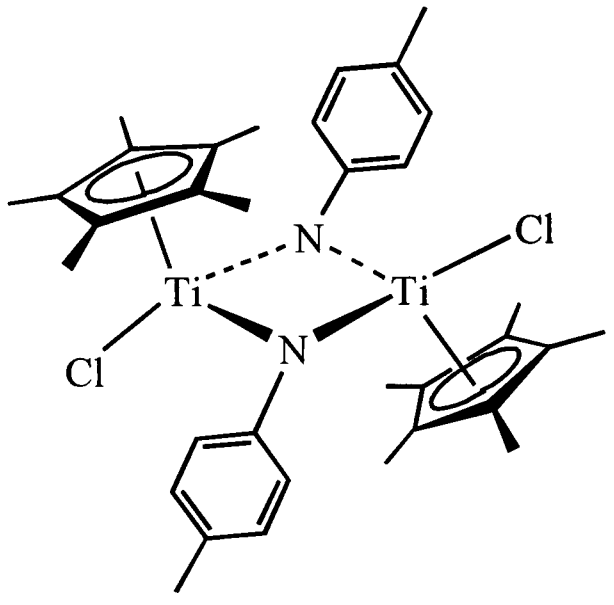
Appearance: Oily brown solid

Molecular formula: $C_{28}H_{32}N_2Ti_2$

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

6.35 – 6.44	10 H, m	*m*-, *p*- 2,6-$C_6H_3Me_2$, $C_5H_2(\beta)H_2(\alpha)Me$
5.61	4 H, s, br	$C_5H_2(\beta)H_2(\alpha)Me$
2.80	12 H, s	2,6-$C_6H_3Me_2$
1.67	6 H, s	$C_5H_2(\beta)H_2(\alpha)Me$

8.17 $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}N\text{-}4\text{-}C_6H_4Me)Cl]_2$ (17)



Appearance: Dark brown powder

Molecular formula: $C_{34}H_{44}Cl_2N_2Ti_2$

Elemental analysis for $C_{34}H_{44}Cl_2N_2Ti_2$:

Satisfactory elemental analysis was not obtained for this compound

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

6.86	4 H, d	J = 8.2 Hz	*m*- 4-C_6H_4Me
6.73	4 H, d	J = 8.2 Hz	*o*- 4-C_6H_4Me
2.05	6 H, s		4-C_6H_4*Me*
1.77	30 H, s		C_5*Me*$_5$

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

153.5	*i*- 4-C_6H_4Me
133.5	*p*- 4-C_6H_4Me
129.1	*m*- 4-C_6H_4Me
127.1	C_5Me_5
123.0	*o*- 4-C_6H_4Me
20.9	4-C_6H_4*Me*
11.7	C_5*Me*$_5$

I.R. data (KBr plates, Nujol mull)

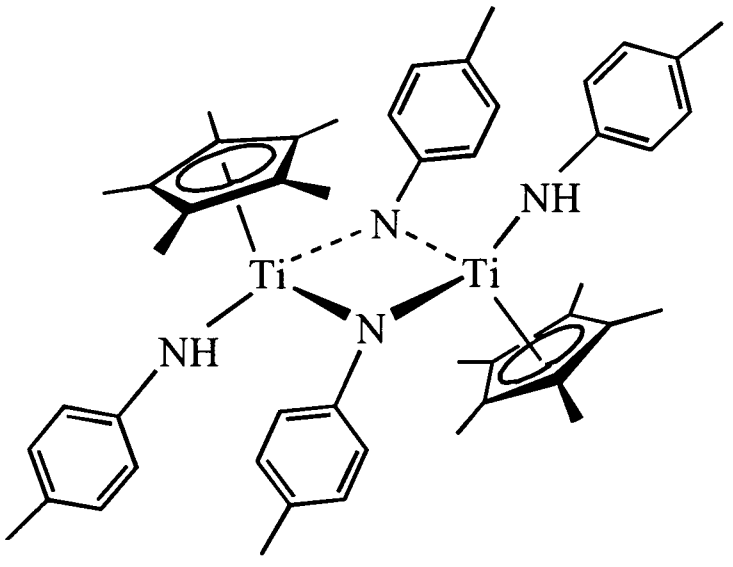
2955 (s), 2727 (w), 2284 (w), 1729 (w), 1603 (m), 1516 (w), 1494 (m), 1445 (m), 1261 (m), 1242 (w), 1220 (w), 1151 (w), 1104 (w), 1067 (w), 1042 (w), 973 (w), 825 (w), 806 (w), 760 (w), 723 (w), 699 (w), 647 (w), 636 (w), 580 (w), 520 (w), 470 (w) cm^{-1}

Mass Spec. (E.I.)

m/z = 647 $[M]^+$

m/z = 610 $[M\text{-}H\text{-}Cl]^+$

8.18 $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}N\text{-}4\text{-}C_6H_4Me)(NH\text{-}4\text{-}C_6H_4Me)]_2$ (18)



Appearance: Red powder

Molecular formula: $C_{48}H_{60}N_4Ti_2$

Elemental analysis for $C_{48}H_{60}N_4Ti_2$:

Found (calculated) % : C 72.8 (73.1); H 7.8 (7.7); N 6.5 (7.1)

^{1}H NMR data (500.0 MHz, 298 K, dichloromethane-d_2)

8.09	2 H, s		NH
7.07	4 H, d	J = 8.0 Hz	*m*- NH-4-C_6H_4Me
6.96	4 H, d	J = 8.0 Hz	*m*- N-4-C_6H_4Me
6.86	4 H, d	J = 8.0 Hz	*o*- NH-4-C_6H_4Me
6.38	4 H, d	J = 8.0 Hz	*o*- N-4-C_6H_4Me
2.30	6 H, s		NH-4-C_6H_4*Me*
2.25	6 H, s		N-4-C_6H_4*Me*
1.63	15 H, s		C_5*Me*$_5$

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, dichloromethane-d_2)

154.1	*i*- NH-4-C_6H_4Me
152.7	*i*- N-4-C_6H_4Me
131.3	*p*- N-4-C_6H_4Me
129.2	*m*- NH-4-C_6H_4Me
128.7	*m*- N-4-C_6H_4Me
126.6	*p*- NH-4-C_6H_4Me
122.7	C_5Me_5
122.5	*o*- N-4-C_6H_4Me
118.2	*o*- NH-4-C_6H_4Me
21.0	N-4-C_6H_4*Me*
20.8	NH-4-C_6H_4*Me*
11.7	C_5*Me*$_5$

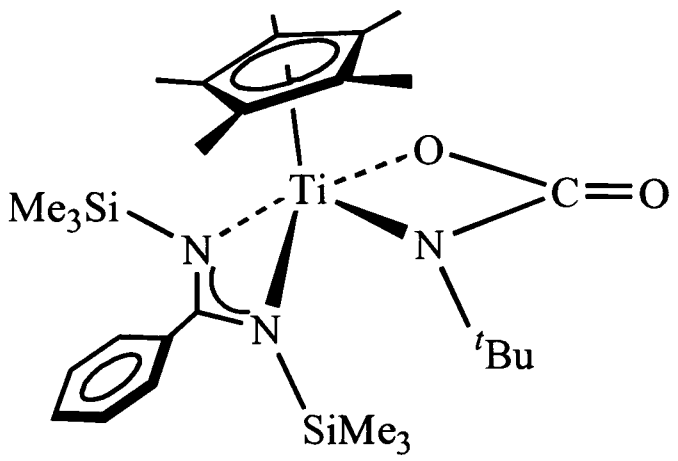
I.R. data (KBr plates, Nujol mull)

3303 (w), 2955 (s), 2726 (w), 1733 (w), 1606 (m), 1572 (w), 1504 (s), 1494 (s), 1352 (w), 1273 (s), 1250 (m), 1175 (w), 1106 (w), 1024 (w), 892 (w), 863 (w), 825 (m), 814 (m), 773 (w), 723 (w), 678 (w), 648 (w), 623 (w), 590 (m), 556 (w), 534 (m), 520 (m), 503 (w), 482 (w), 445 (m) cm^{-1}

Mass Spec. (F.I.)

m/z = 788 $[M]^+$

8.19 Ti(η-C_5Me_5)(N(^{t}Bu)C(O)O){PhC($NSiMe_3$)$_2$} (19)



Appearance: Light red powder

Molecular Formula: $C_{28}H_{47}N_3O_2Si_2Ti$

Elemental Analysis for $C_{28}H_{47}N_3O_2Si_2Ti$:

Found (calculated) % : C 59.9 (59.9); H 8.5 (8.4), 6.4 (7.5)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.00 – 7.03	1 H, m	*p*- C_6H_5
6.95 – 6.99	2 H, m	*o*- C_6H_5
6.84 – 6.91	2 H, m	*m*- C_6H_5
1.99	15 H, s	C_5*Me*$_5$
1.49	9 H, s	N^t*Bu*
0.03	9 H, s	Si*Me*$_3$ (nOe ^{t}Bu)
-0.10	9 H, s	Si*Me*$_3$

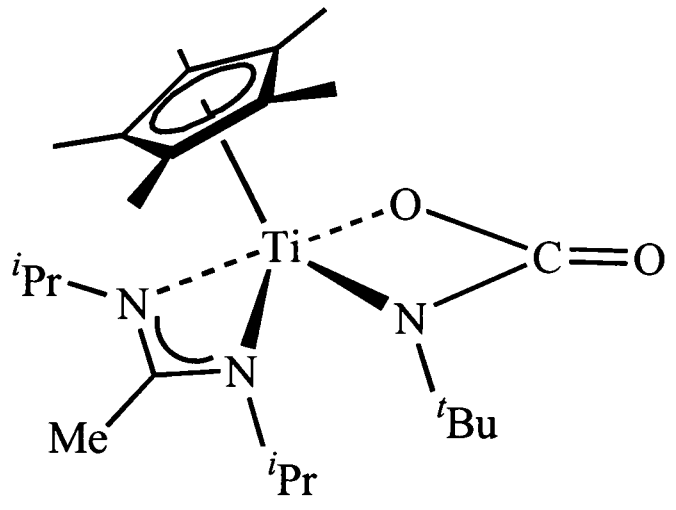
^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

180.5	O*C*(O)
159.4	$C_6H_5CN_2$
138.0	*i*- C_6H_5
129.6	C_5Me_5
129.2, 128.7	*o*- C_6H_5
128.5, 127.7	*m*- C_6H_5
127.4	*p*- C_6H_5
57.8	N*C*Me$_3$
31.5	NC*Me$_3$*
13.0	C_5*Me$_5$*
5.7	Si*Me$_3$*
2.4	Si*Me$_3$*

I.R. data (CsBr plates, Nujol mull)

2855 (s, br), 2726 (w), 2360 (w), 1854 (w), 1839 (w), 1807 (w), 1787 (w), 1766 (w), 1739 (w), 1726 (w), 1711 (w), 1660 (s), 1592 (m), 1549 (w), 1513 (w), 1250 (m, br), 1157 (w, br), 1065 (w), 1002 (w), 988 (m), 938 (m), 920 (w), 838 (s), 798 (w), 787 (w), 767 (m, br), 721 (s), 675 (m), 596 (w), 514 (m), 465 (m), 404 (w) cm^{-1}

8.20 Ti(η-C_5Me_5)(N(^{t}Bu)C(O)O){MeC(N^{i}Pr)$_2$} (20)



Appearance: Cherry red solid

Molecular Formula: $C_{23}H_{41}N_3O_2Ti$

Elemental Analysis for $C_{23}H_{41}N_3O_2Ti$:

Found (calculated) % : C 62.9 (62.9) H 9.3 (9.4) N 9.1 (9.6)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

3.73	1 H, apparent sept	J = 6.4 Hz Hz	NCH_bMe$_a$Me$_b$
3.47	1 H, apparent sept	J = 6.4 Hz	NCH_aMe$_a$Me$_b$
1.90	15 H, s		C$_5$*Me$_5$*
1.50	3 H, s		*Me*CN$_2$
1.39	9 H, s		C$_5$*Me$_5$*
1.15	3 H, d	J = 6.4 Hz	NCH$_b$Me$_a$*Me$_b$*
1.13	3 H, d	J = 6.4 Hz	NCH$_a$Me$_a$*Me$_b$*
1.05	3 H, d	J = 6.4 Hz	NCH$_b$*Me$_a$*Me$_b$
1.04	3 H, d	J = 6.4 Hz	NCH$_a$*Me$_a$*Me$_b$

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

172.4	O*C*(O)
158.8	Me*C*N_2
127.7	*C_5*Me_5
57.5	N*C*Me_3
50.2	N*C*$H_a$$Me_a$$Me_b$
48.3	N*C*$H_b$$Me_a$$Me_b$
30.7	NC*Me_3*
24.8	NCH_b*Me_a*Me_b
24.5	NC$H_b$$Me_a$*$Me_b$*
23.7	NCH_a*Me_a*Me_b
22.9	NC$H_a$$Me_a$*$Me_b$*
16.7	*Me*CN_2
12.5	C_5*Me_5*

I.R. data (KBr plates, Nujol mull)

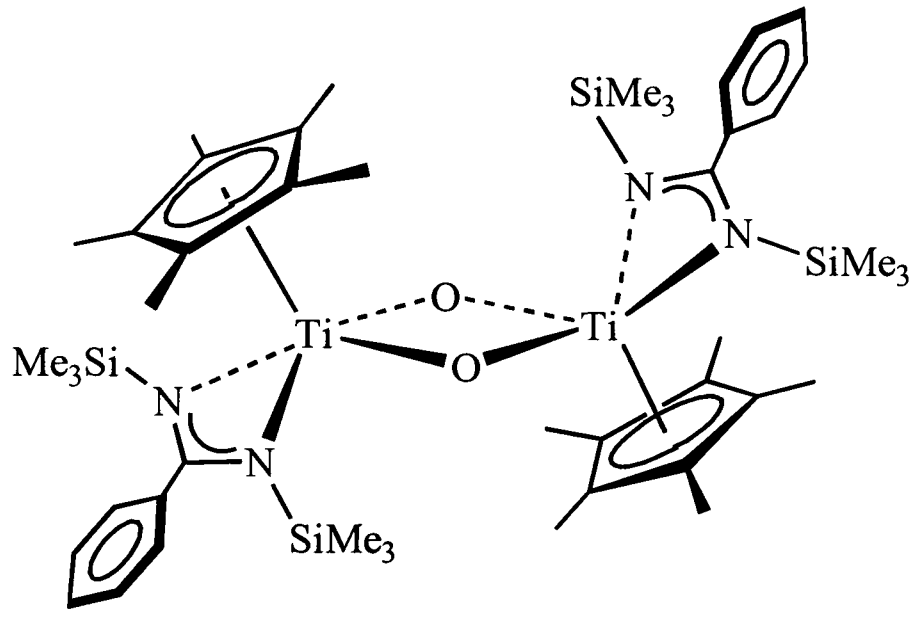
2723 (w), 1662 (s), 1646 (s, br), 1589 (m), 1494 (m), 1355 (s), 1313 (w), 1243 (m), 1208 (m), 1174 (w), 1127 (m), 1066 (w), 1024 (w, br), 940 (m), 923 (w), 826 (w), 797 (m), 782 (w), 722 (m ,br), 681 (w), 656 (w, br), 597 (w), 578 (w), 527 (w, br), 466 (s), 431 (w), 410 (m) cm^{-1}

Mass Spec. (E.I.)

m/z = 439 $[M]^+$

(isotope ratio consistent with that predicted, plus impurity at 441 and above).

8.21 $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$ (21)



Appearance: Yellow powder

Molecular formula: $C_{46}H_{76}N_4O_2Si_4Ti_2$

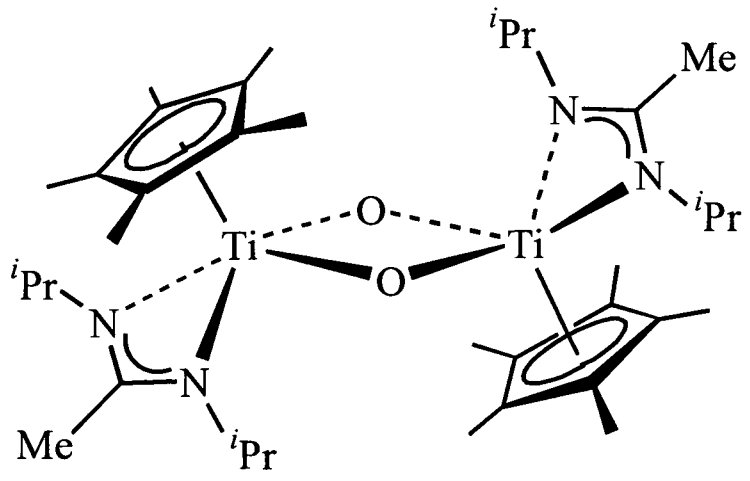
Elemental analysis for $C_{46}H_{76}N_4O_2Si_4Ti_2$:

Found (calculated) % : C 60.2 (59.7); H 8.6 (8.3); N 5.5 (6.1)

I.R. data (KBr plates, Nujol mull)

2955 (s), 2720 (w), 2359 (w), 1952 (w), 1816 (w), 1771 (w), 1682 (w), 1651 (w), 1615 (w), 1575 (w), 1456 (s), 1258 (m), 1244 (m), 1162 (w), 1074 (w), 1020 (w), 1002 (m), 985 (m), 908 (m), 837 (m), 781 (m), 762 (m), 722 (m), 680 (w), 639 (m), 628 (m), 609 (m), 597 (m), 491 (m), 430 (m) cm^{-1}

8.22 *trans* – $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ (22)



Appearance: Yellow powder

Molecular formula: $C_{36}H_{64}N_4O_2Ti_2$

Elemental analysis for $C_{36}H_{64}N_4O_2Ti_2$:

Found (calculated) % : C 63.5 (63.5); H 9.3 (9.5); N 5.3 (8.2)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

3.46	2 H, apparent sept	J = 6.4 Hz	NC*H*MeMe
2.01	15 H, s		C_5Me_5
1.61	3 H, s		*Me*CN_2
1.40	6 H, d	J = 6.4 Hz	NCH*Me*Me
1.16	6 H, d	J = 6.4 Hz	NCHMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

170.0	Me*C*N_2
121.9	C_5Me_5
48.7	N*C*HMeMe
26.4	NCH*Me*Me
24.4	NCHMe*Me*
14.2	C_5Me_5
13.2	*Me*CN_2

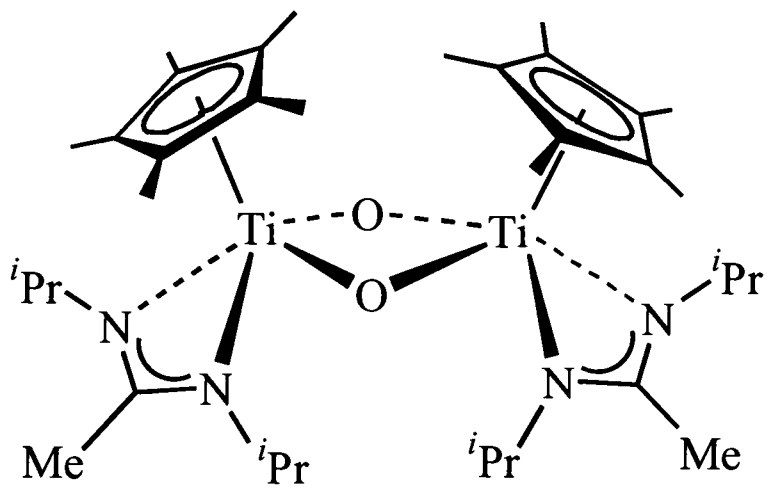
I.R. data (NaCl plates, Nujol mull)

2360 (w), 2342 (w), 1652 (w), 1495 (m), 1325 (m), 1306 (m), 1261 (m), 1201 (m), 1172 (w), 1094 (m, br), 1012 (m), 809 (s), 722 (w), 637 (m), 611 (w), 557 (w), 442 (w), 423 (w) cm^{-1}

Mass Spec. (E.I.)

m/z = 340 $[½M]^+$

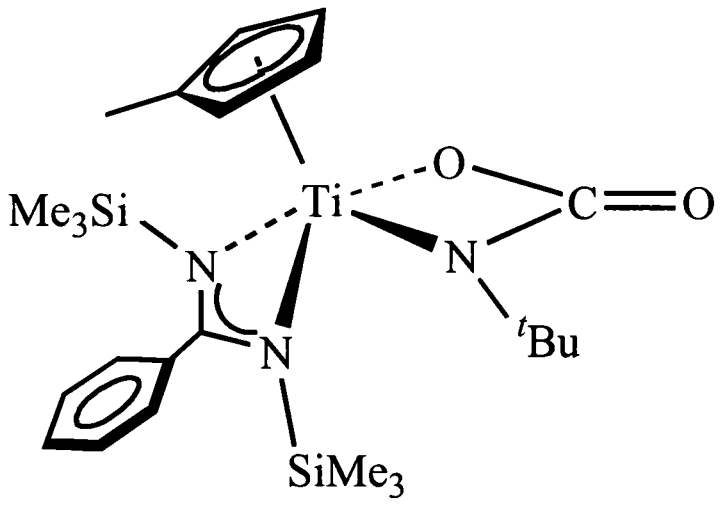
8.23 *cis* – [Ti(η-C_5Me_5)(μ-O){MeC(N^{i}Pr)$_2$}]$_2$ (22a)



^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

3.30	2 H, apparent sept	J = 6.5 Hz	NC*H*MeMe
2.07	15 H, s		C_5*Me*$_5$
1.57	3 H, s		*Me*CN_2
1.28	6 H, d	J = 6.5 Hz	NCH*Me*Me
1.10	6 H, d	J = 6.5 Hz	NCHMe*Me*

8.24 Ti(η-C_5H_4Me){N(^{t}Bu)C(O)O}{PhC($NSiMe_3$)$_2$} (23)



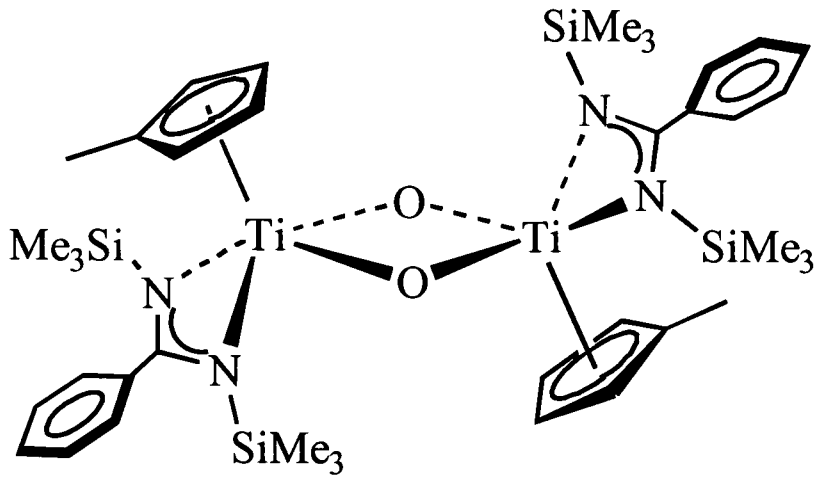
Appearance: Cherry-red solution

Molecular Formula: $C_{24}H_{39}N_3O_2Si_2Ti$

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

6.95	1 H, d	J = 7.3 Hz	C*H*(β_1)CH(β_2)C_2H_2(α)CMe
6.92	3 H, m		*o*-, *p*-C_6H_5
6.80	1 H, d	J = 7.3 Hz	CH(β_1)C*H*(β_2)C_2H_2(α)CMe
6.29	2 H, dd	J = 2.7 Hz	*m*-C_6H_5
6.15	1 H, d	J = 2.4 Hz	C_2H_2(β)C*H*(α_1)CH(α_2)CMe
6.01	1 H, d	J = 2.4 Hz	C_2H_2(β)CH(α_1)C*H*(α_2)CMe
2.19	3 H, s		C_5H_4*Me*
1.42	9 H, s		N^t*Bu*
-0.04	9 H, s		Si*Me*$_3$
-0.08	9 H, s		Si*Me*$_3$

8.25 *trans* – $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$ (24)



Appearance: Yellow powder

Molecular Formula: $C_{38}H_{60}N_4O_2Si_4Ti_2$

Elemental analysis for $C_{38}H_{60}N_4O_2Si_4Ti_2$:

Found (calculated) %: C 56.0 (56.1), H 7.3 (7.4), N 6.7 (6.9)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.31	4 H, m		*m*–C_6H_5
7.04	6 H, m		*o*-, *p*-C_6H_5
6.54	4 H, virtual t	J = 2.6 Hz	C_5H_2(*β*)H_2(α)Me
6.22	4 H, virtual t	J = 2.6 Hz	C_5H_2(β)H_2(*α*)Me
2.35	6 H, s		C_5H_4*Me*
0.12	36 H, s		Si*Me*$_3$

^{13}C-{^{1}H} NMR data (75.5 MHz, 298 K, benzene-d_6)

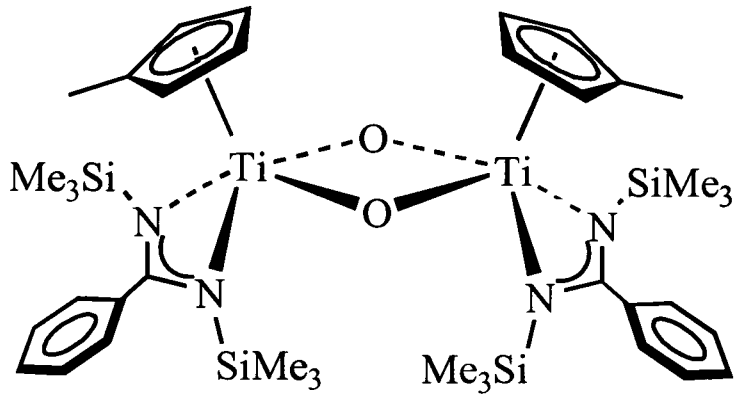
177.9	$C_6H_5CN_2$
140.9	*i*- $C_6H_5CN_2$
128.5	*o*- $C_6H_5CN_2$
126.9	*m*- $C_6H_5CN_2$
126.5	*p*- $C_6H_5CN_2$
114.0	$C_2(\beta)C_2(\alpha)CMe$
112.5	$C_2(\beta)C_2(\alpha)CMe$
16.1	$C_2(\beta)C_2(\alpha)CMe$
2.5	$SiMe_3$

Resonance from $C_2(\beta)C_2(\alpha)CMe$ not observed

IR data (KBr plates, Nujol mull)

2726 (w), 2671 (w), 2094 (w), 1733 (w), 1576 (w), 1500 (m), 1305 (m, br), 1260 (m), 1246 (m), 1175 (w), 1074 (w), 1055 (w), 1038 (w), 1002 (m), 990 (m), 938 (w), 918 (w), 890 (w), 840 (s), 795 (m), 784 (w), 760 (m), 740 (w), 723 (s), 700 (w), 677 (m), 634 (w), 616 (w), 591 (m, br), 503 (s), 433 (w) cm^{-1}

8.26 *cis* – $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$ (24a)



Appearance: Yellow powder

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.46	4 H, d	J = 7.8 Hz	*m*-C_6H_5
7.04	6 H, m		*o*-, *p*-C_6H_5
6.46	4 H, virtual t	J = 2.6 Hz	$C_5H_2(\beta)H_2(\alpha)Me$
6.12	4 H, virtual t	J = 2.6 Hz	$C_5H_2(\beta)H_2(\alpha)Me$
2.30	6 H, s		C_5H_4Me
0.08	36 H, s		$SiMe_3$

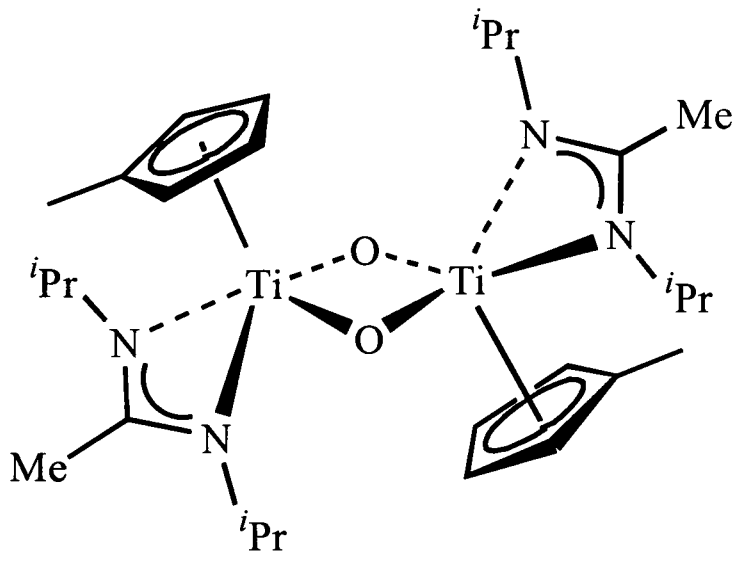
^{13}C-{^{1}H} NMR data (75.5 MHz, 298 K, benzene-d_6)

177.1	$C_6H_5CN_2$
141.4	*i*- $C_6H_5CN_2$
128.5	*o*- $C_6H_5CN_2$
126.7	*m*- $C_6H_5CN_2$

126.4	*p*- $C_6H_5CN_2$
113.7	$C_2(\beta)C_2(\alpha)CMe$
112.3	$C_2(\beta)C_2(\alpha)CMe$
15.3	$C_2(\beta)C_2(\alpha)CMe$
2.2	$SiMe_3$

Resonance from $C_2(\beta)C_2(\alpha)CMe$ not observed

8.27 *trans* – $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ (25)



Appearance: Yellow powder

Molecular Formula: $C_{28}H_{48}N_4O_2Ti_2$

Elemental analysis for $C_{28}H_{48}N_4O_2Ti_2$:

Found (calculated) %: C 59.2 (59.2), H 8.4 (8.5), N 9.9 (9.9)

^{1}H NMR data (300.0 MHz, 298 K, benzene-d_6)

6.33	4 H, virtual t	J = 2.7 Hz	$C_5H_2(\beta)H_2(\alpha)Me$
6.09	4 H, virtual t	J = 2.7 Hz	$C_5H_2(\beta)H_2(\alpha)Me$
3.47	4 H, apparent sept	J = 6.4 Hz	NC*H*MeMe
2.18	6 H, s		$C_5H_2(\beta)H_2(\alpha)Me$
1.52	6 H, s		$MeCN_2$
1.27	12 H, d	J = 6.4 Hz	NCH*Me*Me
1.13	12 H, d	J = 6.4 Hz	NCHMe*Me*

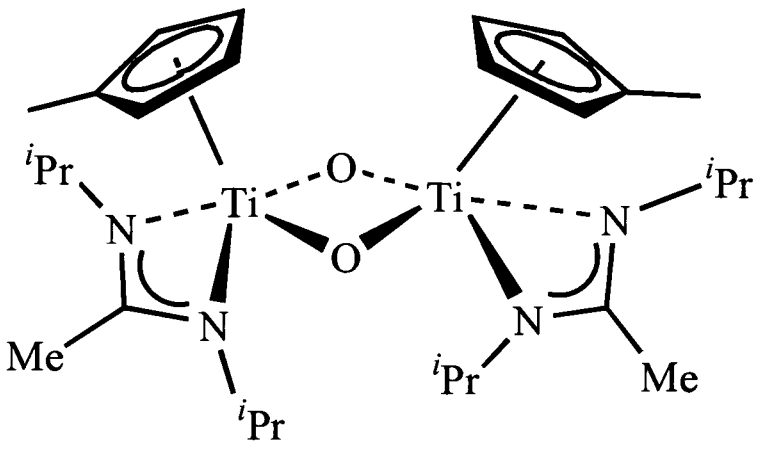
^{13}C-{^{1}H} NMR data (75.5 MHz, 298 K, benzene-d_6)

167.9	Me*C*N_2
126.2	$C_2(\beta)C_2(\alpha)$*C*Me
112.7	$C_2(\beta)$*$C_2(\alpha)$*CMe
112.1	*$C_2(\beta)$*$C_2(\alpha)$CMe
48.4	N*C*HMeMe
25.2	NCH*Me*Me
24.9	NCHMe*Me*
15.8	$C_2(\beta)C_2(\alpha)$C*Me*
10.5	*Me*CN_2

I.R. data (KBr plates, Nujol mull)

2726 (w), 1652 (w), 1338 (m), 1310 (m), 1216 (m), 1173 (w), 1122 (w), 1037 (w), 847 (w), 793 (m), 723 (m), 679 (w), 590 (w), 445 (w), 421 (w) cm^{-1}

8.28 *cis* – [Ti(η-C_5H_4Me)(μ-O){$MeC(N^iPr)_2$}]$_2$ (25a)



Appearance: Yellow powder

Molecular Formula: $C_{28}H_{48}N_4O_2Ti_2$

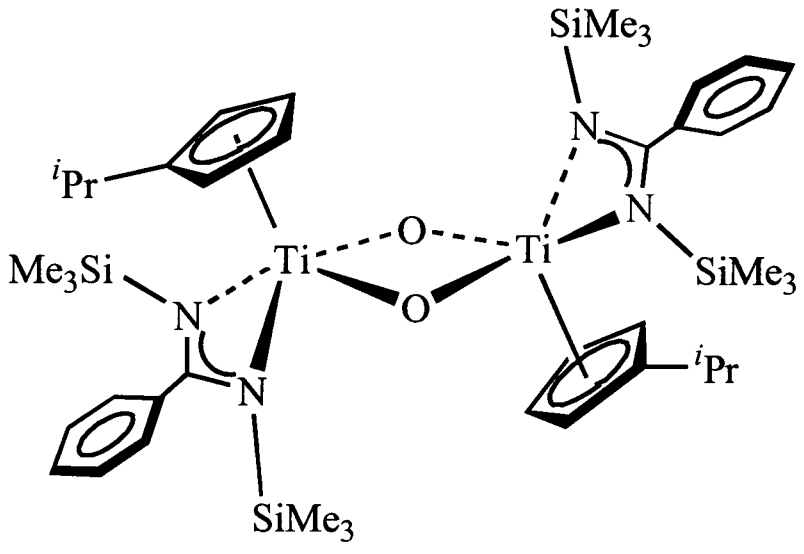
^{1}H NMR data (300.0 MHz, 298 K, benzene-d_6)

6.44	4 H, virtual t	J = 2.7 Hz, 2.4 Hz	$C_5H_2(\beta)H_2(\alpha)Me$
6.08	4 H, virtual t	J = 2.7 Hz, 2.4 Hz	$C_5H_2(\beta)H_2(\alpha)Me$
3.36	4 H, apparent sept	J = 6.4 Hz	NC*H*MeMe
2.15	6 H, s		C_5H_4*Me*
1.45	6 H, s		*Me*CN_2
1.17	12 H, d	J = 6.3 Hz	NCH*Me*Me
1.13	12 H, d	J = 6.3 Hz	NCHMe*Me*

^{13}C-{^{1}H} NMR data (75.5 MHz, 298 K, benzene-d_6)

167.8	Me*C*N_2
126.3	$C_2(\beta)C_2(\alpha)$*C*Me
113.1	$C_2(\beta)$*$C_2(\alpha)$*CMe
111.5	*$C_2(\beta)$*$C_2(\alpha)$CMe
48.1	N*C*HMeMe
25.0	NCH*Me*Me
23.9	NCHMe*Me*
15.1	$C_2(\beta)C_2(\alpha)$C*Me*
10.0	*Me*CN_2

8.29 *trans* – [Ti(η-$C_5H_4{}^iPr$)(μ-O){$PhC(NSiMe_3)_2$}]$_2$ (26)



Appearance: Yellow powder

Molecular Formula: $C_{42}H_{68}N_4O_2Si_4Ti_2$

Elemental analysis for $C_{42}H_{68}N_4O_2Si_4Ti_2$:

Satisfactory elemental analysis was not obtained for this compound

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.2	4 H, m		*m*–C_6H_5
7.05	6 H, m		*o*-, *p*-C_6H_5
6.66	4 H, virtual t	J = 2.7 Hz	C_5H_2(*β*)H_2(α)C^{i}Pr
6.33	4 H, virtual t	J = 2.7 Hz	C_5H_2(β)H_2(*α*)C^{i}Pr
3.20	2 H, sept	J = 6.8 Hz	C*H*Me_2
1.33	12 H, d	J = 6.8 Hz	CH*Me*$_2$
0.12	36 H, s		Si*Me*$_3$

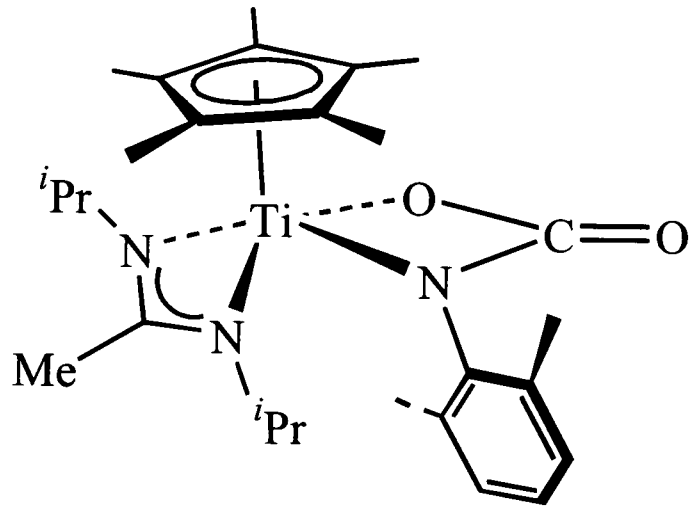
^{13}C-{^{1}H} NMR data (75.5 MHz, 298 K, benzene-d_6)

178.2	$C_6H_5CN_2$
140.7	*i*- $C_6H_5CN_2$
139.1	*i*- $C_5H_4{}^{i}Pr$
128.6	*o*- $C_6H_5CN_2$
128.3	*m*- $C_6H_5CN_2$
126.8	*p*- $C_6H_5CN_2$
112.0	$C_2(\beta)C_2(\alpha)C^{i}Pr$
111.8	$C_2(\beta)C_2(\alpha)C^{i}Pr$
29.7	CH*Me*Me
28.6	CHMe*Me*
23.7	*C*HMe$_2$
2.6	Si*Me*$_3$

I.R. data (NaCl plates, Nujol mull)

2955 (s), 2724 (w), 1946 (w), 1685 (w, br), 1592 (m), 1560 (m), 1524 (m), 1317 (m), 1246 (s), 1175 (m), 1153 (m), 1074 (m), 1031 (m), 1003 (s), 990 (s), 914 (s), 840 (s), 801 (s), 780 (m), 759 (s), 724 (s), 699 (m), 677 (m), 604 (w), 505 (m), 442 (w) cm^{-1}

8.30 Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(O)O}{MeC(N^{i}Pr)$_2$} (27)



Appearance: Red powder

Molecular Formula: $C_{27}H_{41}N_3O_2Ti$

Elemental analysis for $C_{27}H_{41}N_3O_2Ti$:

Found (calculated) % : C 66.1 (66.5); H 9.1 (8.5); N 8.2 (8.6)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

6.95 - 7.00	3 H, m		*m*-, *p*- 2,6-$C_6H_3Me_2$
3.23	1 H, m		NCH_aMeMe
3.05	1 H, m		NCH_bMeMe
2.24	3 H, s		2,6-C_6H_3*Me*Me
1.97	3 H, s		2,6-C_6H_3Me*Me*
1.95	15 H, s		C_5*Me*$_5$
1.41	3 H, s		*Me*CN_2
1.06	3 H, d	J = 6.6 Hz	NCH$_a$*Me*$_a$Me
1.00	3 H, d	J = 6.6 Hz	NCH$_a$Me*Me*$_b$
0.79	3 H, d	J = 6.4 Hz	NCH$_b$*Me*$_a$Me
0.52	3 H, d	J = 6.4 Hz	NCH$_b$Me*Me*$_b$

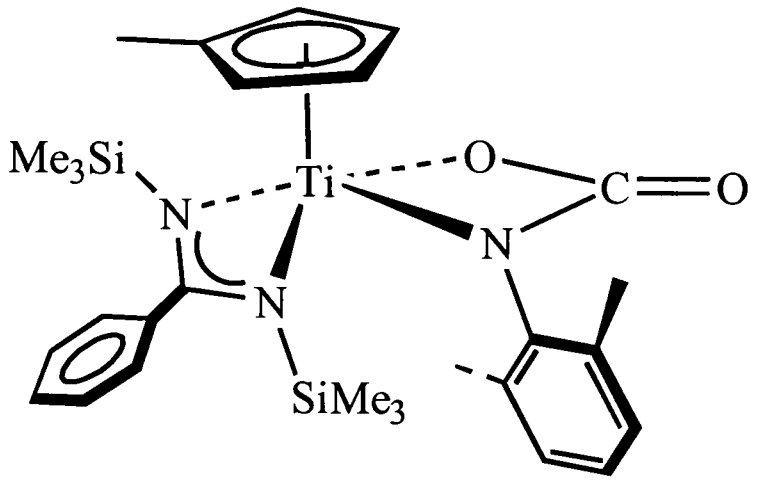
^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

168.5	O*C*O
159.2	Me*C*N_2
147.1	*i*- $C_6H_3Me_2$
134.2	*o*- $C_6H_3Me_2$
133.6	*m*- $C_6H_3Me_2$
129.4	*p*- $C_6H_3Me_2$
124.7	C_5Me_5
50.5	N*C*H_aMeMe
49.3	N*C*H_bMeMe
25.7	NCH$_b$*Me*$_a$Me
24.6	NCH$_a$Me*Me*$_b$
24.2	NCH$_a$*Me*$_a$Me
24.0	NCH$_b$Me*Me*$_b$
19.7	2,6-C_6H_3*Me*Me
19.2	2,6-C_6H_3Me*Me*
13.6	*Me*CN_2
13.0	C_5*Me*$_5$

I.R. data (KBr plates, Nujol mull)

2955 (s), 2726 (w), 1669 (s, br), 1577 (w), 1405 (w), 1328 (w), 1309 (m), 1282 (m), 1247 (m), 1207 (m), 1172 (s, br), 1116 (w), 1002 (w), 910 (m), 821 (m), 790 (m), 762 (m), 723 (m, br), 687 (w), 631 (w), 587 (w), 549 (w), 467 (m), 443 (m) cm^{-1}

8.31 Ti(η-C_5H_4Me){N(-2,6-$C_6H_3Me_2$)C(O)O}{PhC(NSiMe)$_2$} (28)



Appearance: Brown powder

Molecular formula: $C_{28}H_{39}N_3O_2Si_2Ti$

Elemental analysis for $C_{28}H_{39}N_3O_2Si_2Ti$:

Found (calculated) % : C 60.7 (60.7); H 7.1 (7.1); N 7.0 (7.6)

^{1}H NMR data (500.0 MHz, 223 K, dichloromethane-d$_2$)

7.40 – 7.46	3 H, m		*m-*, *p-* C_6H_5
7.20	1 H, d	J = 6.6 Hz	*o-* C_6H_5 (α)
7.14	1 H, d	J = 5.4 Hz	*o-* C_6H_5 (β)
6.97	2 H, d	J = 7.6 Hz	*m-* N-2,6-$C_6H_3Me_2$
6.92	1 H, t	J = 6.6 Hz	*p-* N-2,6-$C_6H_3Me_2$
6.86	1 H, s		C*H*(β_1)CH(β_2)C_2H_2(α)CMe
6.63	1 H, s		CH(β_1)C*H*(β_2)C_2H_2(α)CMe
6.53	1 H, s		C_2H_2(β)C*H*(α_1)CH(α_2)CMe

6.20	1 H, s	$C_2H_2(\beta)CH(\alpha_1)CH(\alpha_2)CMe$
2.46	3 H, s	C_5H_4Me
2.13	3 H, s	N-2,6-C_6H_3MeMe (a)
2.04	3 H, s	N-2,6-C_6H_3MeMe (b)
-0.22	9 H, s	SiMe_3
-0.48	9 H, s	SiMe_3

^{13}C-{^{1}H} NMR data (125.7 MHz, 223 K, dichloromethane-d_2)

173.2	O*C*O
159.1	$C_6H_5CN_2$
144.6	*i*- 2,6-$C_6H_3Me_2$
135.3	*i*- C_6H_5
134.3	*o*- 2,6-$C_6H_3Me_2$ (a)
133.5	*o*- 2,6-$C_6H_3Me_2$ (b)
132.8	C_5Me_5
129.5	*m*- / *p*- C_6H_5
128.4	*p*- / *m*- C_6H_5
127.5	*m*- 2,6-$C_6H_3Me_2$
126.7	*o*- C_6H_5 (β)
125.8	*o*- C_6H_5 (α)
125.0	*p*- 2,6-$C_6H_3Me_2$
121.9	$C_2H_2(\beta)CH(\alpha_1)CH(\alpha_2)CMe$
120.5	$CH(\beta_1)CH(\beta_2)C_2H_2(\alpha)CMe$
116.8	$CH(\beta_1)CH(\beta_2)C_2H_2(\alpha)CMe$

116.3	$C_2H_2(\beta)CH(\alpha_1)CH(\alpha_2)CMe$
19.0	2,6-C_6H_3*Me*Me
18.5	2,6-C_6H_3Me*Me*
15.6	C_5H_4*Me*
0.9	Si*Me*$_3$ (× 2)

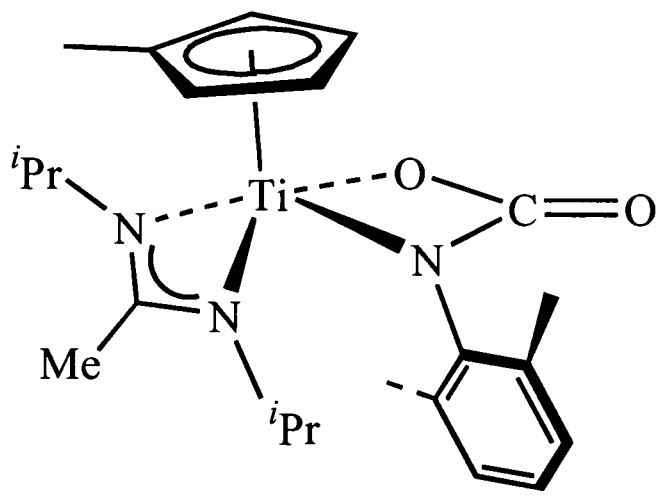
i- C_5H_4Me resonance not observed

I.R. data (KBr plates, Nujol mull)

2954 (s), 2725 (w), 2670 (w), 2361 (w), 2209 (w), 1667 (s), 1610 (m), 1590 (m), 1571 (m), 1496 (m), 1289 (s), 1246 (s), 1185 (w), 1165 (m), 1097 (w), 1067 (w), 1034 (m), 1004 (s), 994 (m), 927 (m), 914 (m), 838 (s), 785 (m), 763 (s), 723 (s), 687 (s), 614 (w), 587 (w), 518 (m), 461 (m), 444 (m) cm^{-1}

8.32 Ti(η-C_5H_4Me){N(-2,6-$C_6H_3Me_2$)C(O)O}{$MeC(N^iPr)_2$}

(29)



Appearance: Green powder

Molecular Formula: $C_{23}H_{33}N_3O_2Ti$

Elemental analysis for $C_{23}H_{33}N_3O_2Ti$:

Satisfactory elemental analysis was not obtained for this compound

^{1}H NMR data (500.0 MHz, 213 K, dichloromethane-d_2)

6.93	1 H, t	J = 4.7 Hz	*p*- 2,6-$C_6H_3Me_2$
6.86	2 H, d	J = 4.7 Hz	*m*- 2,6-$C_6H_3Me_2$
6.80	1 H, m		C*H*(β_1)CH(β_2)C_2H_2(α)CMe
6.49	1 H, m		CH(β_1)C*H*(β_2)C_2H_2(α)CMe
6.35	1 H, m		C_2H_2(β)C*H*(α_1)CH(α_2)CMe
6.23	1H, m		C_2H_2(β)CH(α_1)C*H*(α_2)CMe
3.50	2 H, m		NC*H*MeMe
2.43	3 H, s		C_5H_4*Me*

2.07	3 H, s		2,6-C_6H_3*Me*Me
1.88	3 H, s		*Me*CN_2
1.75	3 H, s		2,6-C_6H_3Me*Me*
1.11	3 H, d	J = 6.7 Hz	NCH_a*Me*Me
1.09	3 H, d	J = 6.7 Hz	NCH_b*Me*Me
0.95	3 H, d	J = 6.7 Hz	NCH_aMe*Me*
0.23	3 H, d	J = 6.7 Hz	NCH_bMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 213 K, dichloromethane-d_2)

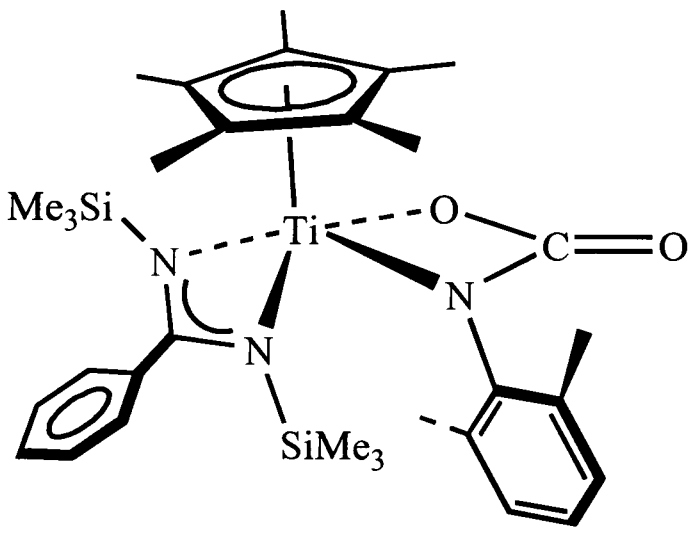
166.4	O*C*O
159.2	Me*C*N_2
144.8	*i*- 2,6-$C_6H_3Me_2$
135.7	*o*- 2,6-$C_6H_3Me_2$
133.5	*o*- 2,6-$C_6H_3Me_2$
132.5	*i*- C_5H_4Me
128.1	*m*- 2,6-$C_6H_3Me_2$
127.2	*p*- 2,6-$C_6H_3Me_2$
124.5	*m*- 2,6-$C_6H_3Me_2$
119.8	$C_2H_2(\beta)CH(\alpha_2)CMe$
117.7	$CH(\beta_1)CH(\alpha)C_2H_2(\alpha)CMe$
117.3	$CH(\beta_2)CH(\beta_2)C_2H_2(\alpha)CMe$
115.5	$C_2H_2(\beta)CH(\alpha_1)CH(\alpha_2)CMe$
50.1	N*C*HMeMe
49.4	N*C*HMeMe

24.2	$NCH_a\mathit{Me}Me$
24.0	$NCH_b\mathit{Me}Me$
23.7	$NCH_aMe\mathit{Me}$
22.9	$NCH_bMe\mathit{Me}$
19.0	2,6-$C_6H_3\mathit{Me}Me$
18.1	2,6-$C_6H_3Me\mathit{Me}$
15.3	$C_5H_4\mathit{Me}$
11.0	$\mathit{Me}CN_2$

I.R. data (KBr plates, Nujol mull)

2955 (s), 2726 (w), 2669 (w), 1733 (w), 1670 (s, br), 1615 (w), 1577 (w), 1499 (m), 1339 (m), 1309 (m), 1294 (m), 1261 (w), 1248 (w), 1218 (m), 1173 (w), 1138 (w), 1120 (w), 1096 (w), 1073 (w), 1020 (w), 1003 (w), 926 (w), 911 (w), 829 (m), 819 (m), 805 (m), 791 (m), 779 (w), 767 (w), 723 (m), 688 (w), 69 (w), 628 (w), 617 (w), 586 (w), 552 (w), 469 (w), 441 (w), 417 (w) cm^{-1}

8.33 Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(O)O}{PhC($NSiMe_3$)$_2$} (30)



Appearance: Brown powder

Molecular formula: $C_{32}H_{47}N_3O_2Si_2Ti$

Elemental analysis for $C_{32}H_{47}N_3O_2Si_2Ti$:

Satisfactory elemental analysis was not obtained for this compound

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.25	1 H, d	J = 7.6 Hz	*m*- 2,6-$C_6H_3Me_2$
7.08	1 H, d	J = 7.6 Hz	*m*- 2,6-$C_6H_3Me_2$
7.02	1 H, t	J = 7.6 Hz	*p*-2,6-$C_6H_3Me_2$
7.02 – 6.94	5 H, m		C_6H_5
2.28	3 H, s		2,6-C_6H_3*Me*Me (a)
2.26	3 H, s		2,6-C_6H_3Me*Me* (b)
1.99	15 H, s		C_5Me_5
-0.11	9 H, s		SiMe_3

-0.36	9 H, s	Si*Me*$_3$

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d$_6$)

177.3	O*C*O
158.8	Ph*C*N$_2$
147.1	*i*- 2,6-C$_6$H$_3$Me$_2$
137.2	*i*- C$_6$H$_5$
134.7	*o*- 2,6-C$_6$H$_3$Me$_2$ (a)
133.5	*o*- 2,6-C$_6$H$_3$Me$_2$ (b)
130.1	*C*$_5$Me$_5$
129.6	*o*- C$_6$H$_5$
128.2	*m*- C$_6$H$_5$
128.0	*p*- 2,6-C$_6$H$_3$Me$_2$
127.9	*m*- 2,6-C$_6$H$_3$Me$_2$ (a)
127.3	*m*- 2,6-C$_6$H$_3$Me$_2$ (b)
125.0	*p*- C$_6$H$_5$
20.7	2,6-C$_6$H$_3$*Me*Me
19.6	2,6-C$_6$H$_3$Me*Me*
13.3	C$_5$*Me*$_5$
3.4	Si*Me*$_3$
3.0	Si*Me*$_3$

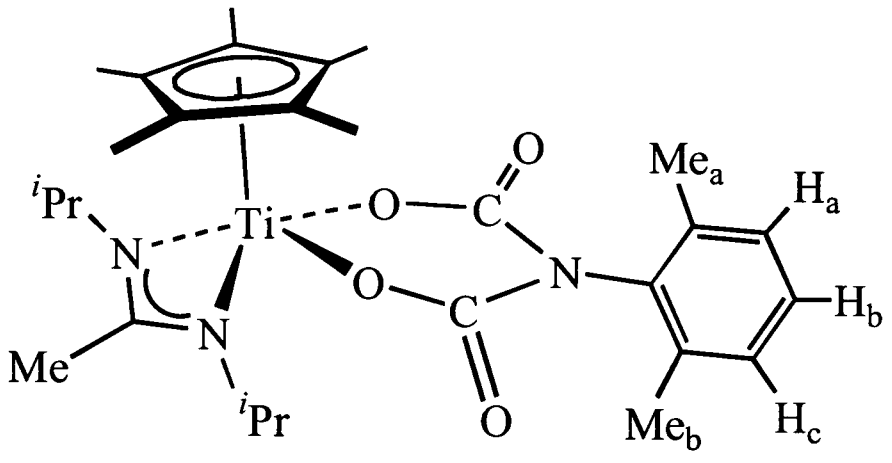
I.R. data (KBr plates, Nujol mull)

2727 (w), 2669 (w), 2208 (w), 1671 (s), 1634 (m), 1608 (m), 1577 (m), 1277 (s), 1260 (s), 1248 (s), 1171 (s), 1158 (m), 1098 (m), 1076 (m), 1004 (s), 991 (s), 913 (s), 841 (s, br), 808 (s), 788 (s), 760 (s), 748 (s), 725 (s), 687 (m), 640 (w), 627 (w), 590 (w), 557 (w), 512 (w), 469 (w), 441 (w) cm^{-1}

Mass Spec. (E.I.)

m/z = 609 $[M]^+$

8.34 Ti(η-C_5Me_5){OC(O)N(-2,6-$C_6H_3Me_2$)C(O)O}{MeC(N^{i}Pr)$_2$} (31)



Appearance: Green powder

Molecular Formula: $C_{28}H_{41}N_3O_4Ti$

Elemental analysis for $C_{28}H_{41}N_3O_4Ti$:

Found (calculated) % : C 63.3 (63.3); H 7.2 (7.8); N 8.1 (7.9)

^{1}H NMR data (300.0 MHz, 298 K, benzene-d_6)

7.12	1 H, d	J = 8.0 Hz	H_a
7.09	1 H, t	J = 8.0 Hz	H_b
7.04	1 H, d	J = 8.0 Hz	H_c
3.51	2 H, apparent sept		NC*H*MeMe
2.55	3 H, s		Me_a
2.20	3 H, s		Me_b
1.97	15 H, s		C_5Me_5

1.42	3 H, s		*Me*CN_2
1.12	6 H, d	J = 7.0 Hz	NCH*Me*Me
1.07	6 H, d	J = 7.0 Hz	NCHMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

169.4	Me*C*N_2
153.3	{O(*C*O)}$_2$N
139.6	*i*- N-2,6-$C_6H_3Me_2$
136.3	*o*- N-2,6-$C_6H_3Me_2$ (adj. Me_a)
135.9	*o*- N-2,6-$C_6H_3Me_2$ (adj. Me_b)
130.9	C_5Me_5
128.6	*m*- N-2,6-$C_6H_3Me_2$ (adj. Me_a)
128.4	*m*- N-2,6-$C_6H_3Me_2$ (adj. Me_b)
127.2	*p*- N-2,6-$C_6H_3Me_2$
50.5	N*C*HMeMe
24.2	NCH*Me*Me
23.3	NCHMe*Me*
18.7	Me_a
18.1	Me_b
14.4	*Me*CN_2
12.7	C_5Me_5

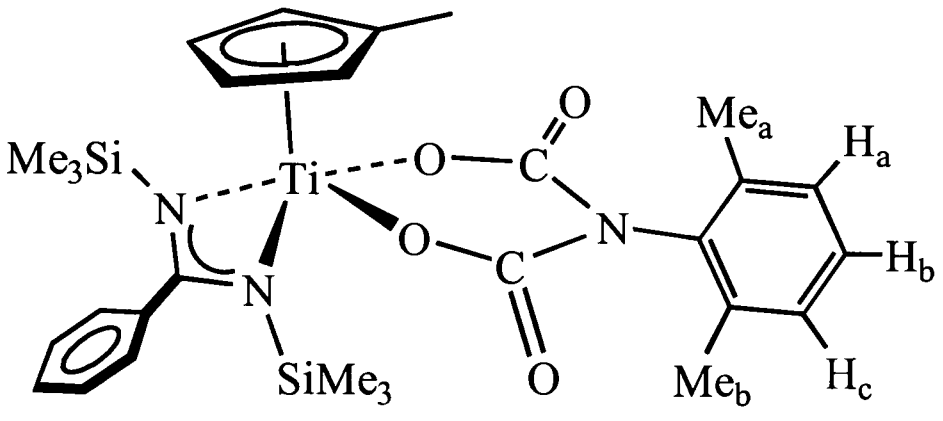
I.R. data (KBr plates, Nujol mull)

2725 (w), 1694 (s), 1651 (s), 1556 (w), 1314 (w), 1262 (w, br), 1234 (w), 1206 (m), 1173 (m), 1158 (m), 1124 (w), 1030 (w), 1004 (s), 811 (m), 782 (w), 771 (m), 742 (w), 724 (m), 685 (w), 652 (w), 611(m), 587 (w), 528 (m), 511 (w), 453 (m, br) cm^{-1}

Mass Spec. (E.I.)

m/z = 531 $[M]^+$

8.35 Ti(η-C_5Me_5){OC(O)N(-2,6-$C_6H_3Me_2$)C(O)O}{$MeC(N^iPr)_2$} (32)



Appearance: Brown powder

Molecular Formula: $C_{29}H_{39}N_3O_4Si_2Ti$

Elemental analysis for $C_{29}H_{39}N_3O_4Si_2Ti$:

Found (calculated) % : C 58.4 (58.3); H 6.5 (6.6); N 6.8 (7.0)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.12	1 H, d	J = 7.3 Hz	H_a
7.09	1 H, t	J = 7.3 Hz	H_b
7.04	1 H, d	J = 7.3 Hz	H_c
6.95 – 6.90	3 H, m		*o*-, *p*- C_6H_5
6.86 – 6.81	2 H, m		*m*- C_6H_5
6.43	2 H, virtual t	J = 2.7 Hz	$C_5H_2(\beta)H_2(\alpha)Me$
6.05	2 H, virtual t	J = 2.7 Hz	$C_5H_2(\beta)H_2(\alpha)Me$
2.48	3 H, s		Me_a

2.34	3 H, s	*Me*$_b$
2.12	3 H, s	$C_5H_2(\beta)H_2(\alpha)$*Me*
-0.02	18 H, s	Si*Me*$_3$

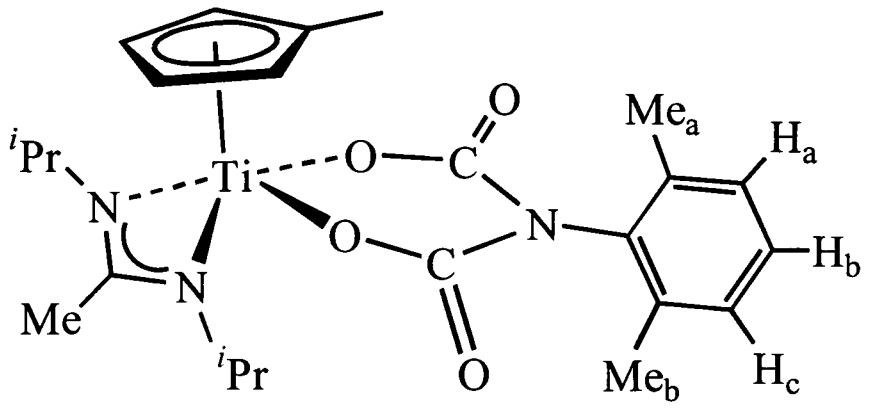
^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d$_6$)

175.0	$C_6H_5CN_2$
152.8	O*C*O
139.1	*i*- 2,6-$C_6H_3Me_2$
136.6	*i*- C_6H_5
136.0	*o*- 2,6-$C_6H_3Me_2$ (adj. Me$_a$)
135.9	*o*- 2,6-$C_6H_3Me_2$ (adj. Me$_b$)
133.8	$C_2(\beta)C_2(\alpha)C$Me
128.6	*m*- 2,6-$C_6H_3Me_2$ (adj. Me$_a$)
128.3	*m*- 2,6-$C_6H_3Me_2$ (adj. Me$_b$)
128.2	*m*- C_6H_5
128.1	*o*- / *p*- C_6H_5
127.9	*p*- / *o*- C_6H_5
127.5	*p*- 2,6-$C_6H_3Me_2$
120.7	$C_2(\beta)C_2(\alpha)$CMe
119.8	$C_2(\beta)C_2(\alpha)$CMe
18.5	*Me*$_a$
18.0	*Me*$_b$
15.7	$C_2(\beta)C_2(\alpha)C$*Me*
1.7	Si*Me*$_3$

I.R. data (KBr plates, Nujol mull)

3106 (w), 2728 (w), 2671 (w), 2336 (w), 2273 (w), 1944 (w), 1703 (s), 1657 (s), 1624 (m), 1590 (m), 1558 (m), 1524 (m), 1500 (m), 1407 (s), 1366 (s), 1301 (s), 1248 (s), 1229 (m), 1172 (m), 1094 (m), 1075 (m), 1032 (m), 1003 (s), 992 (s), 913 (s, br), 842 (s, br), 812 (s), 780 (s), 765 (s), 724 (s), 637 (w), 615 (w), 587 (w), 536 (w), 519 (w), 438 (w) cm^{-1}

8.36 Ti(η-C_5H_4Me){OC(O)N(-2,6-$C_6H_3Me_2$)C(O)O} {$MeC(N^iPr)_2$} (33)



Appearance: Brown powder

Molecular Formula: $C_{24}H_{33}N_3O_4Ti$

Elemental analysis for $C_{24}H_{33}N_3O_4Ti$:

Found (calculated) % : C 61.0 (60.6); H 7.7 (7.0); N 9.1 (8.8)

^{1}H NMR data (300.0 MHz, 298 K, benzene-d_6)

7.10	1 H, d	J = 7.2 Hz	H_a
7.08	1 H, t	J = 7.2 Hz	H_b
7.03	2 H, d	J = 7.2 Hz	H_c
6.30	2 H, virtual t	J = 2.7 Hz	$C_5H_2(\beta)H_2(\alpha)Me$
5.96	2 H, virtual t	J = 2.7 Hz	$C_5H_2(\beta)H_2(\alpha)Me$
3.16	2 H, sept	J = 6.4 Hz	NC*H*MeMe
2.46	3 H, s		Me_a
2.19	3 H, s		Me_b

2.12	3 H, s		$C_5H_2(\beta)H_2(\alpha)\mathit{Me}$
1.13	3 H, s		$\mathit{Me}CN_2$
1.11	6 H, d	J = 6.4 Hz	NCHMeMe
1.04	6 H, d	J = 6.4 Hz	NCHMeMe

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

167.1	Me$\mathit{C}N_2$
152.9	$\{O(\mathit{C}O)\}_2N$
139.3	*i*- 2,6-$C_6H_3Me_2$
136.1	*o*- 2,6-$C_6H_3Me_2$ (adj. Me_a)
136.0	*o*- 2,6-$C_6H_3Me_2$ (adj. Me_b)
134.2	$C_2H_2(\beta)C_2H_2(\alpha)\mathit{C}$Me
128.6	*m*- N-2,6-$C_6H_3Me_2$ (adj. Me_a)
128.5	*m*- N-2,6-$C_6H_3Me_2$ (adj. Me_b)
127.4	*p*- N-2,6-$C_6H_3Me_2$
119.5	$C_2(\beta)\mathit{C_2(\alpha)}$CMe
119.4	$\mathit{C_2(\beta)}C_2(\alpha)$CMe
50.6	NCHMeMe
23.7	NCHMeMe
23.4	NCHMeMe
18.5	$\mathit{Me_a}$
18.4	$\mathit{Me_b}$
18.0	$\mathit{Me}CN_2$
9.9	$C_2(\beta)C_2(\alpha)\mathit{C}Me$

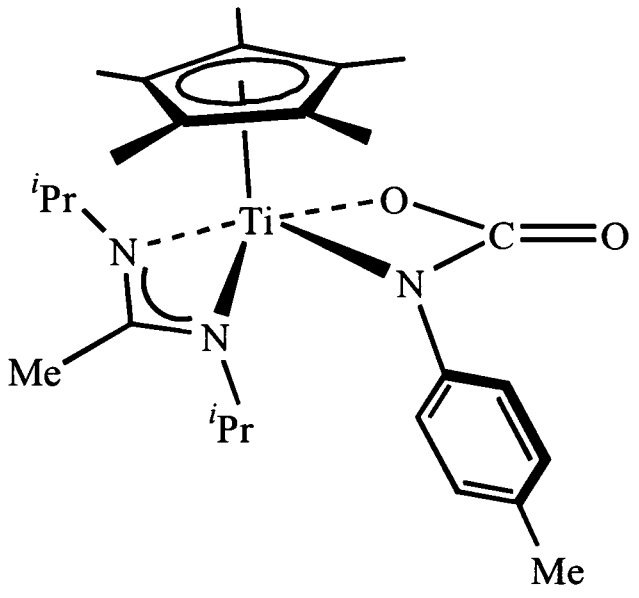
I.R. data (KBr plates, Nujol mull)

2956 (s), 2726 (w), 2671 (w), 1700 (s), 1651 (s, br), 1611 (m), 1583 (m), 1557 (m), 1262 (m), 1244 (m), 1216 (s), 1173 (s), 1122 (m), 1085 (m), 1071 (m), 1031 (m), 1003 (m), 936 (w), 920 (w), 811 (s), 767 (m), 722 (s), 703 (m), 585 (w), 549 (w), 532 9w), 458 (w), 426 (w) cm^{-1}

Mass Spec. (E.I.)

m/z = 475 $[M]^+$

8.37 Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{MeC(N^{i}Pr)$_2$} (34)



Appearance: Brown powder

Molecular formula: $C_{26}H_{39}N_3O_2Ti$

Elemental analysis for $C_{26}H_{39}N_3O_2Ti$:

Found (calculated) % : C 65.6 (65.6); H 8.1 (8.3); N 8.4 (8.9)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.35	2 H, d	J = 8.5 Hz	*m*- 4-C_6H_4Me
7.03	2 H, d	J = 8.5 Hz	*o*- 4-C_6H_4Me
3.65	1 H, m, br		NCH_aMeMe
3.29	1 H, m, br		NCH_bMeMe
2.14	3 H, s		Ar*Me*
1.94	15 H, s		C_5Me_5
1.35	3 H, s		*Me*CN_2
1.08	6 H, d	J = 6.2 Hz	NCH$_b$*MeMe*
0.98	3 H, d	J = 5.9 Hz	NCH$_a$*Me*Me
0.64	3 H, d	J = 6.1 Hz	NCH$_a$Me*Me*

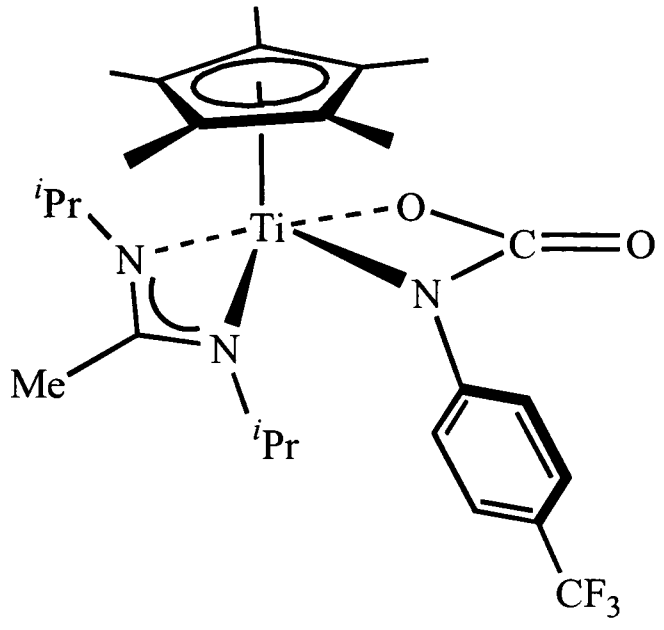
^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

169.9	Me*C*N_2
157.7	O*C*O
146.1	*i*- 4-C_6H_4Me
131.0	*p*- 4-C_6H_4Me
129.4	*o*- 4-C_6H_4Me
129.0	C_5Me_5
122.6	*m*- 4-C_6H_4Me
50.5	N*C*H_bMeMe
49.5	N*C*H_aMeMe
24.3	NCH_a*Me*Me
24.1	NCH_aMe*Me*
23.9	NCH_b*MeMe*
20.9	Ar*Me*
15.0	*Me*CN_2
12.6	C_5*Me*$_5$

I.R. data (KBr plates, Nujol mull)

2955 (s), 2726 (w), 2673 (w), 2360 (w), 1701 (w), 1672 (s), 1609 (w, br), 1575 (w), 1508 (s), 1339 (w), 1307 (m), 1207 (m), 1177 (w), 1160 (w), 1128 (w), 1064 (w), 1006 (m), 934 (w), 915 (m), 818 (m), 791 (m), 724 (s), 681 (w), 612 (w), 586 (w), 516 (w), 476 (m), 424 (w) cm^{-1}

8.38 Ti(η-C_5Me_5){N(-4-$C_6H_4CF_3$)C(O)O}{MeC(N^{i}Pr)$_2$} (35)



Appearance: Brown powder

Molecular formula: $C_{26}H_{36}F_3N_3O_2Ti$

Elemental analysis for $C_{26}H_{36}F_3N_3O_2Ti$:

Found (calculated) % : C 59.5 (59.2); H 7.0 (6.9); N 7.7 (8.0)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.47	2 H, d	J = 8.5 Hz	*m*-4-$C_6H_4CF_3$
7.43	2 H, d	J = 8.8 Hz	*o*-4-$C_6H_4CF_3$
3.57	1 H, m	J = 6.6 Hz	NC*H*$_a$MeMe
3.22	1 H, m	J = 6.6 Hz	NC*H*$_b$MeMe
1.85	15 H, s		C_5*Me*$_5$
1.29	3 H, s		*Me*CN_2
1.04	3 H, d	J = 6.6 Hz	NCH$_b$*Me*Me
1.01	3 H, d	J = 6.6 Hz	NCH$_b$Me*Me*
0.98	3 H, d	J = 6.6 Hz	NCH$_a$*Me*Me
0.44	3 H, d	J = 6.6 Hz	NCH$_a$Me*Me*

^{19}F NMR data (282.4 MHz, 298 K, benzene-d_6)

-61.33	CF_3

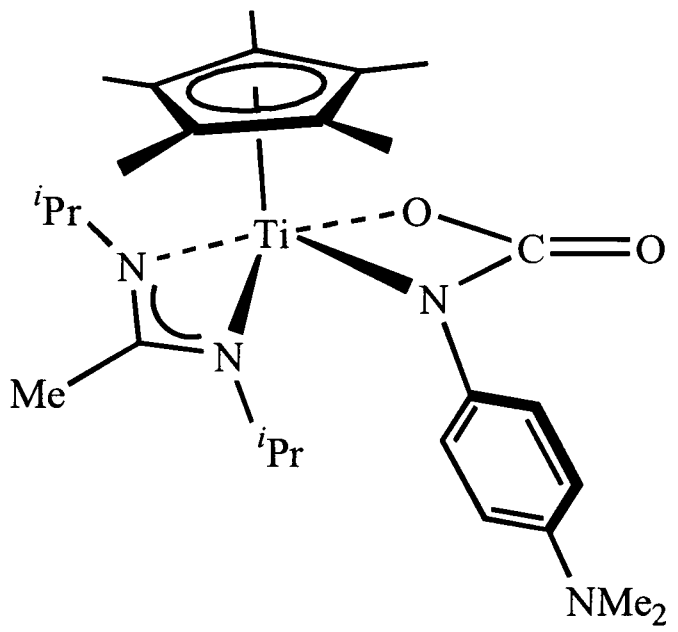
^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

169.6	Me*C*N_2
151.3	O*C*O
130.4	*i*- / *p*- 4-$C_6H_4CF_3$
128.5	C_5Me_5
125.8	*o*- 4-$C_6H_4CF_3$
121.5	*m*- 4-$C_6H_4CF_3$
50.9	N*C*H_bMeMe
49.8	N*C*H_aMeMe
24.3	NCH_a*Me*Me
24.2	NCH_b*MeMe*
23.7	NCH_aMe*Me*
15.8	*Me*CN_2
13.0	C_5*Me*$_5$

I.R. data (KBr plates, Nujol mull)

2727 (w), 1655 (m), 1603 (m), 1499 (m), 1322 (s), 1208 (m), 1160 (m), 1108 (m), 1066 (s), 1012 (m), 914 (w), 890 (w), 846 (w), 789 (w), 723 (w), 678 (w), 663 (w), 644 (w), 632 (w), 580 (w), 508 (w), 469 (w) cm^{-1}

8.39 Ti(η-C_5Me_5){N(-4-$C_6H_4NMe_2$)C(O)O}{MeC(N^{i}Pr)$_2$} (36)



Appearance: Brown powder

Molecular formula: $C_{27}H_{42}N_4O_2Ti$

Elemental analysis for $C_{27}H_{42}N_4O_2Ti$:

Found (calculated) % : C 64.2 (64.5); H 8.3 (8.4); N 10.7 (11.2)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.31	2 H, d	J = 9.0 Hz	*m*- 4-$C_6H_4NMe_2$
6.66	2 H, d	J = 9.0 Hz	*o*- 4-$C_6H_4NMe_2$
3.62	1 H, m, br		NCH_aMeMe
3.27	1 H, m, br		NCH_bMeMe
2.54	6 H, s		NMe_2
1.98	15 H, s		C_5Me_5
1.40	3 H, s		MeCN$_2$
1.15	3 H, d, br		NCH$_b$$Me$Me

1.11	3 H, d, br	NCH_bMeMe
0.98	3 H, d, br	NCH_aMeMe
0.73	3 H, d, br	NCH_aMeMe

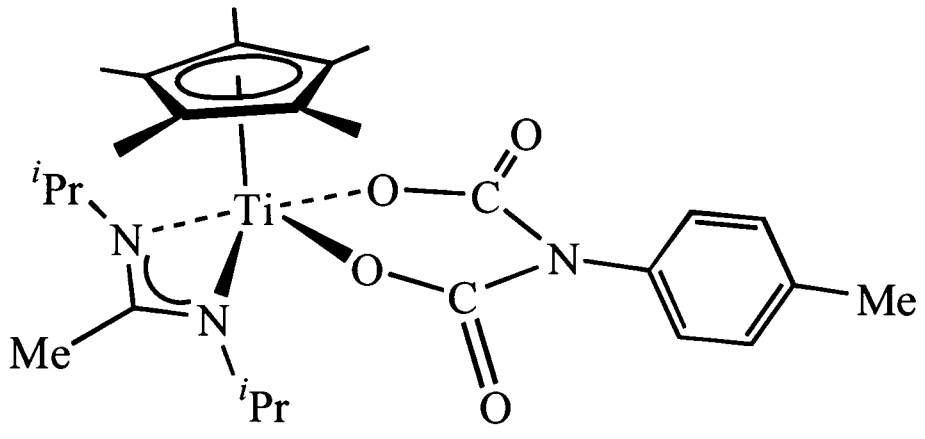
^{13}C-{^{1}H} NMR data (75.5 MHz, 298 K, benzene-d_6)

169.8	$MeCN_2$
158.2	OCO
146.9	*i*- 4-$C_6H_4NMe_2$
139.8	*p*- 4-$C_6H_4NMe_2$
130.0	*o*- 4-$C_6H_4NMe_2$
129.0	C_5Me_5
123.8	*m*- 4-$C_6H_4NMe_2$
50.8	NCH_bMeMe
49.8	NCH_aMeMe
41.3	NMe_2
24.6	NCH_aMeMe
24.5	NCH_aMeMe
24.3	NCH_bMeMe
15.0	$MeCN_2$
13.1	C_5Me_5

I.R. data (KBr plates, Nujol mull)

2726 (w), 2671 (w), 1656 (m), 1603 (m), 1511 (s), 1341 (s), 1309 (s), 1261 (m), 1206 (m), 1162 (m), 1129 (m), 1065 (w), 1022 (w), 947 (m), 908 (w), 817 (m), 789 (w), 723 (m), 596 (w), 533 (w), 464 (w), 404 (w) cm^{-1}

8.40 Ti(η-C_5Me_5){OC(O)N(-4-C_6H_4Me)C(O)O}{MeC(N^{i}Pr)$_2$} (37)



Appearance: Green powder

Molecular Formula: $C_{27}H_{39}N_3O_4Ti$

Elemental analysis for $C_{27}H_{39}N_3O_4Ti$:

Found (calculated) % : C 63.0 (62.7); H 7.9 (7.6); N 7.9 (8.1)

^{1}H NMR data (300.0 MHz, 298 K, benzene-d_6)

7.39	2 H, d	J = 8.4 Hz	*o*- C_6H_4Me
7.04	2 H, d	J = 8.4 Hz	*m*- C_6H_4Me
3.42	1 H, apparent sept	J = 6.8 Hz	NC*H*MeMe
2.05	3 H, s		C_6H_4*Me*
1.94	15 H, s		C_5*Me*$_5$
1.32	3 H, s		*Me*CN_2
1.10	6 H, d	J = 6.8 Hz	NCH*Me*Me
1.07	6 H, d	J = 6.8 Hz	NCHMe*Me*

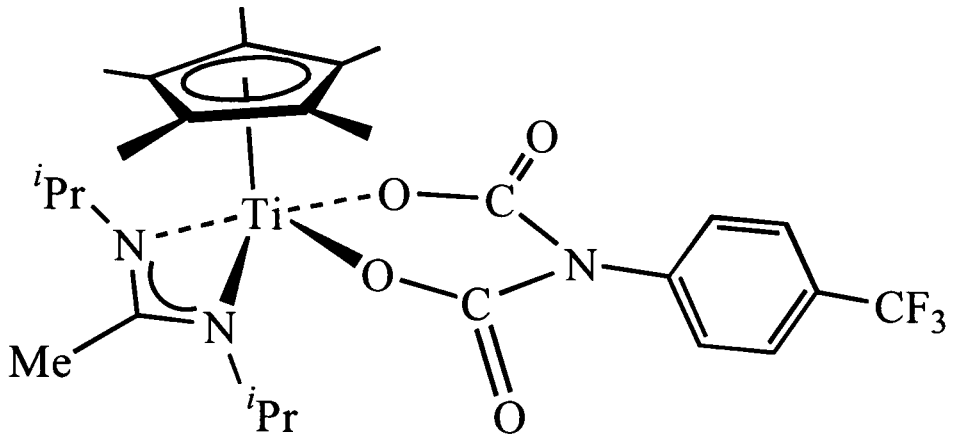
^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

169.5	Me*C*N_2
154.4	{O(*C*O)}$_2$N
139.2	*i*- 4-C_6H_4Me
136.3	*p*- 4-C_6H_4Me
130.9	C_5Me$_5$
129.4	*o*- 4-C_6H_4Me
129.3	*o*- 4-C_6H_4Me
128.3	*m*- 4-C_6H_4Me
50.5	N*C*HMeMe
24.0	NCH*Me*Me
23.8	NCHMe*Me*
21.0	C_6H_4*Me*
13.2	*Me*CN_2
12.7	C_5*Me*$_5$

I.R. data (KBr plates, Nujol mull)

2955 (s), 1698 (m), 1656 (m), 1265 (m), 1206 (w), 1154 (m), 1124 (w), 1005 (m), 784 (w), 723 (w), 610 (w), 526 (w) cm^{-1}

8.41 Ti(η-C_5Me_5){OC(O)N(-4-$C_6H_4CF_3$)C(O)O}{$MeC(N^iPr)_2$} (38)



Appearance: Brown powder

Molecular Formula: $C_{27}H_{36}F_3N_3O_4Ti$

Elemental analysis for $C_{27}H_{36}F_3N_3O_4Ti$:

Found (calculated) % : C 57.6 (56.8); H 6.6 (6.4); N 7.0 (7.3)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.40	2 H, d	J = 8.5 Hz	*o*- 4-$C_6H_4CF_3$
7.34	2 H, d	J = 8.5 Hz	*m*- 4-$C_6H_4CF_3$
3.41	2 H, apparent sept	J = 6.5 Hz	NC*H*MeMe
1.92	15 H, s		C_5Me_5
1.31	3 H, s		*Me*CN_2
1.08	6 H, d	J = 6.5 Hz	NCH*Me*Me
1.05	6 H, d	J = 6.5 Hz	NCHMe*Me*

^{19}F NMR data (282.4 MHz, 298 K, benzene-d_6)

-62.40	CF_3

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

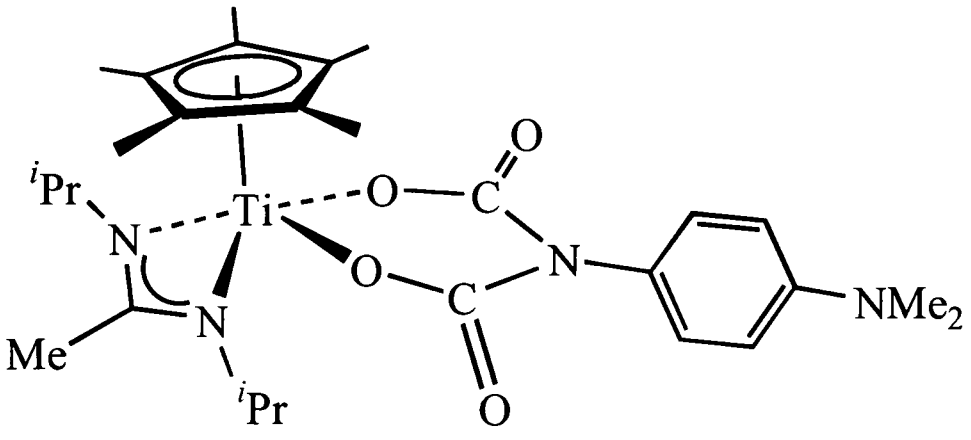
169.5	Me*C*N_2
153.8	{O(*C*O)}$_2$N
144.7	*i*- 4-$C_6H_4CF_3$
131.5	C_5Me_5
130.1	*o*- 4-$C_6H_4CF_3$
125.8	*m*- 4-$C_6H_4CF_3$
50.6	N*C*HMeMe
24.0	NCH*Me*Me
23.7	NCHMe*Me*
14.1	*Me*CN_2
12.7	C_5*Me*$_5$

CF_3, *p*- 4-$C_6H_4CF_3$ resonances not observed

I.R. data (CsBr plates, Nujol mull)

2955 (s), 2728 (w), 1704 (s), 1658 (s), 1642 (s), 1632 (s), 1604 (s), 1548 (m), 1513 (m), 1494 (s), 1411 (s), 1323 (s), 1261 (s), 1208 (m), 1159 (s), 1107 (s), 1067 (s), 1007 (m), 918 (w), 890 (w), 846 (w), 795 (m), 723 (w), 677 (w), 663 (w), 633 (w), 595 (w), 534 (w), 454 (w), 409 (w) cm^{-1}

8.42 Ti(η-C_5Me_5){OC(O)N(-4-$C_6H_4NMe_2$)C(O)O}{MeC(N^{i}Pr)$_2$} (39)



Appearance: Dark red powder

Molecular Formula: $C_{28}H_{42}N_4O_4Ti$

Elemental analysis for $C_{28}H_{42}N_4O_4Ti$:

Found (calculated) % : C 62.0 (61.5); H 7.8 (7.8); N 10.7 (10.3)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.43	2 H, d	J = 8.9 Hz	*o*- 4-$C_6H_4NMe_2$
6.62	2 H, d	J = 8.9 Hz	*m*- 4-$C_6H_4NMe_2$
3.43	2 H, apparent sept	J = 6.8 Hz	NC*H*MeMe
2.44	6 H, s		N*Me*$_2$
1.97	15 H, s		C_5*Me*$_5$
1.32	3 H, s		*Me*CN_2
1.11	6 H, d	J = 6.8 Hz	NCH*Me*Me
1.08	6 H, d	J = 6.8 Hz	NCHMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

154.8	{O(*C*O)}$_2$N
131.1	*i*- 4-$C_6H_4NMe_2$
130.7	*p*- 4-$C_6H_4NMe_2$
129.8	*o*- 4-$C_6H_4NMe_2$
124.7	C_5Me_5
113.0	*m*- 4-$C_6H_4NMe_2$
50.5	N*C*HMeMe
40.4	N*Me*$_2$
24.1	NCH*Me*Me
23.9	NCHMe*Me*
14.1	*Me*CN_2
12.7	C_5*Me*$_5$

Me*C*N_2 resonance not observed

I.R. data (KBr plates, Nujol mull)

2727 (w), 1774 (w), 1698 (s), 1653 (s), 1614 (m), 1558 (w), 1521 (m), 1263 (m), 1212 (m), 1183 (m), 1157 (m), 1129 (m), 1067 (m), 1025 (w), 998 (m), 947 (w), 918 (w), 820 (m), 790 (s), 751 (w), 723 (m), 676 (w), 596 (m), 533 (m), 454 (m) cm^{-1}

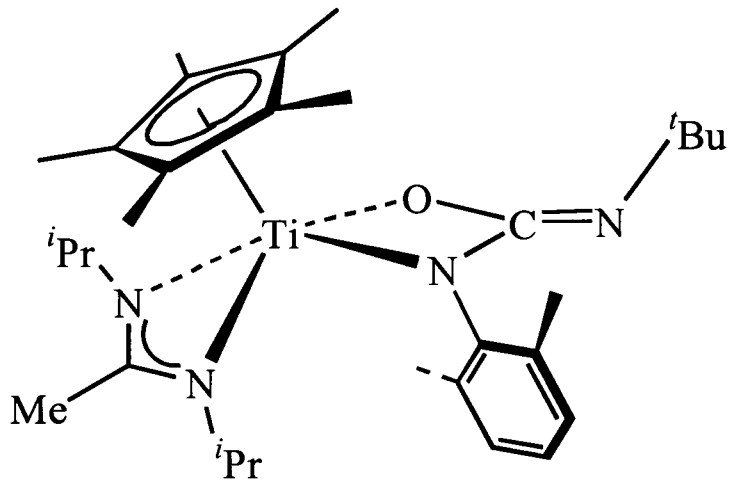
Mass Spec. (E.I.)

m/z = 546 $[M]^+$

Accurate Mass Spectrum: Found (Calculated): 546.2689 (546.2686)

8.43 Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N^{t}Bu)O}{MeC(N^{i}Pr)$_2$}

(40)



Appearance: Sticky brown solid

Molecular Formula: $C_{31}H_{50}N_4OTi$

Elemental analysis for $C_{31}H_{50}N_4OTi$:

Satisfactory elemental analysis was not obtained for this compound

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

6.98	1 H, d	J = 7.3 Hz	*m*- 2,6-$C_6H_3Me_2$
6.94	1 H, d	J = 7.3 Hz	*m*- 2,6-$C_6H_3Me_2$
6.88	1 H, t	J = 7.3 Hz	*p*- 2,6-$C_6H_3Me_2$
3.32	1 H, apparent sept	J = 6.4 Hz	NCH_aMeMe
3.14	1 H, apparent sept	J = 6.4 Hz	NCH_bMeMe
2.32	3 H, s		2,6-C_6H_3*Me*Me
1.99	3 H, s		2,6-C_6H_3Me*Me*

1.97	15 H, s		C_5Me_5
1.66	9 H, s		^tBu
1.44	3 H, s		$MeCN_2$
1.15	3 H, d	J = 6.4 Hz	NCH_aMeMe
0.99	3 H, d	J = 6.4 Hz	NCH_bMeMe
0.78	3 H, d	J = 6.4 Hz	NCH_bMeMe
0.50	3 H, d	J = 6.4 Hz	NCH_bMeMe

^{13}C-{^1H} NMR data (125.7 MHz, 298 K, benzene-d_6)

166.9	$MeCN_2$
152.5	OCN
148.8	*i*- 2,6-$C_6H_3Me_2$
133.6	*o*- 2,6-$C_6H_3Me_2$
133.0	*o*- 2,6-$C_6H_3Me_2$
127.4	C_5Me_5
127.6	*m*- 2,6-$C_6H_3Me_2$
124.1	*p*- 2,6-$C_6H_3Me_2$
51.9	NCH_aMeMe
49.7	NCH_bMeMe
32.9	$NCMe_3$
25.5	NCH_bMeMe , NCH_aMeMe (broad)
24.2	NCH_aMeMe , NCH_bMeMe (broad)
19.6	2,6-$C_6H_3Me_2$

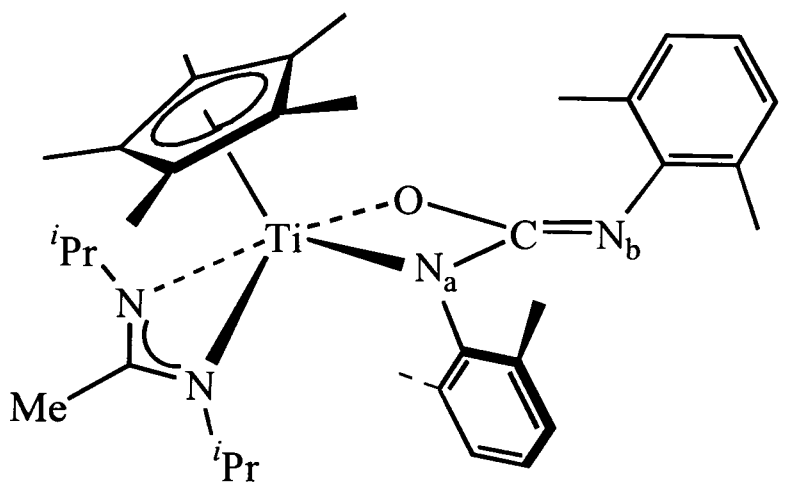
13.5	$MeCN_2$
12.8	C_5Me_5

$NCMe_3$ resonance not observed

I.R. data (KBr plates, Nujol mull)

2957 (s), 2721 (w), 2602 (w), 2359 (w), 2140 (m), 1904 (w), 1652 (m), 1610 (m, br), 1549 (m), 1366 (m), 1349 (w), 1334 (m), 1313 (w), 1284 (m), 1262 (w), 1250 (w), 1232 (w), 1206 (s, br), 1174 (m, br), 1138 (w), 1123 (w), 1097 (w), 1049 (m), 1017 (m), 955 (w), 940 (w), 919 (w), 860 (w), 792 (m), 764 (m), 732 (w), 634 (m, br), 610 (w), 594 (w), 558 (w), 529 (w), 499 (m), 477 (m), 423 (w) cm^{-1}

8.44 Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N-2,6-$C_6H_3Me_2$)O} {MeC(N^{i}Pr)$_2$} (41)



Appearance: Brown powder

Molecular Formula: $C_{35}H_{50}N_4OTi$

Elemental analysis for $C_{35}H_{50}N_4OTi$:

Found (calculated): C 71.2 (71.2); H 8.2 (8.5); N 9.4 (9.5)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.24	2 H, d	J = 7.6 Hz	*m*- N_b-2,6-$C_6H_3Me_2$
7.09	1 H, m		*m*- N_a-2,6-$C_6H_3Me_2$
7.04	1 H, m		*m*- N_a-2,6-$C_6H_3Me_2$
7.00	2 H, t	J = 7.6 Hz	*p*-N_b-2,6-$C_6H_3Me_2$, *p*-N_a-2,6-$C_6H_3Me_2$
3.20	1 H, apparent sept	J = 6.4 Hz	NCH_aMeMe
3.17	1 H, apparent sept	J = 6.4 Hz	NCH_bMeMe
2.50	6 H, s		N_b-2,6-$C_6H_3Me_2$

2.40	3 H, s		N_a-2,6-C_6H_3*Me*Me
2.07	3 H, s		N_a-2,6-C_6H_3Me*Me*
1.83	15 H, s		C_5*Me*$_5$
1.41	3 H, s		*Me*CN_2
0.93	3 H, d	J = 6.4 Hz	NCH_a*Me*Me
0.92	3 H, d	J = 6.4 Hz	NCH_aMe*Me*
0.75	3 H, d	J = 6.4 Hz	NCH_b*Me*Me
0.55	3 H, d	J = 6.4 Hz	NCH_bMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

166.3	Me*C*N_2
153.3	O*C*N
148.3	*i*- 2,6-$C_6H_3Me_2$
148.2	*i*- 2,6-$C_6H_3Me_2$
134.0	*o*- N_a-2,6-$C_6H_3Me_2$
133.5	*o*- N_a-2,6-$C_6H_3Me_2$
130.1	*o*- N_b-2,6-$C_6H_3Me_2$
128.4	*p*- N_b-2,6-$C_6H_3Me_2$
128.3	*p*- N_a-2,6-$C_6H_3Me_2$
127.7	*m*- N_a-2,6-$C_6H_3Me_2$
127.6	*m*- N_a-2,6-$C_6H_3Me_2$
124.6	*C*$_5$Me$_5$
121.0	*m*- N_b-2,6-$C_6H_3Me_2$
49.6	N*C*H_aMeMe

48.8	N*C*H_aMeMe
25.1	NCH$_b$*Me*Me
24.9	NCH$_a$Me*Me*
24.6	NCH$_b$*Me*Me
24.1	NCH$_b$Me*Me*
20.4	N$_b$-2,6-C_6H_3*Me*$_2$
19.6	N$_a$-2,6-C_6H_3*Me*Me
19.2	N$_a$-2,6-C_6H_3Me*Me*
14.0	*Me*CN_2
12.9	C_5*Me*$_5$

I.R. data (KBr plates, Nujol mull)

2722 (w), 1610 (s), 1580 (s), 1495 (m), 1404 (w), 1338 (w), 1316 (m), 1302 (m), 1259 (w), 1226 (w), 1210 (m), 1192 (w), 1168 (w), 1114 (w), 1094 (w), 995 (m), 925 (m), 819 (w), 789 (w), 761 (m), 725 (m), 708 (w), 588 (w), 559 (w), 498 (w), 456 (m), 442 (m) cm^{-1}

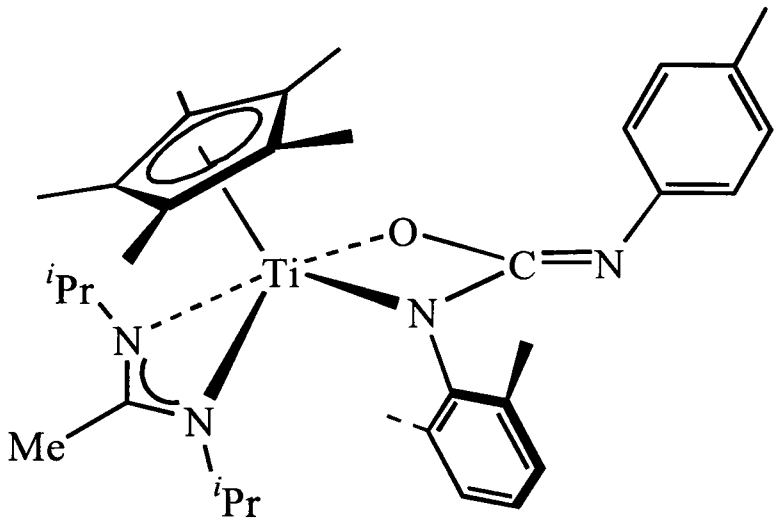
Mass Spec. (E.I.)

m/z = 591 $[M+H]^+$

m/z = 575 $[M-Me]^+$

m/z = 545 $[M-3Me]^+$

8.45 Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N-4-C_6H_4Me)O} {MeC(N^{i}Pr)$_2$} (42)



Appearance: Brown powder

Molecular Formula: $C_{34}H_{48}N_4OTi$

Elemental analysis for $C_{34}H_{48}N_4OTi$:

Satisfactory elemental analysis was not obtained for this compound

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.66	2 H, d	J = 8.2 Hz	*o*- 4-C_6H_4Me
7.14	2 H, d	J = 8.2 Hz	*m*- 4-C_6H_4Me
7.04	1 H, d	J = 7.2 Hz	*o*- 2,6-$C_6H_3Me_2$
6.99	1 H, d	J = 7.2 Hz	*o*- 2,6-$C_6H_3Me_2$
6.95	1 H, t	J = 7.2 Hz	*p*- 2,6-$C_6H_3Me_2$
3.26	1 H, apparent sept	J = 6.6 Hz	NCH_aMeMe
3.09	1 H, apparent sept	J = 6.4 Hz	NCH_bMeMe

2.37	3 H, s		4-C_6H_4*Me*
2.21	3 H, s		2,6-C_6H_3*Me*Me
2.02	3 H, s		2,6-C_6H_3Me*Me*
1.96	15 H, s		C_5*Me*$_5$
1.43	3 H, s		*Me*CN_2
1.07	3 H, d	J = 6.6 Hz	NCH_a*Me*Me
0.97	3 H, d	J = 6.6 Hz	NCH_aMe*Me*
0.84	3 H, d	J = 6.4 Hz	NCH_b*Me*Me
0.56	3 H, d	J = 6.4 Hz	NCH_bMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

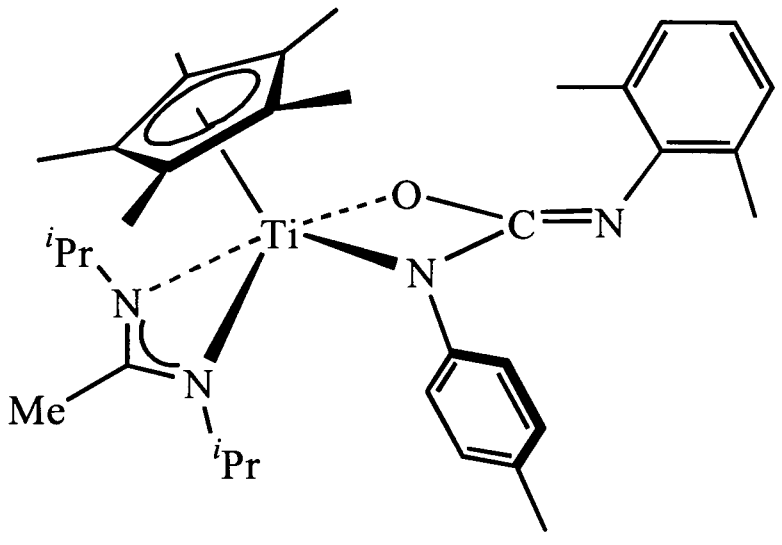
167.9	Me*C*N_2
154.9	O*C*N
148.3	*i*- NAr
147.9	*i*- NAr
133.7	*o*- 2,6-$C_6H_3Me_2$
133.4	*o*- 2,6-$C_6H_3Me_2$
129.4	*p*- 4-C_6H_4Me
129.0	*m*- 4-C_6H_4Me
128.6	*m*- 2,6-$C_6H_3Me_2$
128.3	*m*- 2,6-$C_6H_3Me_2$
128.1	*C*$_5$Me$_5$
125.6	*o*- 4-C_6H_4Me
124.5	*p*- 2,6-$C_6H_3Me_2$

50.3	N*C*H$_a$MeMe
49.3	N*C*H$_b$MeMe
25.9	NCH$_b$*Me*Me
24.8	NCH$_a$Me*Me*
24.2	NCH$_a$*Me*Me
24.0	NCH$_b$Me*Me*
21.0	2,6-C$_6$H$_3$*Me*Me
19.7	4-C$_6$H$_4$*Me*
19.4	2,6-C$_6$H$_3$Me*Me*
13.6	*Me*CN$_2$
13.0	C$_5$*Me*$_5$

I.R. data (KBr plates, Nujol mull)

2727 (w), 1655 (w), 1615 (w), 1595 (m), 1576 (s), 1504 (s), 1410 (m), 1338 (m), 1311 (m), 1295 (m), 1247 (m), 1208 (m), 1170 (w), 1118 (w), 1069 (w), 996 (w), 927 (w), 847 (w), 811 (w), 787 (w), 757 (w), 724 (w), 631 (w), 592 (w), 550 (w), 537 (w), 522 (w), 499 (w) cm^{-1}

8.46 Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-2,6-$C_6H_3Me_2$)O} {$MeC(N^iPr)_2$} (43)



Appearance: Brown powder

Molecular Formula: $C_{34}H_{48}N_4OTi$

Elemental analysis for $C_{34}H_{48}N_4OTi$:

Found (calculated): C 70.7 (70.8); H 8.9 (8.4); N 9.3 (9.7)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.57	2 H, d	J = 8.2 Hz	*m*- 4-C_6H_4Me
7.23	2 H, d	J = 7.6 Hz	*m*- 2,6-$C_6H_3Me_2$
7.09	2 H, d	J = 8.2 Hz	*o*- 4-C_6H_4Me
6.99	1 H, t	J = 7.6 Hz	*p*- 2,6-$C_6H_3Me_2$
3.61	1 H, s (br)		NCH_aMeMe
3.25	1 H, s (br)		NCH_bMeMe
2.51	6 H, s		2,6-$C_6H_3Me_2$
2.19	3 H, s		4-C_6H_4Me

1.91	15 H, s	C_5Me_5
1.42	3 H, s	$MeCN_2$
0.95	6 H, s (br)	$NCH_{a,b}MeMe$
0.87	3 H, s (br)	NCH_bMeMe
0.61	3 H, s (br)	NCH_aMeMe

^{13}C-{^1H} NMR data (125.7 MHz, 298 K, benzene-d_6)

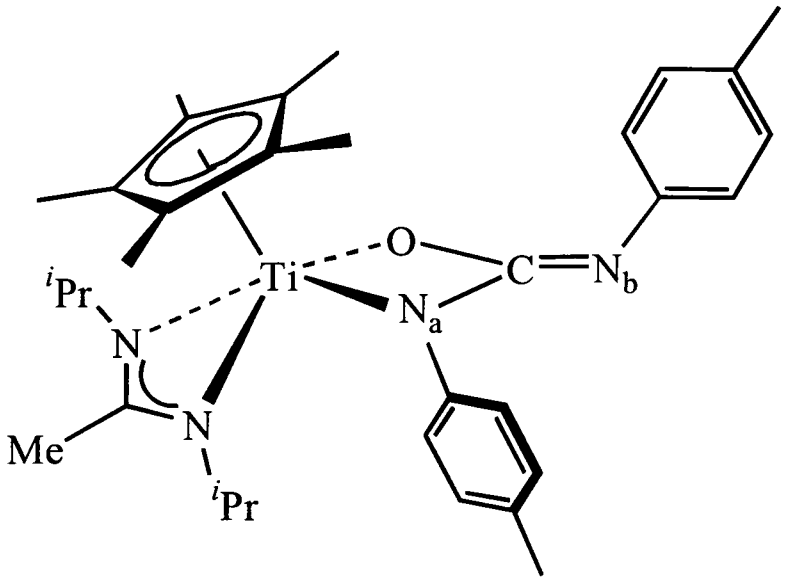
167.3	$MeCN_2$
150.1	OCN
148.2	*i*- NAr
146.7	*i*- NAr
130.7	*o*- 4-C_6H_4Me
130.2	*o*- 4-C_6H_4Me
128.7	*p*- 4-C_6H_4Me
128.6	*m*- 2,6-$C_6H_3Me_2$
127.6	*o*- 2,6-$C_6H_3Me_2$
123.4	*m*- 4-C_6H_4Me
123.3	*m*- 4-C_6H_4Me
121.0	*p*- 2,6-$C_6H_3Me_2$
49.8	NCH_bMeMe
49.4	NCH_aMeMe
24.6	NCH_bMeMe
23.9	$NCH_{a,b}MeMe$
23.6	NCH_aMeMe

21.0	4-C_6H_4Me
19.8	2,6-$C_6H_3Me_2$
15.4	$MeCN_2$
12.6	C_5Me_5

I.R. data (KBr plates, Nujol mull)

2957 (s), 2721 (w), 2670 (w), 1883 (w), 1732 (w), 1616 (s), 1582 (s), 1507 (s), 1350 (m), 1326 (s), 1257 (m), 1228 (m), 1214 (m), 1181 (w), 1169 (w), 1158 (w), 1144 (w), 1118 (w), 1106 (w), 1094 (w), 1076 (w), 1019 (w), 990 (m), 932 (w), 920 (m), 820 (m), 803 (m), 791 (w), 773 (w), 753 (m), 728 (m), 716 (m), 655 (w), 619 (w), 610 (w), 580 (w), 556 (w), 517 (w) cm^{-1}

8.47 Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O} {$MeC(N^iPr)_2$} (44)



Appearance: Brown powder

Molecular Formula: $C_{33}H_{46}N_4OTi$

Elemental analysis for $C_{33}H_{46}N_4OTi$

Found (calculated): C 70.3 (70.5); H 8.4 (8.2); N 9.9 (10.0)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.81	2 H, d	J = 8.3 Hz	*o*- N_b-4-C_6H_4Me
7.41	2 H, d	J = 8.3 Hz	*o*- N_a-4-C_6H_4Me
7.22	2 H, d	J = 8.3 Hz	*m*- N_b-4-C_6H_4Me
7.06	2 H, d	J = 8.3 Hz	*m*- N_a-4-C_6H_4Me
3.61	1 H, sept	J = 6.8 Hz	NCH_aMeMe
3.26	1 H, sept	J = 6.6 Hz	NCH_bMeMe
2.21	3 H, s		N_b-4-C_6H_4Me

2.17	3 H, s		N_a-4-C_6H_4*Me*
1.94	15 H, s		C_5*Me*$_5$
1.36	3 H, s		*Me*CN_2
1.05	3 H, d	J = 6.6 Hz	NCH_b*Me*Me
1.00	3 H, d	J = 6.6 Hz	NCH_bMeMe
0.92	3 H, d	J = 6.8 Hz	NCH_a*Me*Me
0.66	3 H, d	J = 6.8 Hz	NCH_aMeMe

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

169.1	Me*C*N_2
153.5	O*C*N
148.1	*i*- N-4-C_6H_4Me
146.5	*i*- N-4-C_6H_4Me
131.2	*p*- N-4-C_6H_4Me
129.5	*p*- N-4-C_6H_4Me
129.2	*m*- N_b-4-C_6H_4Me
128.7	*m*- N_a-4-C_6H_4Me
128.5	*C*$_5$Me$_5$
125.7	*o*- N_b-4-C_6H_4Me
123.7	*o*- N_a-4-C_6H_4Me
50.3	N*C*H_bMeMe
49.4	N*C*H_aMeMe
24.3	NCH_a*MeMe*
23.9	NCH_b*MeMe*

21.1	N-4-C_6H_4*Me*
21.1	N-4-C_6H_4*Me*
14.6	*Me*CN_2
12.6	C_5*Me*$_5$

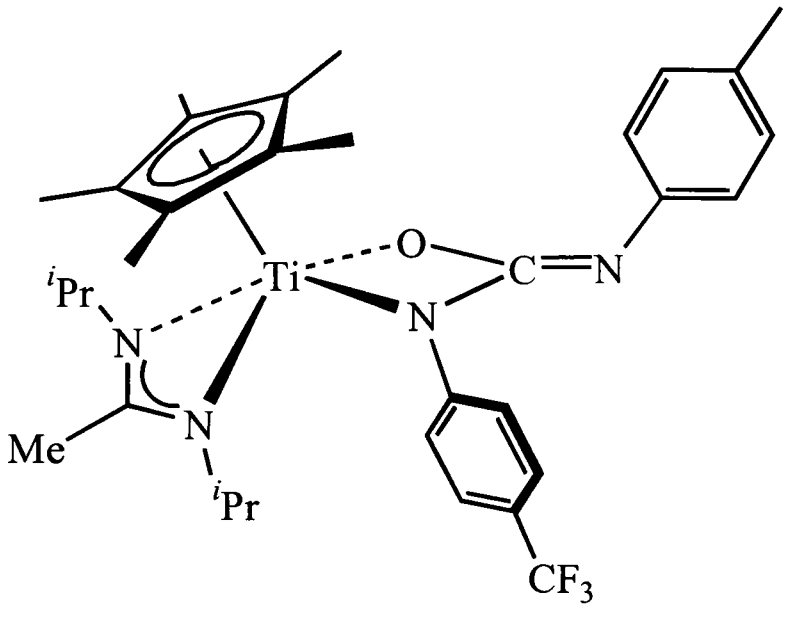
I.R. data (KBr plates, Nujol mull)

2727 (w), 2360 (w), 2342 (w), 1886 (w), 1609 (m), 1569 (s), 1500 (s), 1338 (s), 1322 (s), 1245 (m), 1208 (s), 1127 (m), 1107 (m), 1076 (w), 1018 (w), 996 (m), 918 (s), 817 (s), 785 (m), 724 (m), 698 (w), 681 (w), 642 (w), 620 (w), 611 (w), 578 (w), 544 (w), 515 (m), 487 (m), 440 (m), 408 (m) cm^{-1}

Mass Spec. (F.I.)

m/z = 562 $[M]^+$

8.48 Ti(η-C_5Me_5){N(-4-$C_6H_4CF_3$)C(N-4-C_6H_4Me)O} {$MeC(N^iPr)_2$} (45)



Appearance: Brown powder

Molecular Formula: $C_{33}H_{43}F_3N_4OTi$

Elemental analysis for $C_{33}H_{43}F_3N_4OTi$:

Found (calculated): C 64.1 (64.1); H 7.3 (7.4); N 9.1 (8.6)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.75	2 H, d	J = 8.3 Hz	*o*- 4-C_6H_4Me
7.65	2 H, d	J = 8.6 Hz	*o*- 4-$C_6H_4CF_3$
7.47	2 H, d	J = 8.6 Hz	*m*- 4-$C_6H_4CF_3$
7.23	2 H, d	J = 8.3 Hz	*m*- 4-C_6H_4Me
3.62	1 H, apparent sept	J = 6.8 Hz	NCH_aMeMe
3.25	1 H, apparent sept	J = 6.8 Hz	NCH_bMeMe
2.22	3 H, s		4-C_6H_4*Me*

1.85	15 H, s		C_5Me_5
1.29	3 H, s		$MeCN_2$
0.97	3 H, d	J = 6.8 Hz	NCH_bMeMe
0.95	6 H, d	J = 6.8 Hz	NCH_bMeMe, NCH_aMeMe
0.43	3 H, d	J = 6.8 Hz	NCH_aMeMe

^{19}F NMR data (282.4 MHz, 298 K, benzene-d_6)

-61.21	CF_3

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

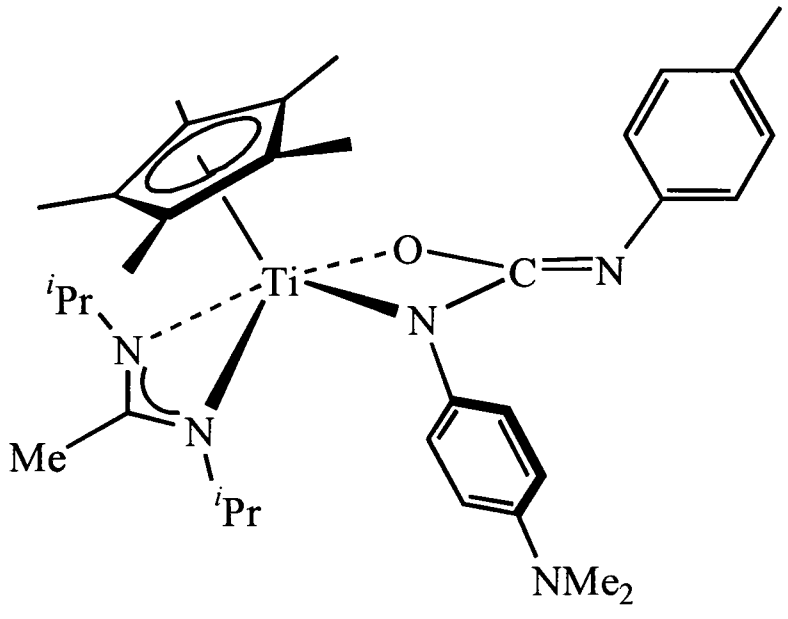
168.7	$MeCN_2$
151.6	OCN
151.1	*i*- NAr
147.2	*i*- NAr
130.2	*p*- 4-$C_6H_4CF_3$
129.4	*p*- 4-C_6H_4Me
129.3	*m*- 4-C_6H_4Me
128.5	C_5Me_5
125.5	*o*- 4-C_6H_4Me, *m*- 4-$C_6H_4CF_3$
122.2	*o*- 4-$C_6H_4CF_3$
50.6	NCH_bMeMe
49.6	NCH_aMeMe

24.4	NCH_bMeMe, NCH_aMeMe
24.2	NCH_bMeMe
23.8	NCH_aMeMe
21.5	$4\text{-}C_6H_4Me$
16.1	$MeCN_2$
12.9	C_5Me_5

I.R. data (KBr plates, Nujol mull)

1618 (m), 1608 (m), 1578 (s), 1504 (m, br), 1410 (w), 1320 (s), 1250 (m), 1208 (m), 1158 (m), 1106 (s, br), 1066 (s), 998 (m), 924 (w), 838 (m), 820 (w), 810 (w), 786 (w), 734 (w), 723 (w), 687 (m), 591 (w), 533 (w) cm^{-1}

8.49 Ti(η-C_5Me_5){N(-4-$C_6H_4NMe_2$)C(N-4-C_6H_4Me)O} {MeC(N^{i}Pr)$_2$} (46)



Appearance: Brown powder

Molecular Formula: $C_{34}H_{49}N_5OTi$

Elemental analysis for $C_{34}H_{49}N_5OTi$:

Found (calculated): C 68.2 (69.0); H 9.0 (8.4); N 11.5 (11.8)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.87	2 H, d	J = 8.3 Hz	*o*- 4-C_6H_4Me
7.34	2 H, d	J = 8.5 Hz	*o*- 4-$C_6H_4NMe_2$
7.22	2 H, d	J = 8.3 Hz	*m*- 4-C_6H_4Me
6.69	2 H, d	J = 8.5 Hz	*m*- 4-$C_6H_4NMe_2$
3.60	1 H, apparent sept	J = 7.1 Hz	NCH_aMeMe
3.28	1 H, apparent sept	J = 6.6 Hz	NCH_bMeMe
2.56	6 H, s		NMe_2

2.22	3 H, s		4-C_6H_4*Me*
1.98	15 H, s		C_5*Me*$_5$
1.40	3 H, s		*Me*CN_2
1.09	3 H, d	J = 6.6 Hz	NCH_b*Me*Me
1.04	3 H, d	J = 6.6 Hz	NCH_bMe*Me*
0.93	3 H, d	J = 6.6 Hz	NCH_a*Me*Me
0.74	3 H, d	J = 6.6 Hz	NCH_aMe*Me*

^{13}C-{^{1}H} NMR data (75.5 MHz, 298 K, benzene-d_6)

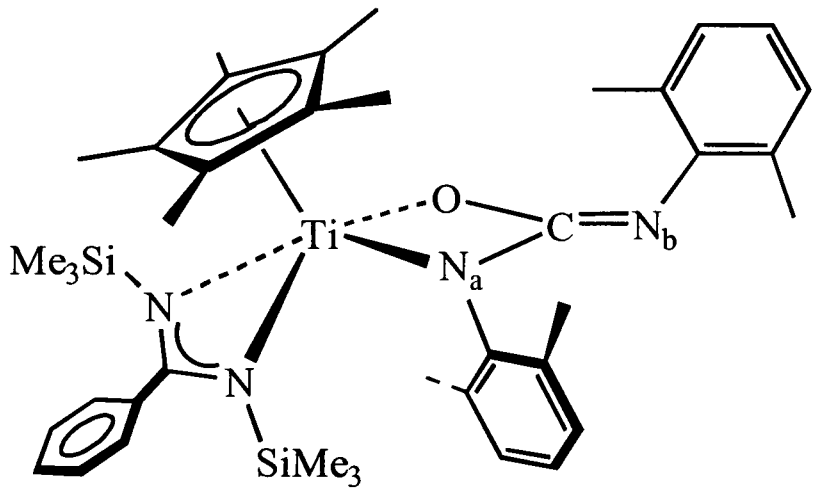
169.1	Me*C*N_2
148.2	*i*- 4-C_6H_4Me
147.1	*p*- 4-$C_6H_4NMe_2$
140.1	*i*- 4-$C_6H_4NMe_2$
129.2	*p*- 4-C_6H_4Me
128.6	*m*- 4-C_6H_4Me
128.1	C_5Me_5
125.7	*o*- 4-C_6H_4Me
124.8	*o*- 4-$C_6H_4NMe_2$
113.0	*m*- 4-$C_6H_4NMe_2$
50.6	N*C*H_bMeMe
49.8	N*C*H_aMeMe
41.4	N*Me*$_2$
25.0	NCH_aMe*Me*
24.7	NCH_a*Me*Me

24.4	NCH_b*MeMe*
21.5	4-C_6H_4*Me*
14.6	*Me*CN_2
13.0	C_5*Me*$_5$

I.R. data (KBr plates, Nujol mull)

2955 (s), 2727 (w),1655 (w), 1613 (w), 1568 (m, sh), 1503 (m, br), 1341 (w), 1317 (w), 1260 (w), 1207 (w), 1178 (w), 1161 (w), 1128 (w), 1064 (w), 1020 (w), 994 (w), 949 (w), 934 (w), 913 (w), 818 (w), 790 (w), 754 (w), 723 (w), 643 (w), 600 (w), 523 (w), 491 (m) cm^{-1}

8.50 Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N-2,6-$C_6H_3Me_2$)O} {PhC($NSiMe_3$)$_2$} (47)



Appearance: Brown powder

Molecular Formula: $C_{40}H_{56}N_4OSi_2Ti$

Elemental analysis for $C_{40}H_{56}N_4OSi_2Ti$:

Satisfactory elemental analysis was not obtained for this compound

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.32 – 7.29	1 H , m		*p*- C_6H_5
7.25	2 H, d	J = 7.6 Hz	*m*- N_b-2,6-$C_6H_3Me_2$
7.11	1 H, d	J = 8.1 Hz	*m*- N_a-2,6-$C_6H_3Me_2$
7.06	1 H, d	J = 6.8 Hz	*m*- N_a-2,6-$C_6H_3Me_2$
7.04 – 6.97	6 H, m		Ar*H*
2.49	6 H, s		N_b-2,6-C_6H_3*Me*$_2$
2.46	3 H, s		N_a-2,6-C_6H_3*Me*Me

2.40	3 H, s	N_a-2,6-C_6H_3Me*Me*
1.89	15 H, s	C_5*Me*$_5$
-0.11	9 H, s	Si*Me*$_3$
-0.30	9 H, s	Si*Me*$_3$

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

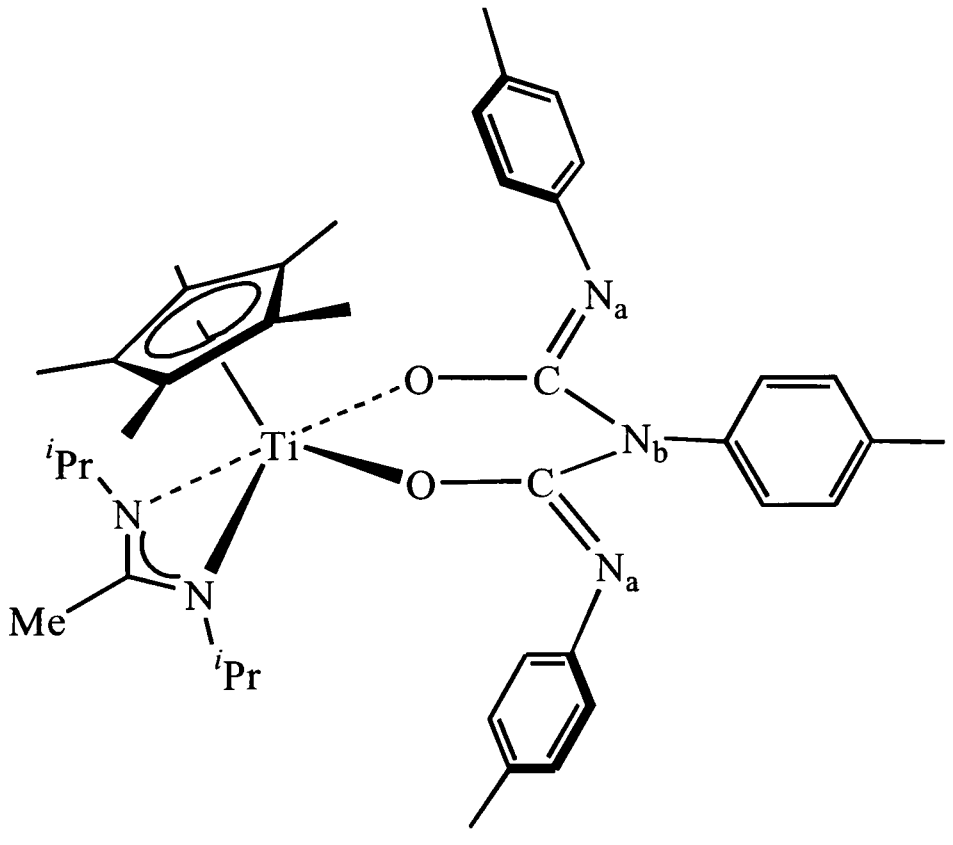
176.3	$C_6H_5CN_2$
153.1	O*C*N
148.3	*i*- N-2,6-$C_6H_3Me_2$
147.9	*i*- N-2,6-$C_6H_3Me_2$
137.3	*i*- C_6H_5
134.2	*o*- N-2,6-$C_6H_3Me_2$
133.7	*o*- N-2,6-$C_6H_3Me_2$
130.1	*o*- N-2,6-$C_6H_3Me_2$
129.5	*o*- C_6H_5
129.1	C_5Me_5
128.7	*p*- N_b-2,6-$C_6H_3Me_2$
128.3	*p*- N_a-2,6-$C_6H_3Me_2$
128.1	*m*- C_6H_5
127.9	*m*- N_a-2,6-$C_6H_3Me_2$
127.5	*m*- N_a-2,6-$C_6H_3Me_2$
125.0	*p*- C_6H_5
121.3	*m*- N_b-2,6-$C_6H_3Me_2$

20.6	N_b-2,6-C_6H_3*Me*$_2$
20.4	N_a-2,6-C_6H_3*Me*Me
19.6	N_a-2,6-C_6H_3Me*Me*
13.2	C_5*Me*$_5$
3.6	Si*Me*$_3$
3.3	Si*Me*$_3$

I.R. data (KBr plates, Nujol mull)

2727 (w), 2671 (w), 2359 (w), 2283 (w), 1895 (w), 1608 (s), 1580 (s), 1290 (m), 1259 (m), 1247 (s), 1231 (m), 1192 (w), 1157 (w), 1095 (m), 1077 (m), 1023 (m), 1003 (s), 990 (s), 952 (w), 928 (s), 840 (s), 786 (m), 758 (s), 725 (s), 708 (m), 625 (w), 590 (w), 556 (w), 509 (m), 499 (m), 456 (m), 427 (w), 403 (w) cm^{-1}

8.51 Ti(η-C_5Me_5){OC(N-4-C_6H_4Me)N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (48)



Appearance: Brown powder

Molecular formula: $C_{41}H_{53}N_5O_2Ti$

Elemental analysis for $C_{41}H_{53}N_5O_2Ti$:

Found (calculated) % : C 70.8 (70.8); H 7.8 (7.7); N 9.7 (10.1)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.61	2 H, d	J = 8.6 Hz	*o*- N_b-4-C_6H_4Me
7.16	4 H, d	J = 8.6 Hz	*o*- N_a-4-C_6H_4Me
7.10	2 H, d	J = 8.6 Hz	*m*- N_b-4-C_6H_4Me
7.02	4 H, d	J = 8.6 Hz	*m*- N_a-4-C_6H_4Me
3.43	2 H, apparent sept	J = 7.1 Hz	NC*H*MeMe

2.17	6 H, s		N_a-4-C_6H_4*Me*
2.05	3 H, s		N_b-4-C_6H_4*Me*
1.85	15 H, s		C_5*Me*$_5$
1.44	3 H, s		*Me*CN_2
0.91	6 H, d	J = 7.1 Hz	NCH*Me*Me
0.83	6 H, d	J = 6.8 Hz	NCHMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d$_6$)

169.5	Me*C*N_2
153.1	*i*- N_a-4-C_6H_4Me
147.7	*p*- N_a-4-C_6H_4Me
142.2	*i*- N_b-4-C_6H_4Me
135.2	*p*- N_b-4-C_6H_4Me
130.0	*o*- N_b-4-C_6H_4Me
129.7	*m*- N_b-4-C_6H_4Me
129.4	*m*- N_a-4-C_6H_4Me
128.6	*o*- N_a-4-C_6H_4Me
124.3	C_5Me$_5$
49.5	N*C*HMeMe
23.9	NCH*Me*Me
23.5	NCHMe*Me*
21.1	N_b-4-C_6H_4*Me*
21.0	N_a-4-C_6H_4*Me*
16.4	*Me*CN_2

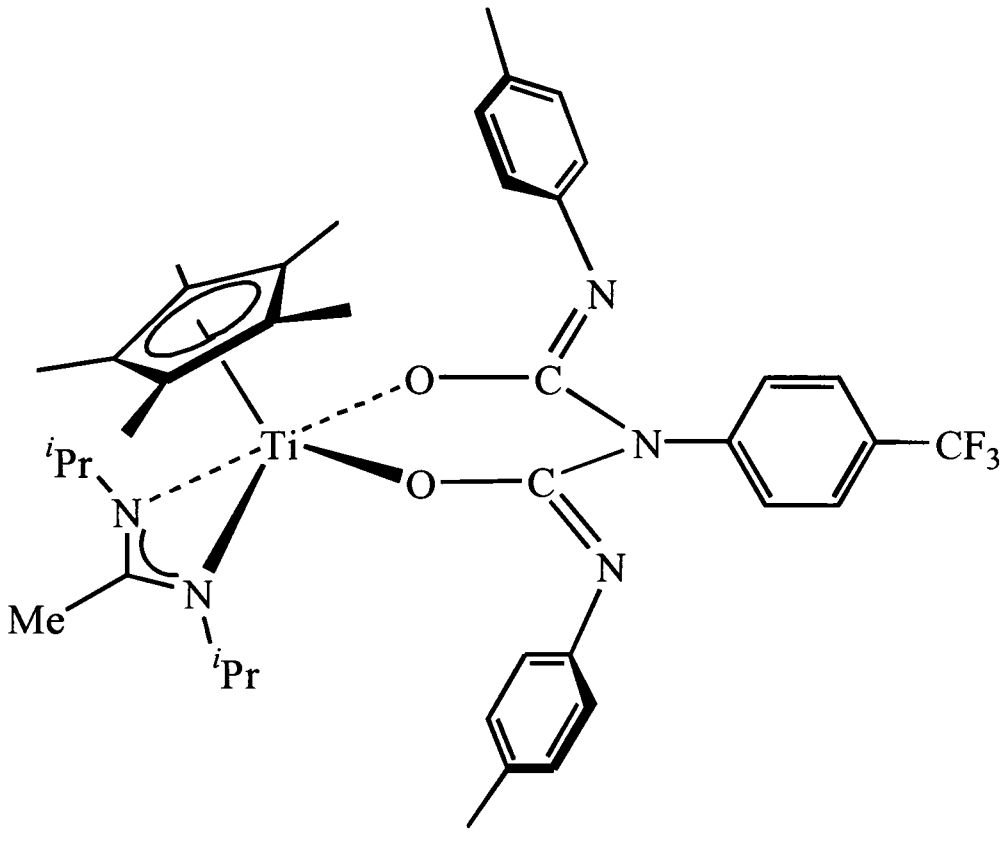
12.31 C_5Me_5

OC(N)(N) resonance not observed

I.R. data (KBr plates, Nujol mull)

2728 (w), 2671 (w), 1882 (w), 1733 (w), 1655 (s), 1609 (m), 1572 (m), 1538 (s), 1505 (s), 1292 (m, br), 1209 (w), 1145 (w), 1107 (w), 1072 (w), 1021 (w), 998 (w), 946 (m), 891 (w), 813 (s), 791 (m), 723 (m), 670 (w), 638 (w), 616 (w), 584 (w), 549 (w), 519 (w), 442 (w), 417 (w), 407 (w) cm^{-1}

8.52 Ti(η-C_5Me_5){OC(N-4-C_6H_4Me)N(-4-$C_6H_4CF_3$)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (49)



Appearance: Brown powder

Molecular formula: $C_{41}H_{50}F_3N_5O_2Ti$

Elemental analysis for $C_{41}H_{50}F_3N_5O_2Ti$:

Found (calculated) % : C 65.7 (65.0); H 6.7 (6.6); N 8.8 (9.3)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.58	2 H, d	J = 8.5 Hz	*o*- 4-$C_6H_4CF_3$
7.48	2 H, d	J = 8.5 Hz	*m*- 4-$C_6H_4CF_3$
7.12	4 H, d	J = 8.3 Hz	*o*- 4-C_6H_4Me
7.02	4 H, d	J = 8.3 Hz	*m*- 4-C_6H_4Me

3.41	2 H, apparent sept	J = 6.8 Hz	NC*H*MeMe
2.17	6 H, s		4-C_6H_4*Me*
1.83	15 H, s		C_5*Me*$_5$
1.41	3 H, s		*Me*CN_2
0.89	6 H, d	J = 6.8 Hz	NCH*Me*Me
0.82	6 H, d	J = 6.8 Hz	NCHMe*Me*

^{19}F NMR data (282.4 MHz, 298 K, benzene-d_6)

-62.08	CF_3

^{13}C-{^{1}H} NMR data (75.5 MHz, 298 K, benzene-d_6)

169.3	Me*C*N_2
152.5	*i*- 4-C_6H_4Me
147.1	*p*- 4-C_6H_4Me
130.8	*o*- 4-$C_6H_4CF_3$
130.2	*i*- 4-$C_6H_4CF_3$
130.1	*p*- 4-$C_6H_4CF_3$
128.7	*m*- 4-C_6H_4Me
128.5	*C*$_5$Me$_5$
125.7	*m*- 4-$C_6H_4CF_3$
124.2	*o*- 4-C_6H_4Me
50.0	NCHMeMe

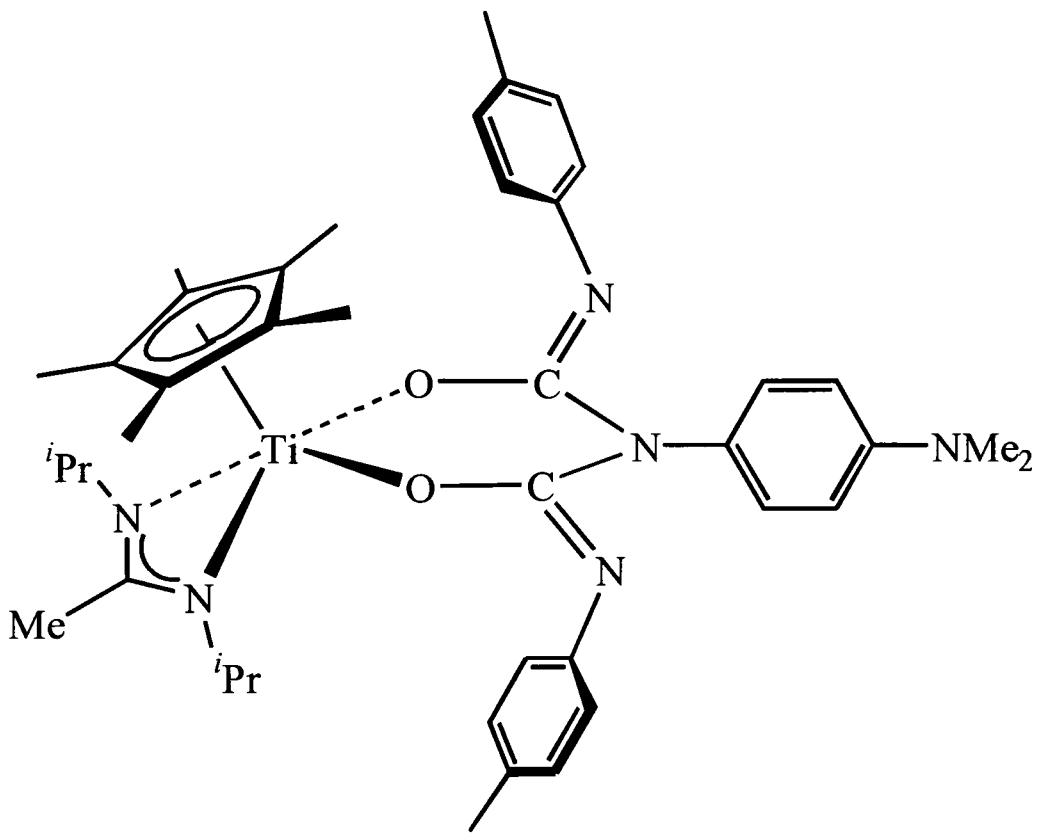
24.3	NCH*Me*Me
23.9	NCHMe*Me*
21.4	4-C_6H_4*Me*
16.8	*Me*CN_2
12.8	C_5*Me*$_5$

CF_3, OC(N)(N) resonances not observed

I.R. data (KBr plates, Nujol mull)

2955 (s), 2727 (w), 1628 (w), 1577 (m, sh), 1508 (w), 1323 (s), 1262 (w), 1209 (w), 1161 (w), 1121 (m), 1105 (m), 1081 (w), 1066 (m), 1001 (w), 944 (w), 886 (w), 810 (m), 795 (m), 724 (m), 685 (w), 663 (w), 643 (w), 596 (w), 548 (w), 501 (w), 470 (w) cm^{-1}

8.53 Ti(η-C_5Me_5){OC(N-4-C_6H_4Me)N(-4-$C_6H_4NMe_2$)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (50)



Appearance: Brown powder

Molecular formula: $C_{42}H_{56}N_6O_2Ti$

Elemental analysis for $C_{42}H_{56}N_6O_2Ti$:

Found (calculated) % : C 69.0 (69.6); H 7.1 (7.8); N 11.6 (11.6)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.63	2 H, d	J = 8.8 Hz	*o*- 4-$C_6H_4NMe_2$
7.19	4 H, d	J = 8.1 Hz	*o*- 4-C_6H_4Me
7.03	4 H, d	J = 8.1 Hz	*m*- 4-C_6H_4Me
6.68	2 H, d	J = 8.8 Hz	*m*- 4-$C_6H_4NMe_2$
3.44	2 H, apparent sept	J = 6.9 Hz	NC*H*MeMe

2.45	6 H, s		N*Me*$_2$
2.18	6 H, s		4-C_6H_4*Me*
1.87	15 H, s		C_5*Me*$_5$
1.44	3 H, s		*Me*CN_2
0.92	6 H, d	J = 6.9 Hz	NCH*Me*Me
0.84	6 H, d	J = 6.9 Hz	NCHMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d$_6$)

169.2	Me*C*N_2
153.3	*i*- 4-C_6H_4Me
148.9	*p*- 4-$C_6H_4NMe_2$
148.0	*p*- 4-C_6H_4Me
134.4	*i*- 4-$C_6H_4NMe_2$
130.4	*o*- 4-$C_6H_4NMe_2$
129.5	C_5Me_5
128.6	*m*- 4-C_6H_4Me
124.4	*o*- 4-C_6H_4Me
113.2	*m*- 4-$C_6H_4NMe_2$
49.8	N*C*HMeMe
40.8	N*Me*$_2$
24.4	NCH*Me*Me
24.0	NCHMe*Me*
21.5	4-C_6H_4*Me*
16.9	*Me*CN_2

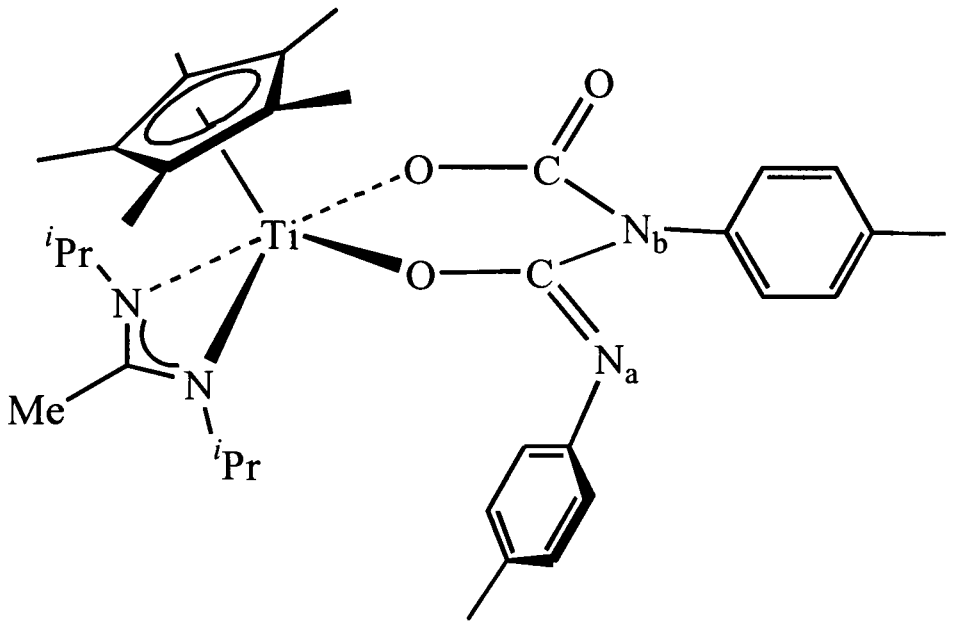
12.8 C_5Me_5

OC(N)(N) resonance not observed

I.R. data (CsBr plates, Nujol mull)

2955 (s), 2924 (s), 2727 (w), 2359 (w), 1716 (w), 1570 (s), 1507 (s), 1312 (m), 1261 (m), 1204 (m), 1182 (m), 1163 (m), 1128 (m), 1105 (m), 1076 (m), 1019 (m), 996 (m), 948 (m), 918 (w), 879 (m), 810 (s), 792 (s), 756 (w), 723 (s), 681 (w), 643 (w), 591 (w), 547 (w), 503 (w), 471 (w), 450 (w), 421 (w), 405 (w) cm^{-1}

8.54 Ti(η-C_5Me_5){OC(O)N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O} {$MeC(N^iPr)_2$} (51)



Appearance: Red-brown powder

Molecular formula: $C_{34}H_{46}N_4O_3Ti$

Elemental analysis for $C_{34}H_{46}N_4O_3Ti$:

Found (calculated) % : C 67.2 (67.2); H 8.1 (7.6); N 8.5 (9.2)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.51	2 H, d	J = 8.0 Hz	*o*- N_a-4-C_6H_4Me
7.08	2 H, d	J = 8.1 Hz	*o*- N_b-4-C_6H_4Me
7.06*	2 H, d	J = 8.0 Hz	*m*- N_a-4-C_6H_4Me
7.02	2 H, d	J = 8.1 Hz	*m*- N_b-4-C_6H_4Me
3.47	1 H, apparent sept	J = 6.9 Hz	NCH_aMeMe
3.38	1 H, apparent sept	J = 6.9 Hz	NCH_bMeMe
2.17	3 H, s		N_b-4-C_6H_4Me

2.05	3 H, s		N_a-4-C_6H_4*Me*
1.89	15 H, s		C_5*Me*$_5$
1.36	3 H, s		*Me*CN_2
1.10	3 H, d	J = 6.8 Hz	NCH_a*Me*Me
1.09	3 H, d	J = 6.8 Hz	NCH_aMe*Me*
0.89	3 H, d	J = 6.8 Hz	NCH_b*Me*Me
0.86*	3 H, d	J = 6.8 Hz	NCH_b*Me*Me

* indicates cross peak in NOESY experiment

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

169.5	Me*C*N_2
154.3	O*C*O
153.5	*i*- N_a-4-C_6H_4Me
147.5	*p*- N_a-4-C_6H_4Me
140.7	*p*- N_b-4-C_6H_4Me
135.7	*i*- N_b-4-C_6H_4Me
130.4	*C*$_5$Me$_5$
129.6	*m*- N_a-4-C_6H_4Me
129.4	*o*- N_b-4-C_6H_4Me
127.5	*m*- N_b-4-C_6H_4Me
123.9	*o*- N_a-4-C_6H_4Me
50.3	N*C*H_aMeMe
49.9	N*C*H_bMeMe

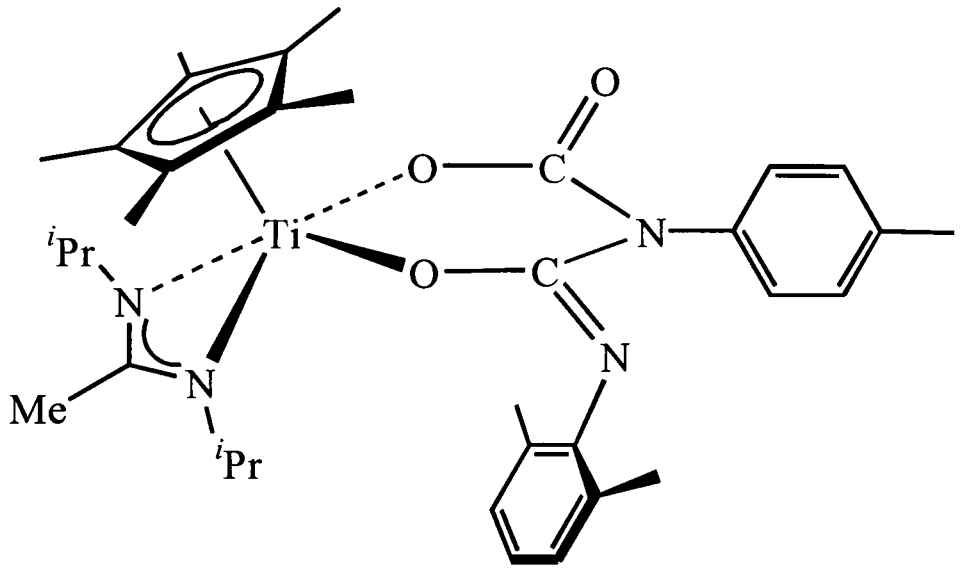
24.3	$NCH_a\mathit{Me}Me$
23.9	$NCH_b\mathit{Me}Me$
23.7	$NCH_{a,b}Me\mathit{Me}$
21.1	N_a-4-$C_6H_4\mathit{Me}$
21.0	N_b-4-$C_6H_4\mathit{Me}$
14.9	$\mathit{Me}CN_2$
12.5	$C_5\mathit{Me}_5$

OC(N)(N) resonance not observed

I.R. data (KBr plates, Nujol mull)

2955 (s), 2726 (w), 2272 (w), 1681 (m), 1618 (m), 1592 (m, br), 1507 (m), 1408 (w), 1258 (w), 1206 (w), 1183 (w), 1103 (w), 1068 (w), 1024 (w), 1001 (m), 933 (w), 883 (w), 859 (w), 812 (m), 788 (m), 736 (w), 723 (w), 680 (w), 643 (w), 604 (w), 587 (w), 545 (w), 533 (w), 474 (w), 445 (w) cm^{-1}

8.55 Ti(η-C_5Me_5){OC(O)N(-4-C_6H_4Me)C(N-2,6-$C_6H_3Me_2$)O} {$MeC(N^iPr)_2$} (52)



Appearance: Brown powder

Molecular formula: $C_{35}H_{48}N_4O_3Ti$

Elemental analysis for $C_{35}H_{48}N_4O_3Ti$:

Found (calculated) % : C 67.7 (67.3); H 7.8 (7.8); N 9.0 (8.6)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.53	2 H, d	J = 8.1 Hz	*o*- 4-C_6H_4Me
7.13	2 H, d	J = 8.1 Hz	*m*- 4-C_6H_4Me
7.03	1 H, d, br	J = 7.1 Hz	*m*- 2,6-$C_6H_3Me_2$
6.93	1 H, d, br	J = 7.1 Hz	*m*- 2,6-$C_6H_3Me_2$
6.87	1 H, t	J = 7.1 Hz	*p*- 2,6-$C_6H_3Me_2$
3.37	1 H, apparent sept	J = 6.6 Hz	NCH_aMeMe
3.02	1 H, apparent sept	J = 6.6 Hz	NCH_bMeMe

2.29	3 H, s, br		2,6-C_6H_3*Me*Me
2.11	3 H, s		C_6H_4*Me*
1.99	3 H, s, br		2,6-C_6H_3Me*Me*
1.94	15 H, s		C_5*Me*$_5$
1.39	3 H, s		*Me*CN_2
1.15	3 H, d	J = 6.6 Hz	NCH_a*Me*Me
1.08	3 H, d	J = 6.6 Hz	NCH_aMe*Me*
0.85	3 H, d	J = 6.5 Hz	NCH_b*Me*Me
0.58	3 H, d	J = 6.5 Hz	NCH_bMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

169.1	Me*C*N_2
154.2	O*C*O
151.2	*i*- 2,6-$C_6H_3Me_2$
147.5	*o*- 2,6-$C_6H_3Me_2$
140.8	*i*- 4-C_6H_4Me
135.9	*p*- 4-C_6H_4Me
131.1	*C*$_5$Me$_5$
129.5	*o*- 4-C_6H_4Me
129.4	*m*- 4-C_6H_4Me
128.9	*m*- 2,6-$C_6H_3Me_2$
125.5	*m*- 2,6-$C_6H_3Me_2$
121.3	*p*- 2,6-$C_6H_3Me_2$
51.5	N*C*H_aMeMe

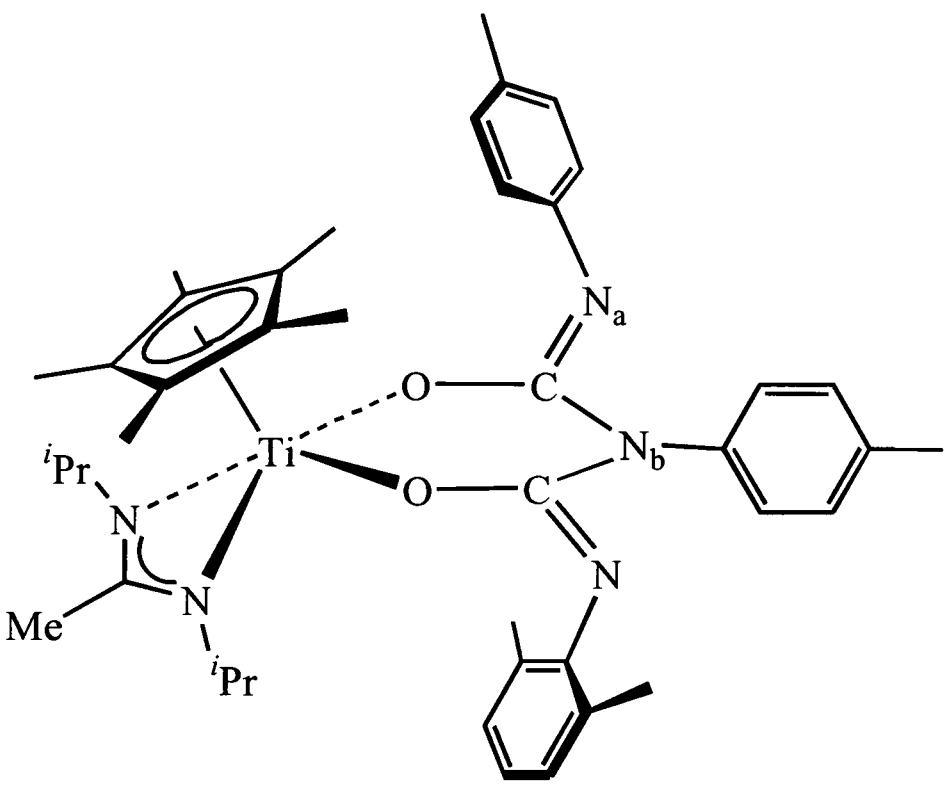
51.0	N*C*H_bMeMe
26.9	NCH$_b$*Me*Me
24.2	NCH$_a$Me*Me*
24.1	NCH$_a$*Me*Me
23.4	NCH$_b$Me*Me*
21.5	4-C_6H_4*Me*
19.5	2,6-C_6H_3*Me*Me
19.3	2,6-C_6H_3Me*Me*
13.4	C_5*Me*$_5$
13.3	*Me*CN_2

OC(N)(N) resonance not observed

I.R. data (KBr plates, Nujol mull)

2926 (s), 2725 (w), 1680 (s), 1620 (s), 1587 (s), 1514 (m, sh), 1313 (m), 1243 (m), 1203 (m), 1184 (m), 1105 (w), 1083 (w), 1025 (w), 1001 (s), 932 (w), 919 (w), 876 (w), 857 (w), 819 (m, br), 795 (m), 773 (m), 733 (w), 678 (w), 605 (w), 587 (w), 567 (w), 537 (w), 523 (w), 481 (w), 410 w cm^{-1}

8.56 Ti(η-C_5Me_5){OC(N-4-C_6H_4Me)N(-4-C_6H_4Me)C(N-2,6-$C_6H_3Me_2$)O}{$MeC(N^iPr)_2$} (53)



Appearance: Red-brown powder

Molecular formula: $C_{42}H_{55}N_5O_2Ti$

Elemental analysis for $C_{42}H_{55}N_5O_2Ti$:

Found (calculated) % : C 71.3 (71.1); H 7.6 (7.8); N 9.1 (9.9)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.61	2 H, d	J = 8.1 Hz	*o*- N_b-C_6H_4Me
7.15 – 7.13	4 H, m		*o*- N_a-C_6H_4Me,
			m- N-$C_6H_4Me_a$
7.04	2 H, d	J = 8.1 Hz	*m*- N_b-C_6H_4Me
7.02	1 H, m		*m*- 2,6-$C_6H_3Me_2$

6.94	1 H , m		*m*- 2,6-$C_6H_3Me_2$
6.86	1 H, t	J = 7.5 Hz	*p*- 2,6-$C_6H_3Me_2$
3.50	1 H, apparent sept	J = 6.7 Hz	NCH_aMeMe
3.05	1 H, apparent sept	J = 6.7 Hz	NCH_bMeMe
2.35	3 H, s, br		2,6-C_6H_3*Me*Me
2.23	3 H, s		N_a-C_6H_4*Me*
2.14	3 H, s		N_b-C_6H_4*Me*
2.07	3 H, s, br		2,6-C_6H_3Me*Me*
1.85	15 H, s		C_5*Me*$_5$
1.51	3 H, s		*Me*CN_2
1.06	3 H, d	J = 6.8 Hz	NCH_a*Me*Me
1.01	3 H, d	J = 6.8 Hz	NCH_aMe*Me*
0.91	3 H, d	J = 6.1 Hz	NCH_b*Me*Me
0.61	3 H, d	J = 6.1 Hz	NCH_bMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

168.9	Me*C*N_2
153.4	*i*- N_a-C_6H_4Me
150.7	*i*- 2,6-$C_6H_3Me_2$
148.2	*o*- 2,6-$C_6H_3Me_2$
147.9	*p*- N_a-C_6H_4Me
142.6	*p*- N_b-C_6H_4Me
135.3	*i*- N_b-C_6H_4Me

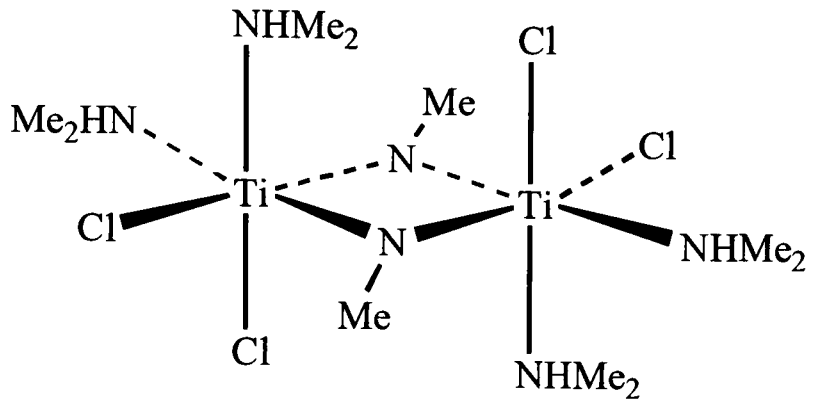
130.7	*o*- N_b-C_6H_4Me
129.9	C_5Me_5
129.6	*o*- 2,6-$C_6H_3Me_2$
129.4	*m*- N_b-C_6H_4Me
128.9	*m*- N_a-C_6H_4Me
128.3	*m*- 2,6-$C_6H_3Me_2$
127.9	*m*- 2,6-$C_6H_3Me_2$
124.2	*o*- N_a-C_6H_4Me
121.1	*p*- 2,6-$C_6H_3Me_2$
50.5	NCH_aMeMe
50.3	NCH_bMeMe
26.4	NCH_b*Me*Me
23.7	NCH_a*Me*Me
23.6	NCH_aMe*Me*
22.5	NCH_bMe*Me*
21.2	N_b-C_6H_4*Me*
21.1	N_a-C_6H_4*Me*
19.1	2,6-C_6H_3*Me*Me
19.1	2,6-C_6H_3Me*Me*
14.0	*Me*CN_2
12.7	C_5*Me*$_5$

O*C*(N)(N) resonances not observed

I.R. data (KBr plates, Nujol mull)

2725 (w), 2360 (w), 2273 (w), 1637 (m), 1614 (m), 1597 (m), 1581 (s), 1507 (m), 1311 (m), 1261 (m), 1252 (m), 1202 (s), 1171 (w), 1127 (w), 1103 (w), 1070 (m), 1031 (w), 997 (m), 931 (w), 875 (w), 848 (w), 811 (w), 785 (w), 759 (w), 729 (m), 678 (w), 659 (w), 604 (w), 586 (w), 566 (w), 541 (w), 520 (w), 475 (m), 446 (m) cm^{-1}

8.57 $[Ti(\mu\text{-}NMe)Cl_2(NHMe_2)_2]_2$ (54)



Appearance: Red powder

Molecular Formula: $C_{10}H_{34}Cl_4N_6Ti_2$

Elemental analysis for $C_{10}H_{34}Cl_4N_6Ti_2$:

Found (calculated) % : C 25.2 (25.2); H 7.2 (7.2); N 16.5 (17.7)

^{1}H NMR data (500.0 MHz, 298 K, dichloromethane-d_2)

4.26	6 H, s		N*Me*	
3.88	2 H, s, br		N*H*Me_2	- axial / equatorial
3.45	2 H, s, br		N*H*Me_2	- equatorial / axial
2.92	12 H, d	J = 6.1 Hz	NH*Me*$_2$	- axial / equatorial
2.69	12 H, d	J = 6.1 Hz	NH*Me*$_2$	- equatorial / axial

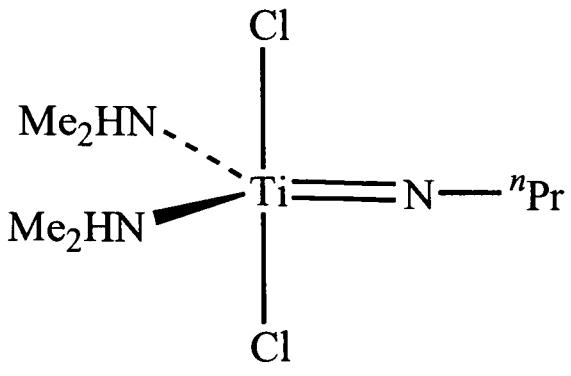
^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, dichloromethane-d_2)

60.27	N*Me*
42.33	NH*Me*$_2$ - axial / equatorial
40.83	NH*Me*$_2$ - equatorial / axial

I.R. data (KBr plates, Nujol mull)

3171 (m), 2727 (w), 1307 (w), 1282 (w), 1260 (w), 1212 (w), 1115 (m), 1078 (m), 1062 (m), 1018 (m), 894 (m), 844 (w), 806 (w), 723 (w), 682 (w), 587 (m, br), 521 (w), 464 (w) cm^{-1}

8.58 $Ti(N^nPr)Cl_2(NHMe_2)_2$ (55)



Appearance: Red powder

Molecular Formula: $C_{14}H_{42}Cl_4N_6Ti_2$

Elemental analysis for $C_{14}H_{42}Cl_4N_6Ti_2$:

Satisfactory elemental analysis was not obtained for this compound

^1H NMR data (500.0 MHz, 298 K, benzene-d_6)

3.13	4 H, t	J = 6.9 Hz	$NC\mathit{H}_2CH_2CH_3$
2.67	4 H, s, br		$N\mathit{H}Me_2$
2.27	24 H, d	J = 6.2 Hz	$\mathit{N}H\mathit{Me}_2$
1.35	4 H, apparent qt	J = 6.9 Hz	$NCH_2C\mathit{H}_2CH_3$
0.97	6 H, t	J = 6.9 Hz	$NCH_2CH_2C\mathit{H}_3$

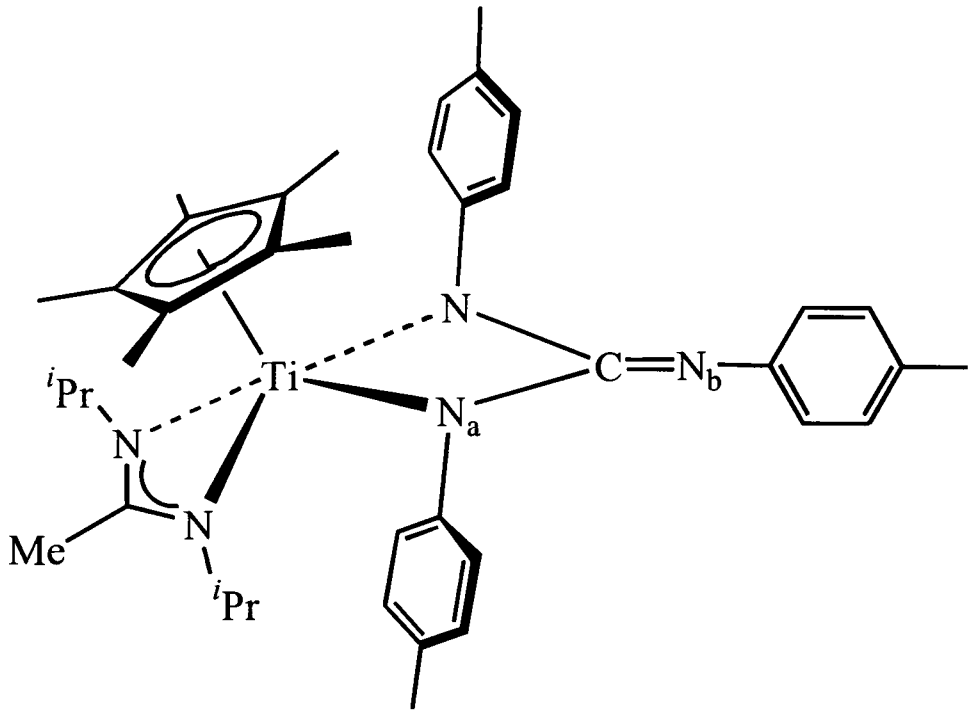
^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

71.3	$NCH_2CH_2CH_3$
39.5	$NHMe_2$
25.7	$NCH_2CH_2CH_3$
10.8	$NCH_2CH_2CH_3$

I.R. data (KBr plates, Nujol mull)

3234 (w), 3169 (m), 2726 (w), 1398 (w), 1322 (w), 1286 (w), 1259 (w), 1259 (m), 1235 (m), 1168 (w), 1115 (w), 1098 (w), 1061 (m), 1021 (m), 897 (m), 807 (w), 723 (m), 578 (m), 463 (m) cm^{-1}

8.59 Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-4-C_6H_4Me)N(-4-C_6H_4Me)}{MeC(N^{i}Pr)$_2$} (56)



Appearance: Brown powder

Molecular formula: $C_{40}H_{53}N_5Ti$

Elemental analysis for $C_{40}H_{53}N_5Ti$:

Found (calculated) % : C 73.1 (73.7); H 8.7 (8.2); N 10.8 (10.8)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d$_6$)

7.24	4 H, d (br)		*m*- N_a-4-C_6H_4Me
6.97	2 H, d	J = 8.3 Hz	*m*- N_b-4-C_6H_4Me
6.92	4 H, d	J = 7.8 Hz	*o*- N_a-4-C_6H_4Me
6.85	2 H, d	J = 8.3 Hz	*o*- N_b-4-C_6H_4Me
3.69	2 H, apparent sept	J = 7.1 Hz	NC*H*MeMe

2.11	6 H, s		N_a-4-C_6H_4*Me*
2.02	3 H, s		N_b-4-C_6H_4*Me*
1.87	15 H, s		C_5*Me*$_5$
1.54	3 H, s		*Me*CN_2
1.02	6 H, d	J = 7.1 Hz	NCH*Me*Me
0.73	6H, d	J = 7.1 Hz	NCHMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

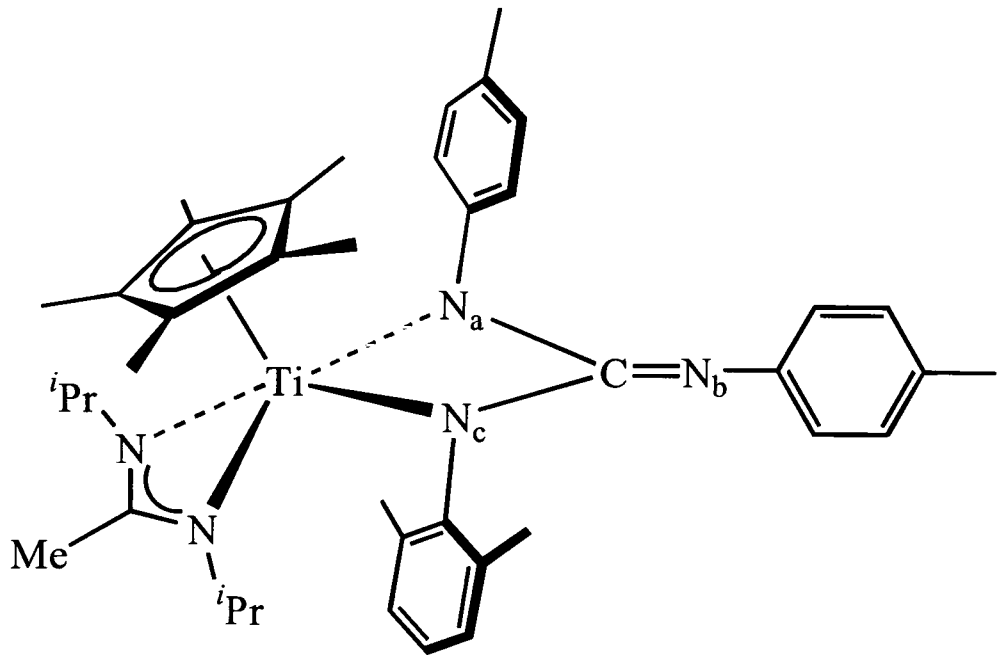
173.6	N_2*C*N
166.6	Me*C*N_2
149.7	*i*- N_b-4-C_6H_4Me
148.3	*p*- N_b-4-C_6H_4Me
147.6	*i*- N_a-4-C_6H_4Me
130.1	*p*- N_a-4-C_6H_4Me
128.6	*o*- N_b-4-C_6H_4Me
128.3	*o*- N_a-4-C_6H_4Me
127.7	*C*$_5$Me$_5$
123.8	*m*- N_a-4-C_6H_4Me
122.6	*m*- N_b-4-C_6H_4Me
49.3	N*C*HMeMe
24.1	NCH*Me*Me
23.1	NCHMe*Me*
20.9	N_a-4-C_6H_4*Me*

20.9	N_b-4-C_6H_4*Me*
18.8	*Me*CN_2
12.7	C_5*Me*$_5$

I.R. data (KBr plates, Nujol mull)

2728 (w), 2671 (w), 1882 (w), 1733 (w), 1655 (s), 1609 (m), 1572 (m), 1538 (s), 1505 (s), 1292 (m, br), 1209 (w), 1145 (w), 1107 (w), 1072 (w), 1021 (w), 998 (w), 946 (m), 891 (w), 813 (s), 791 (m), 723 (m), 670 (w), 638 (w), 616 (w), 584 (w), 549 (w), 519 (w), 442 (w), 417 (w), 407 (w) cm^{-1}

8.60 Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N-4-C_6H_4Me)N(-4-C_6H_4Me)}{$MeC(N^iPr)_2$} (57)



Appearance: Brown powder

Molecular formula: $C_{41}H_{55}N_5Ti$

Elemental analysis for $C_{41}H_{55}N_5Ti$:

Found (calculated) % : C 72.7 (74.0); H 8.6 (8.3); N 10.2 (10.5)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.41	2 H, d (br)	*m*- N_a-4-C_6H_4Me
7.01	2 H, d	*o*- N_a-4-C_6H_4Me
6.79	1 H, m	*p*- N-2,6-$Me_2C_6H_3$
6.72	2 H, d	*m*- N_b-4-C_6H_4Me
6.67	2 H, m	*m*-N-2,6-$Me_2C_6H_3$
6.62	2 H, d	*o*- N_b-4-C_6H_4Me

3.89	1 H, apparent sept		NC*H*$_a$MeMe
3.11	1 H, apparent sept		NC*H*$_b$MeMe
2.26	3 H, s		N$_a$-4-C$_6$H$_4$*Me*
2.19	6 H, s		N-2,6-C$_6$H$_3$*Me*$_2$
2.07	3 H, s		N$_b$-4-C$_6$H$_4$*Me*
1.81	15 H, s		C$_5$*Me*$_5$
1.56	3 H, s		*Me*CN$_2$
1.15	3 H, d	J = 6.8 Hz	NCH$_a$*Me*Me
1.06	3 H, d	J = 6.8 Hz	NCH$_a$Me*Me*
0.89	3 H, d	J = 6.8 Hz	NCH$_b$*Me*Me
0.31	3 H, s (br)		NCH$_b$Me*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d$_6$)

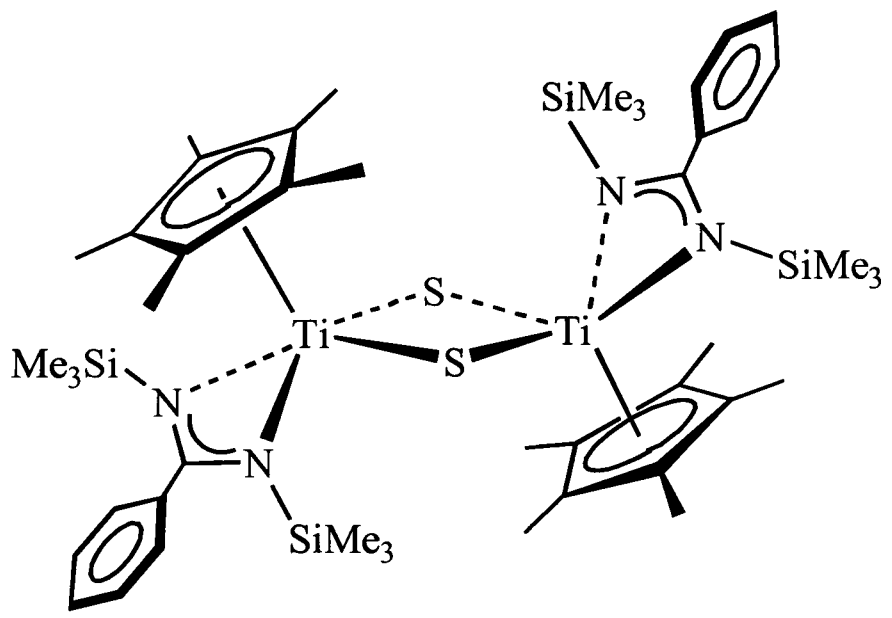
166.6	MeCN$_2$
149.9	*o*- 2,6-Me$_2$C$_6$H$_3$
149.0	*i*- N$_a$-4-C$_6$H$_4$Me
147.9	*m*-,*p*- 2,6-Me$_2$C$_6$H$_3$
133.6	*o*- 2,6-Me$_2$C$_6$H$_3$
131.4	*p*- N$_a$-4-C$_6$H$_4$Me
128.4	*m*- N$_a$-4-C$_6$H$_4$Me
128.3	*i*- N$_b$-4-C$_6$H$_4$Me
128.1	*o*- N$_a$-4-C$_6$H$_4$Me
127.4	*p*- N$_b$-4-C$_6$H$_4$Me

127.2	*o* -N_b-4-C_6H_4Me
126.8	C_5Me_5
121.1	*m*- N_b-4-C_6H_4Me
50.1	N*C*H_aMeMe
49.0	N*C*H_bMeMe
24.8	NCH_b*Me*Me
24.7	NCH_aMe*Me*
23.9	NCH_bMe*Me*
23.0	NCH_a*Me*Me
21.0	N_b-4-C_6H_4*Me*
20.9	2,6-C_6H_3*Me*Me
20.4	N_a-4-C_6H_4*Me*
19.5	2,6-C_6H_3Me*Me*
18.6	*Me*CN_2
12.8	C_5*Me*$_5$

I.R. data (KBr plates, Nujol mull)

2728 (w), 2671 (w), 1882 (w), 1733 (w), 1655 (s), 1609 (m), 1572 (m), 1538 (s), 1505 (s), 1292 (m, br), 1209 (w), 1145 (w), 1107 (w), 1072 (w), 1021 (w), 998 (w), 946 (m), 891 (w), 813 (s), 791 (m), 723 (m), 670 (w), 638 (w), 616 (w), 584 (w), 549 (w), 519 (w), 442 (w), 417 (w), 407 (w) cm^{-1}

8.61 $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}S)\{PhC(NSiMe_3)_2\}]_2$ (58)



Appearance: Red brown powder

Molecular formula: $C_{46}H_{76}N_4S_2Si_4Ti_2$

Elemental analysis for $C_{46}H_{76}N_4S_2Si_4Ti_2$:

Found (calculated) % : C 57.7 (57.7); H 7.5 (8.0); N 5.7 (5.9)

I.R. data (KBr plates, Nujol mull)

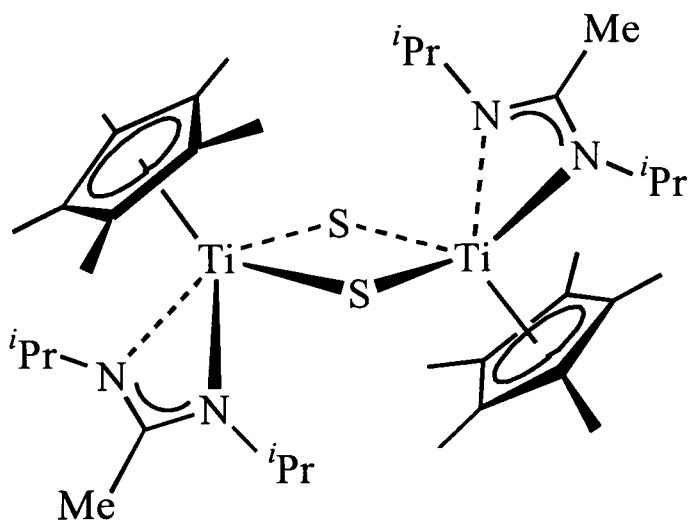
2726 (w), 1456 (s, br), 1259 (m), 1244 (s), 1160 (w), 1095 (m, br), 1020 (m, br), 1002 (w), 983 (s), 920 (w), 835 (s, br), 781 (w), 761 (m), 722 (m, br), 681 (w, br), 627 (w), 609 (w), 598 (w), 500 (m), 413 (m) cm^{-1}

Mass Spec. (E.I.)

m/z = 821 $[M\text{-}C_5Me_5]^+$

m/z = 789 $[M\text{-}C_5Me_5\text{-}S]^+$

8.62 $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}S)\{MeC(N^iPr)_2\}]_2$ (59)



Appearance: Brown powder

Molecular formula: $C_{36}H_{64}N_4S_2Ti_2$

Elemental analysis for $C_{36}H_{64}N_4S_2Ti_2$:

Found (calculated) % : C 60.7 (60.7); H 9.1 (9.1); N 7.5 (7.9)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

3.59	4 H, apparent sept	J = 6.6 Hz	NC*H*MeMe
2.28	30 H, s		C_5Me_5
1.81	6 H, s		$MeCN_2$
1.32	12 H, d	J = 6.6 Hz	NCH*Me*Me
1.26	12 H, d	J = 6.6 Hz	NCHMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

167.2	Me*C*N_2
125.7	*C*$_5$Me$_5$
49.6	N*C*HMeMe
25.7	NCHMe*Me*
24.8	NCH*Me*Me
15.5	*Me*CN_2
14.8	C_5*Me*$_5$

I.R. data (KBr plates, Nujol mull)

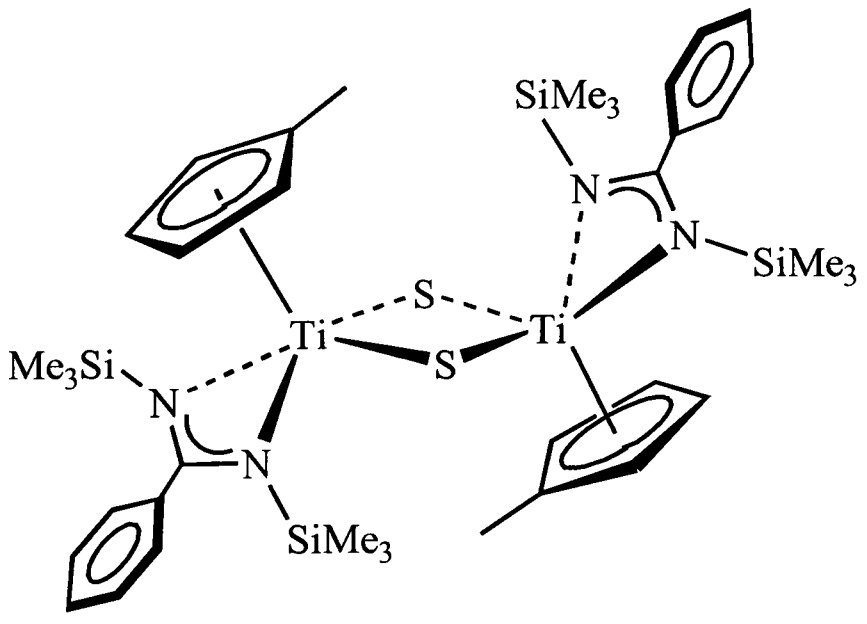
2721 (w), 1645 (w), 1558 (w), 1329 (s), 1296 (m), 1262 (m), 1206 (s), 1190 (s), 1169 (m), 1143 (m), 1114 (m), 1019 (m), 808 (m), 795 (m), 768 (w), 723 (w), 675 (w), 629 (w), 571 (w), 548 (w), 414 (s) cm^{-1}

Mass Spec (E.I.)

m/z = 712 $[M]^+$

m/z = 356 $[½M]^+$

8.63 $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}S)\{PhC(NSiMe_3)_2\}]_2$ (60)



Appearance: Dark yellow powder

Molecular Formula: $C_{38}H_{60}N_4S_2Si_4Ti_2$

Elemental analysis for $C_{38}H_{60}N_4S_2Si_4Ti_2$:

Found (calculated) %: C 57.3 (57.3), H 5.7 (7.6), N 7.0 (7.0)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.59	2 H, d	J = 6.8 Hz	*o*- C_6H_5
7.05	6 H, m		*m*-, *p*- C_6H_5
6.86	2 H, d	J = 6.8 Hz	*o*- C_6H_5
6.80	4 H, virtual triplet	J = 2.7 Hz	$C_5H_2(\beta)H_2(\alpha)Me$
6.35	4 H, virtual triplet	J = 2.7 Hz	$C_5H_2(\beta)H_2(\alpha)Me$
2.70	6 H, s		$C_5H_2(\beta)H_2(\alpha)Me$
0.01	18 H, s		$SiMe_3$

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

175.2	$C_6H_5CN_2$
139.9	*i*- $C_6H_5CN_2$
128.7	*o*- $C_6H_5CN_2$
128.6	*m*- $C_6H_5CN_2$
128.3	*p*- $C_6H_5CN_2$
126.5	$C_2(\beta)C_2(\alpha)CMe$
116.1	$C_2(\beta)C_2(\alpha)CMe$
114.9	$C_2(\beta)C_2(\alpha)CMe$
18.3	$C_2(\beta)C_2(\alpha)CMe$
3.06	$SiMe_3$

I.R. data (KBr plates, Nujol mull)

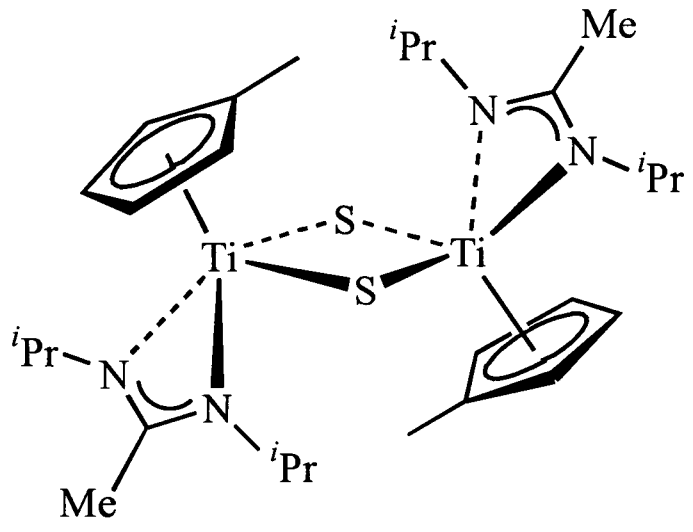
2726 (w), 2044 (w), 1600 (w), 1499 (m), 1244(s), 1170 (m), 1071 (w), 1055 (w), 1041 (w), 1031 (w), 1002 (m), 983 (s), 917 (m), 838 (s, br), 803 (s), 783 (m), 760 (s), 737 (m), 721 (s), 679 (w), 607 (w, br), 504 (s), 417 (s) cm^{-1}

Mass Spec. (E.I.)

m/z = 844 $[M]^+$

m/z = 422 $[½M]^+$

8.64 $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}S)\{PhC(NSiMe_3)_2\}]_2$ (61)



Appearance: Brown powder

Molecular formula: $C_{28}H_{48}N_4S_2Ti_2$

Elemental analysis for $C_{28}H_{48}N_4S_2Ti_2$:

Satisfactory elemental analysis was not obtained for this compound

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

6.57	4 H, virtual t		$C_5H_2(\beta)H_2(\alpha)Me$
6.39	4 H, virtual t		$C_5H_2(\beta)H_2(\alpha)Me$
3.45	4 H, apparent sept	J = 6.6 Hz	NC*H*MeMe
2.59	6 H, s		$C_5H_2(\beta)H_2(\alpha)Me$
1.55	6 H, s		$MeCN_2$
1.38	12 H, d	J = 6.6 Hz	NCH*Me*Me
1.12	12 H, d	J = 6.6 Hz	NCHMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

166.3	Me*C*N_2
127.4	$C_2(\beta)C_2(\alpha)$*C*Me
115.1	$C_2(\beta)$*$C_2(\alpha)$*CMe
114.3	*$C_2(\beta)$*$C_2(\alpha)$CMe
49.7	N*C*HMeMe
24.9	NCH*Me*Me
23.6	NCHMe*Me*
18.2	$C_2(\beta)C_2(\alpha)$C*Me*
9.99	*Me*CN_2

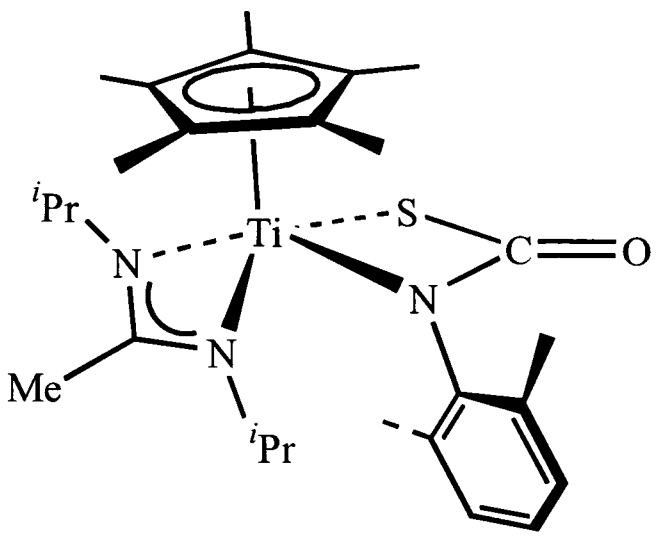
I.R. data (KBr plates, Nujol mull)

1340 (m), 1313 (w), 1261 (m), 1210 (w), 1173 (w), 1069 (w), 1038 (w), 935 (w), 859 (w), 804 (m), 723 (w), 684 (w) cm^{-1}

Mass Spec. (E.I.)

m/z = 600 $[M]^+$

8.65 Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(O)S}{MeC(N^{i}Pr)$_2$ (62)



Appearance: Dark brown powder

Molecular formula: $C_{27}H_{41}N_3OSTi$

Elemental analysis for $C_{27}H_{41}N_3OSTi$:

Found (calculated) % : C 64.5 (64.4); H 8.3 (8.2); N 8.1 (8.3); S 7.6 (6.4)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.03	1 H, m		*p*- 2,6-$C_6H_3Me_2$
6.99	2 H, m		*m*- 2,6-$C_6H_3Me_2$
3.25	1 H, apparent sept		NCH_aMeMe
2.97	1 H, apparent sept		NCH_bMeMe
2.32	3 H, s		2,6-C_6H_3*Me*Me
1.98	3 H, s		2,6-C_6H_3Me*Me*
1.92	15 H, s		C_5Me_5
1.36	3 H, s		*Me*CN_2
1.06	3 H, d	J = 6.6 Hz	NCH_a*Me*Me

1.03	3H, d	J = 6.6 Hz	NCH_aMeMe
0.76	3H, d	J = 6.4 Hz	NCH_bMeMe
0.43	3H, d	J = 6.4 Hz	NCH_bMeMe

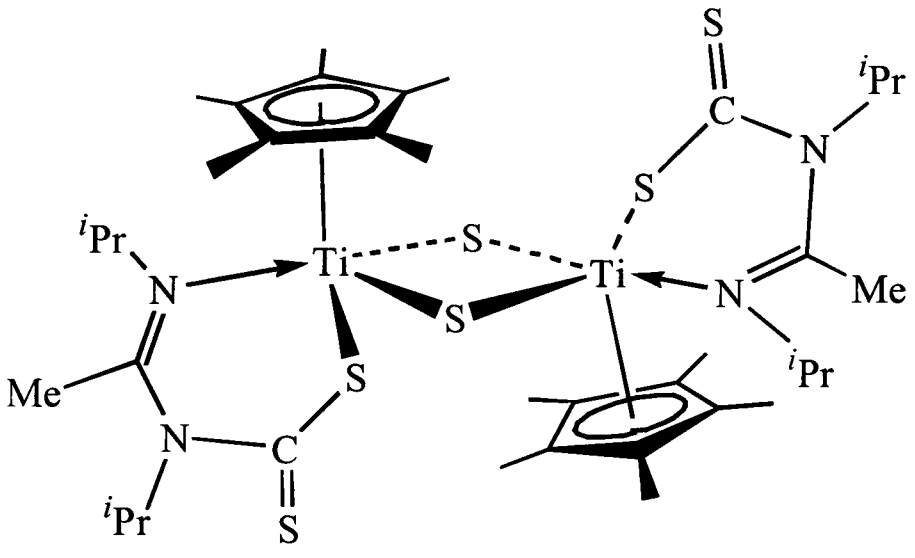
^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

195.8	S*C*O
169.4	Me*C*N_2
146.7	*i*- 2,6-$C_6H_3Me_2$
133.6	*o*- 2,6-$C_6H_3Me_2$
133.3	*o*- 2,6-$C_6H_3Me_2$
130.6	*m*- 2,6-$C_6H_3Me_2$
128.5	*m*- 2,6-$C_6H_3Me_2$
125.7	C_5Me_5
51.8	NCH_aMeMe
49.9	NCH_bMeMe
26.5	NCH_bMeMe
25.2	NCH_aMeMe
24.5	NCH_aMeMe
24.1	NCH_bMeMe
20.0	2,6-C_6H_3MeMe
19.6	2,6-C_6H_3MeMe
14.1	$MeCN_2$
13.5	C_5Me_5

I.R. data (KBr plates, Nujol mull)

2724(w), 2363 (w), 2274 (w), 1832 (w), 1718 (w), 1672 (m), 1648 (w), 1616 (s), 1581 (m, br), 1494 (m), 1403 (m), 1319 (s, br), 1253 (m), 1232 (s), 1205 (s), 1114 (w), 1094 (w), 1061 (w), 1011 (m, br), 956 (w), 938 (s), 883 (w), 819 (m), 790 (m), 763 (m), 724 (m), 698 (w), 676 (w), 631 (w), 581 (m), 550 (w), 491 (w), 447 (m), 417 (m), 402 (m) cm^{-1}

8.66 [Ti(η-C_5Me_5)(μ-S){N(^{i}Pr)C(Me)N(^{i}Pr)C(S)S}{MeC(N^{i}Pr)$_2$}]$_2$ (63)



Appearance: Brown powder

Molecular formula: $C_{38}H_{64}N_4S_6Ti_2$

Elemental analysis for $C_{38}H_{64}N_4S_6Ti_2$:

Found (calculated) % : C 52.6 (52.8); H 9.3 (7.5); N 6.0 (6.5) S 23.5 (22.2)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

5.19	4 H, apparent sept	J = 6.8 Hz	CNC*H*Me$_2$
3.38	4 H, apparent sept	J = 6.6 Hz	TiNC*H*Me$_2$
2.39	30 H, s		C_5*Me*$_5$
1.98	6 H, s		*Me*CN$_2$
1.25	6 H, d		CNCH*Me*Me
1.17	6 H, d		CNCHMe*Me*
1.06	12 H, d	J = 6.6 Hz	TiNCH*MeMe*

^{13}C-{^{1}H} NMR data (125 MHz, 298K, benzene-d_6)

202.3	*C*(S)S
154.1	Me*C*N_2
127.0	*C*$_5$Me$_5$
53.4	CN*C*HMeMe
51.7	TiN*C*HMeMe
23.2	TiNCH*MeMe*
20.7	CNCH*MeMe*
20.1	*Me*CN_2
14.6	C$_5$*Me*$_5$

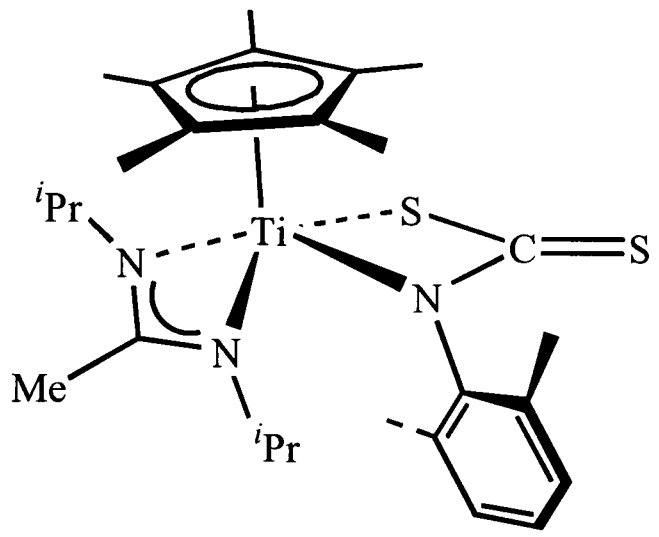
I.R. data (KBr plates, Nujol mull)

2955 (s), 2726 (w), 1398 (m), 1357 (s), 1343 (w), 1315 (w), 1261 (w), 1227 (m, br), 1169 (w), 1147 (m), 1123 (w), 1110 (w, br), 1063 (w), 1020 (w), 962 (w), 864 (w), 804 (w, br), 723 (m, br), 667 (w), 605 (w), 521 (w), 496 (w), 433 (m, br), 404 (m) cm^{-1}

Mass Spec. (E.I.)

m/z = 864 $[M]^+$

8.67 Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(S)S}{MeC(N^{i}Pr)$_2$ (64)



Appearance: Brown powder

Molecular formula: $C_{27}H_{41}N_3S_2Ti$

Elemental analysis for $C_{27}H_{41}N_3S_2Ti$:

Found (calculated) % : C 62.3 (62.4); H 8.3 (8.0); N 8.0 (8.1)

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.02 – 7.00	3 H, m		*m*-, *p*- 2,6-$C_6H_3Me_2$
3.08	1 H, apparent sept	J = 6.6 Hz	NCH_aMeMe
3.07	1 H, apparent sept	J = 6.6 Hz	NCH_bMeMe
2.23	3 H, s		2,6-C_6H_3*Me*Me
2.12	3 H, s		2,6-C_6H_3Me*Me*
1.85	15 H, s		C_5Me_5
1.45	3 H, s		*Me*CN_2
0.98	3 H, d	J = 6.6 Hz	NCH$_a$*Me*Me
0.91	3 H, d	J = 6.6 Hz	NCH$_a$Me*Me*

0.72	3 H, d	J = 6.6 Hz	NCH_bMeMe
0.34	3 H, d	J = 6.6 Hz	NCH_bMeMe

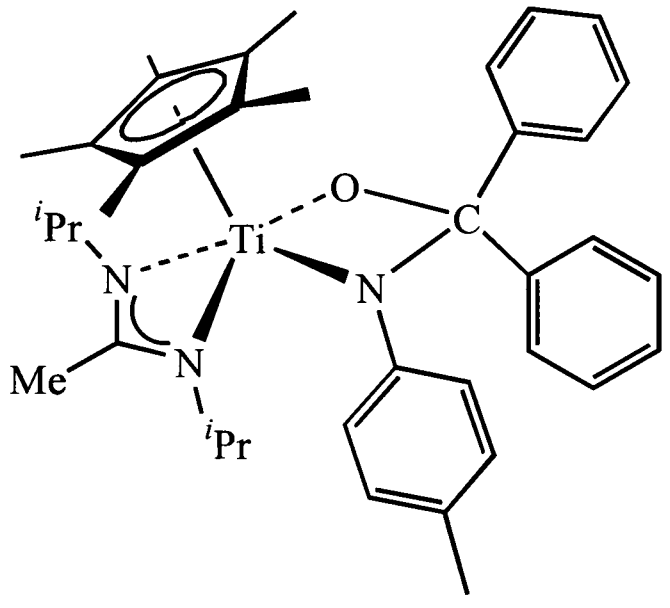
^{13}C-{^1H} NMR data (125.7 MHz, 298 K, benzene-d_6)

201.8	S*C*S
169.2	Me*C*N_2
148.2	*i*- 2,6-$C_6H_3Me_2$
135.1	*o*- 2,6-$C_6H_3Me_2$
134.1	*o*- 2,6-$C_6H_3Me_2$
133.3	*m*- 2,6-$C_6H_3Me_2$
130.3	C_5Me_5
125.7	*m*- 2,6-$C_6H_3Me_2$
125.4	*p*- 2,6-$C_6H_3Me_2$
52.5	NCH_bMeMe
49.7	NCH_aMeMe
26.0	NCH_bMeMe
24.5	NCH_aMeMe
23.7	NCH_bMeMe
23.1	NCH_aMeMe
19.3	2,6-C_6H_3MeMe
19.0	2,6-C_6H_3MeMe
14.8	$MeCN_2$
13.6	C_5Me_5

I.R. data (KBr plates, Nujol mull)

2721 (w), 2589 (w), 2364 (w), 1903 (w), 1762 (w), 1653 (w, br), 1623 (w), 1590 (w), 1563 (w, br), 1403 (s), 1344 (s), 1324 (s), 1296 (s), 1252 (s), 1198 (s), 1177 (s), 1125 (m), 1093 (s), 1055 (m), 1007 (s, br), 954 (w), 921 (w), 821 (s), 793 (s), 764 (s), 757 (s), 723 (m), 702 (m), 677 (m), 628 (w), 616 (w), 598 (w), 580 (w), 556 (m), 519 (m), 480 (w), 437 (s), 422 (s) cm^{-1}

8.68 Ti(η-C_5Me_5){N(-4-C_6H_4Me)C$(Ph)_2$O}{MeC(N^{i}Pr)$_2$ (65)



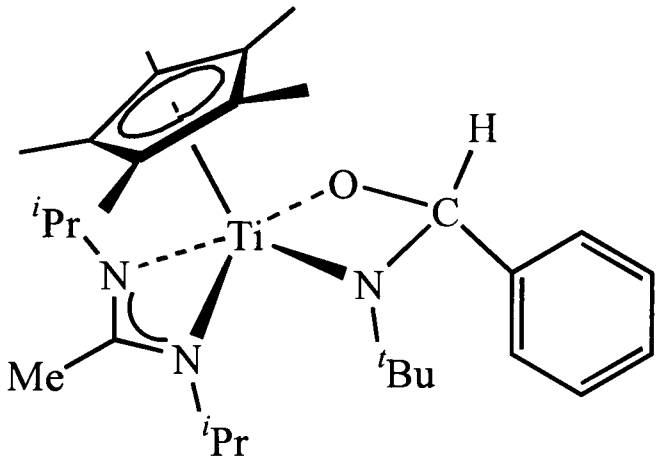
Molecular formula: $C_{38}H_{49}N_3OTi$

^{1}H NMR data (500.0 MHz, 233 K, toluene-d_8)

8.05 – 8.03	2 H, m		*o*- 4-C_6H_4Me
7.70	2 H, d	J = 7.6 Hz	*o*- C_6H_5 (a)
7.37 – 7.35	2 H, m		*o*- C_6H_5 (b)
7.21 – 7.19	2 H, m		*m*- 4-C_6H_4Me
7.13	1 H, t	J = 7.6 Hz	*p*- C_6H_5 (a)
7.10 – 7.07	3 H, m		*m*-, *p*- C_6H_5 (b)
7.05 – 7.01	2 H, m		*m*- C_6H_5 (a)
4.14	1 H, apparent sept	J = 7.0 Hz	NCH_aMeMe
3.55	1 H, apparent sept	J = 7.0 Hz	NCH_bMeMe
2.16	3 H, s		4-C_6H_4Me
1.95	15 H, s		C_5Me_5
1.67	3 H, s		$MeCN_2$

1.30	3 H, d	J = 7.0 Hz	NCH_aMeMe
1.19	3 H, d	J = 7.0 Hz	NCH_bMeMe
0.96	3 H, d	J = 7.0 Hz	NCH_bMeMe
0.72	3 H, d	J = 7.0 Hz	NCH_aMeMe

8.69 Ti(η-C_5Me_5){N(^{t}Bu)C(Ph)(H)O}{MeC(N^{i}Pr)$_2$ (66)

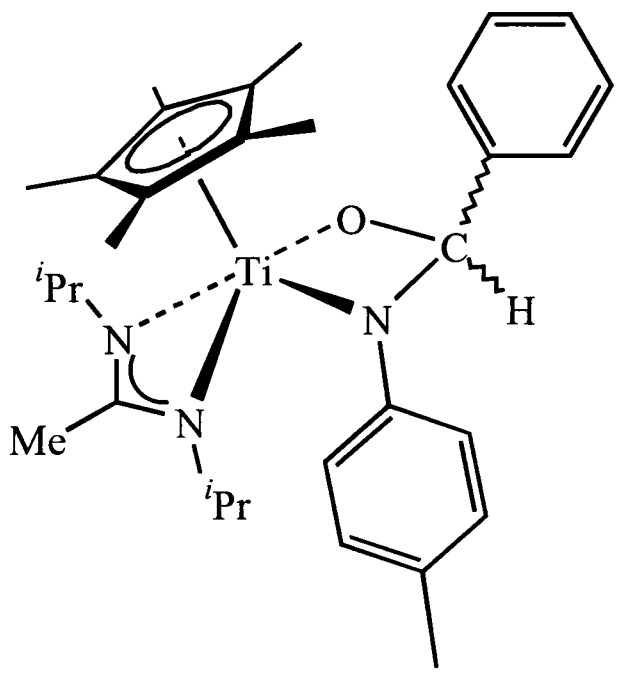


Molecular formula: $C_{29}H_{47}N_3OTi$

^{1}H NMR data (500.0 MHz, 289 K, benzene-d$_6$)

7.39	2 H, d	J = 7.1 Hz	*o*- C_6H_5
7.20 – 7.08	3 H, m		*m*-, *p*- C_6H_5
6.01	1 H, s		OC(H)
3.90	1 H, apparent sept	J = 6.8 Hz	NC*H$_a$*MeMe
3.58	1 H, apparent sept	J = 6.8 Hz	NC*H$_b$*MeMe
2.01	15 H, s		C_5*Me$_5$*
1.73	3 H, s		*Me*CN_2
1.31	3 H, d	J = 6.8 Hz	NCH$_a$*Me*Me
1.24	3 H, d	J = 6.8 Hz	NCH$_a$Me*Me*
1.12	3 H, d	J = 6.8 Hz	NCH$_b$*Me*Me
1.09	9 H, s		^{t}*Bu*
1.01	3 H, d	J = 6.5 Hz	NCH$_b$Me*Me*

8.70 Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(Ph)(H)O}{$MeC(N^iPr)_2$} (67A)



Appearance: Appears as first product

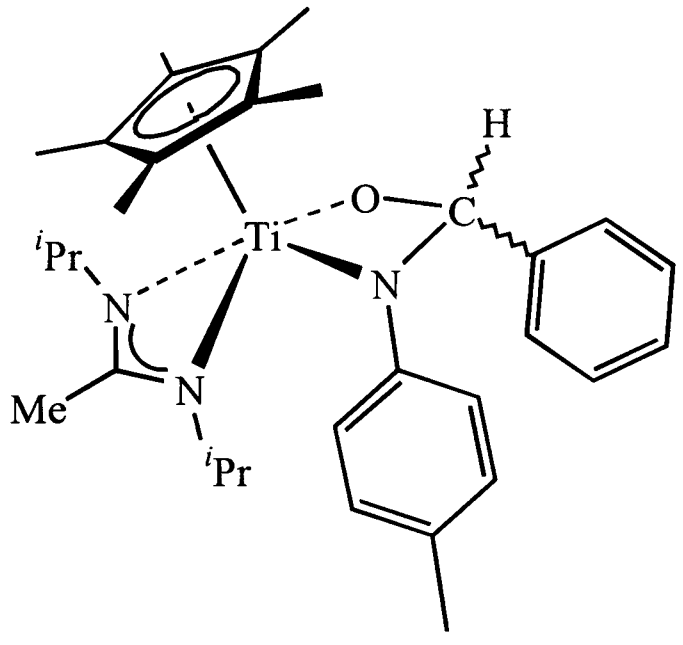
Molecular formula: $C_{32}H_{44}N_3OTi$

^{1}H NMR data (500.0 MHz, 289 K, benzene-d_6)

7.40	2 H, d	J = 6.8 Hz	*o*- C_6H_5
7.15 – 7.10	3 H, m		*m*-, *p*- C_6H_5
6.93	2 H, d	J = 8.5 Hz	*o*- 4-C_6H_4Me
6.65	2 H, d	J = 8.5 Hz	*m*- 4-C_6H_4Me
6.18	1 H, s		OC(H)
4.14	1 H, apparent sept	J = 7.0 Hz	NCH_aMeMe
3.54	1 H, apparent sept	J = 7.0 Hz	NCH_bMeMe
2.13	3 H, s		4-C_6H_4Me
1.97	15 H, s		C_5Me_5

1.58	3 H, s		MeCN$_2$
1.25	3 H, d	J = 7.1 Hz	NCH$_a$$Me$Me
1.12	3 H, d	J = 6.6 Hz	NCH$_b$$Me$Me
0.93	3 H, d	J = 7.0 Hz	NCH$_a$MeMe
0.81	3 H, d	J = 6.8 Hz	NCH$_b$MeMe

8.71 Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(Ph)(H)O}{$MeC(N^iPr)_2$} (67B)



Appearance: Appears as second product

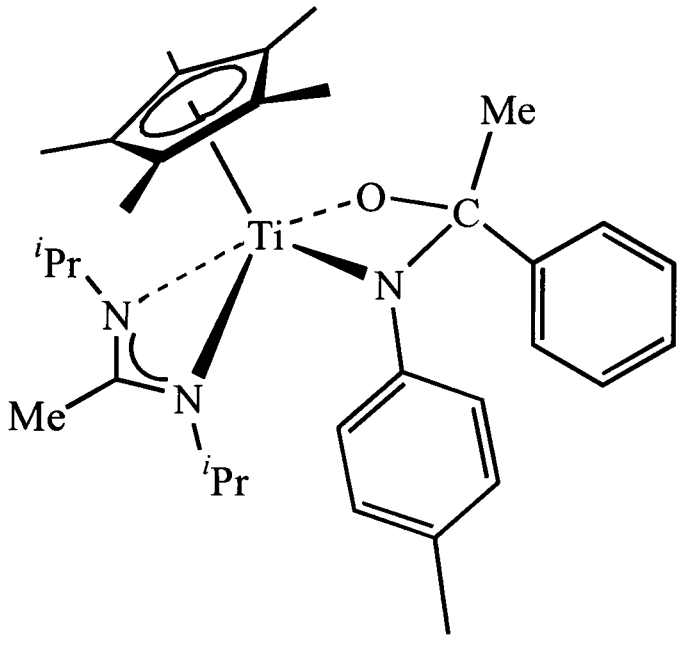
Molecular formula: $C_{32}H_{44}N_3OTi$

^{1}H NMR data (500.0 MHz, 289 K, benzene-d_6)

7.22	2 H, m		*o*- C_6H_5
7.15 – 7.10	3 H, m		*m*-, *p*- C_6H_5
6.84	2 H, d	J = 8.5 Hz	*o*- 4-C_6H_4Me
6.67	2 H, d	J = 8.5 Hz	*m*- 4-C_6H_4Me
6.24	1 H, s		OC(H)
3.30	1 H, apparent sept	J = 6.4 Hz	NCH_aMeMe
3.25	1 H, apparent sept	J = 6.4 Hz	NCH_bMeMe
2.10	3 H, s		4-C_6H_4*Me*
2.04	15 H, s		C_5*Me*$_5$
1.65	3 H, d	J = 6.7 Hz	NCH$_a$*Me*Me

1.14	3 H, d	J = 6.7 Hz	$NCH_aMe\mathit{Me}$
1.12	3 H, s		$\mathit{Me}CN_2$
1.04	3 H, d	J = 6.6 Hz	$NCH_b\mathit{Me}Me$
0.85	3 H, d	J = 6.4 Hz	$NCH_bMe\mathit{Me}$

8.72 Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(Ph)(Me)O}{MeC(N^{i}Pr)$_2$} (68)



Appearance: Brown waxy solid

Molecular formula: $C_{33}H_{47}N_3OTi$

^{1}H NMR data (500.0 MHz, 289 K, benzene-d_6)

7.37	2 H, d	J = 8.1 Hz	*o*- C_6H_5
7.18 – 7.13	1 H, m		*p*- C_6H_5
7.08	2 H, m		*m*- C_6H_5
6.89	2 H, d	J = 8.1 Hz	*o*- 4-C_6H_4Me
6.53	2 H, d	J = 8.1 Hz	*m*- 4-C_6H_4Me
6.18	1 H, s		OC(H)
4.10	1 H, apparent sept	J = 6.7 Hz	NCH_aMeMe
3.10	1 H, apparent sept	J = 6.7 Hz	NCH_bMeMe
2.14	3 H, s		4-C_6H_4Me
2.06	15 H, s		C_5Me_5

2.05	3 H, s		OC*Me*
1.53	3 H, s		*Me*CN_2
1.25	3 H, d	J = 6.7 Hz	NCH_a*Me*Me
1.12	3 H, d	J = 6.7 Hz	NCH_aMe*Me*
0.93	3 H, d	J = 6.7 Hz	NCH_b*Me*Me
0.81	3 H, d	J = 6.7 Hz	NCH_bMe*Me*

^{13}C-{^{1}H} NMR data (125.7 MHz, 289 K, benzene-d_6)

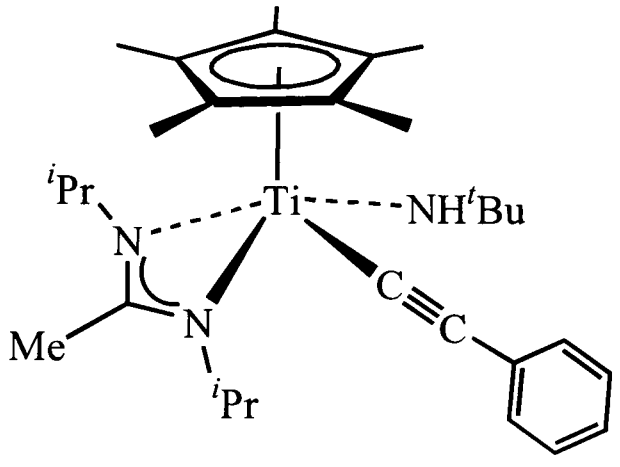
164.3	Me*C*N_2
148.6	*i*- / *p*- 4-C_6H_4Me
148.1	*p*- / *i*- 4-C_6H_4Me
128.9	*o*- 4-C_6H_4Me
128.5	*i*- C_6H_5
128.4	*p*- C_6H_5
127.6	*o*- C_6H_5
127.1	*m*- C_6H_5
124.3	C_5Me_5
118.4	*m*- 4-C_6H_4Me
84.1	O*C*Me
49.1	N*C*H_bMeMe
48.2	N*C*H_aMeMe
25.4	OC*Me*
24.5	NCH_bMe*Me*

24.4	NCH_aMeMe
23.6	NCH_bMeMe
23.2	NCH_aMeMe
20.7	$4\text{-}C_6H_4Me$
16.6	$MeCN_2$
12.4	C_5Me_5

IR data (KBr plates, Nujol mull)

1654 (m), 1636 (m), 1610 (m), 1578 (w), 1505 (s), 1311 (m), 1288 (m), 1262 (m), 1206 (w), 1171 (w), 1115 (m), 1088 (m), 1071 (m), 1027 (m), 914 (w), 899 (w), 841(w), 792 (m), 763 (w), 735 (w), 723 (w), 697 (w), 669 (w), 655 (w), 628 (w), 610 (w), 594 (w), 572 (w), 527 (w), 498 (w), 435 (w), 402 (w) cm^{-1}

8.73 Ti(η-C_5Me_5)(NH^{t}Bu)(η^1-C_2Ph){MeC(N^{i}Pr)$_2$ (69)

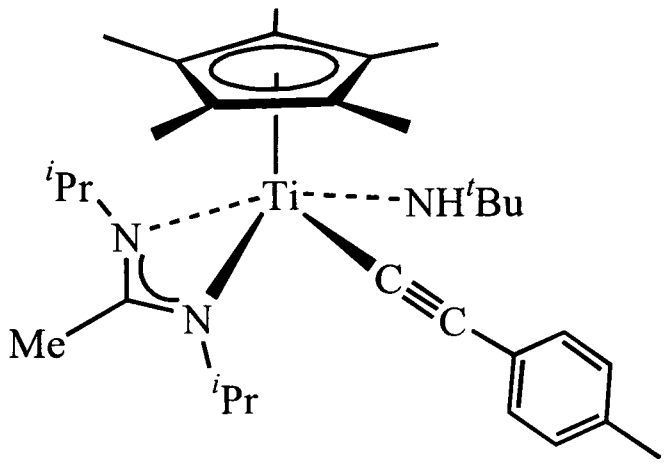


Molecular Formula: $C_{30}H_{47}N_3Ti$

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.93	1 H, s, br		N*H*^{t}Bu
7.59	2 H, d	J = 7.5 Hz	*o*- C_6H_5
7.15	3 H, m		*m*-, *p*- C_6H_5
4.13	1 H, apparent sept	J = 7.0 Hz	C*H*$_a$MeMe
3.18	1 H, apparent sept	J = 7.0 Hz	C*H*$_b$MeMe
2.06	15 H, s		C_5*Me*$_5$
1.66	3 H, s		*Me*CN_2
1.51	3 H, d	J = 7.0 Hz	NCH$_a$*Me*Me
1.33	9 H, s		^{t}*Bu*
1.27	3 H, d	J = 7.0 Hz	NCH$_a$Me*Me*
1.19	3 H, d	J = 7.0 Hz	NCH$_b$*Me*Me
1.05	3 H, d	J = 7.0 Hz	NCH$_b$Me*Me*

8.74 Ti(η-C_5Me_5)(NH^{t}Bu)(η^1-C_2-4-C_6H_4Me){MeC(N^{i}Pr)$_2$ (70)



Molecular Formula: $C_{31}H_{49}N_3Ti$

^{1}H NMR data (500.0 MHz, 298 K, benzene-d_6)

7.92*	1 H, s, br		N*H*^{t}Bu
7.56	2 H, d	J = 8.2 Hz	*o*- 4-C_6H_4Me
7.00	2 H, d	J = 8.2 Hz	*m*- 4-C_6H_4Me
4.15	1 H, apparent sept	J = 7 Hz	C*H*$_a$MeMe
3.18	1 H, apparent sept	J = 7 Hz	C*H*$_b$MeMe
2.08*	15 H, s		C_5*Me*$_5$
2.06	3 H, s		4-C_6H_4*Me*
1.67	3 H, s		*Me*CN_2
1.55	3 H, d	J = 7.0 Hz	NCH$_a$*Me*Me
1.35*	9 H, s		^{t}Bu
1.29	3 H, d	J = 7.0 Hz	NCH$_a$Me*Me*
1.20*	3 H, d	J = 7.0 Hz	NCH$_b$*Me*Me
1.06	3 H, d	J = 7.0 Hz	NCH$_b$Me*Me*

* denotes cross peak in NOESY experiment

^{13}C-{^{1}H} NMR data (125.7 MHz, 298 K, benzene-d_6)

168.4	*Me*CN_2
134.5	*p*- 4-C_6H_4Me
130.3	*o*- 4-C_6H_4Me
129.0	*m*- 4-C_6H_4Me
126.3	*i*- 4-C_6H_4Me
121.3	C_5Me_5
60.0	NH*C*Me_3
50.6	N*C*H_aMeMe
48.1	N*C*H_bMeMe
31.1	NHC*Me*$_3$
26.4	NCH_bMe*Me*
25.3	NCH_b*Me*Me
23.8	NCH_a*Me*Me
23.6	NCH_aMe*Me*
20.9	4-C_6H_4*Me*
14.9	*Me*CN_2
13.3	C_5*Me*$_5$

APPENDIX A – X-RAY STRUCTURE ANALYSIS OF Ti(η-C_5H_4Me)(N^tBu){$PhC(NSiMe_3)_2$} (3)

A.1 Crystal data, data collection and refinement

Empirical formula	$C_{46}H_{78}N_6Si_4Ti_2$	
Formula weight	923.31	
Temperature	150 K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.171(4) Å	α= 90°
	b = 26.614(3) Å	β= 90.810(6)°
	c = 15.496(4) Å	γ = 90°
Volume	5431.3(6) $Å^3$	
Z	8	
Density (calculated)	1.13 Mg/m^3	
Absorption coefficient	0.42 mm^{-1}	
F(000)	1987.25	
Crystal size	0.50 x 0.40 x 0.40 mm	
Theta range for data collection	0.00 to 26.57°	
Index ranges	$0\leq h\leq 16$, $0\leq k\leq 30$, $-19\leq l\leq 19$	
Reflections collected	40229	
Independent reflections	10015 [R(int) = 0.04]	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.85 and 0.85	
Refinement method	Full-matrix least-squares on F	
Data / parameters	7769 / 551	
Goodness-of-fit on F	0.8011	
R indices (all data)	R1 = 0.0603, wR2 = 0.0864	
Largest diff. peak and hole	1.08 and -0.59 $e.Å^{-3}$	

A.2 Bond lengths (Å) and angles (°)

Ti(1)-$Cp_{(cent)}$	2.082		
Ti(1)-N(11)	1.708(2)	Ti(1)-N(13)	2.098(2)
Ti(1)-N(15)	2.111(2)	Ti(1)-C(14)	2.471(2)
Ti(1)-C(16)	2.453(3)	Ti(1)-C(17)	2.410(3)
Ti(1)-C(18)	2.355(3)	Ti(1)-C(19)	2.362(3)
Ti(1)-C(110)	2.409(3)	Ti(2)-N(21)	1.708(2)
Ti(2)-N(23)	2.112(2)	Ti(2)-N(25)	2.098(2)
Ti(2)-C(24)	2.467(2)	Ti(2)-C(26)	2.463(3)
Ti(2)-C(27)	2.416(3)	Ti(2)-C(28)	2.357(3)
Ti(2)-C(29)	2.360(3)	Ti(2)-C(210)	2.404(3)
Si(13)-N(13)	1.739(2)	Si(13)-C(131)	1.864(4)
Si(13)-C(132)	1.854(4)	Si(13)-C(133)	1.857(3)
Si(15)-N(15)	1.743(2)	Si(15)-C(151)	1.868(3)
Si(15)-C(152)	1.864(3)	Si(15)-C(153)	1.862(3)
Si(23)-N(23)	1.743(2)	Si(23)-C(231)	1.877(3)
Si(23)-C(232)	1.860(3)	Si(23)-C(233)	1.863(3)
Si(25)-N(25)	1.740(2)	Si(25)-C(251)	1.856(3)
Si(25)-C(252)	1.862(4)	Si(25)-C(253)	1.864(3)
N(11)-C(12)	1.441(3)	N(13)-C(14)	1.328(3)
N(15)-C(14)	1.335(3)	N(21)-C(22)	1.444(4)
N(23)-C(24)	1.336(3)	N(25)-C(24)	1.325(3)
C(12)-C(121)	1.523(4)	C(12)-C(122)	1.524(4)
C(12)-C(123)	1.531(5)	C(14)-C(141)	1.504(4)
C(16)-C(17)	1.428(5)	C(16)-C(110)	1.399(5)
C(16)-C(161)	1.465(5)	C(17)-C(18)	1.390(5)
C(18)-C(19)	1.379(5)	C(19)-C(110)	1.397(5)
C(22)-C(221)	1.539(5)	C(22)-C(222)	1.542(5)
C(22)-C(223)	1.501(5)	C(22)-C(224)	1.524(7)
C(22)-C(225)	1.563(7)	C(22)-C(226)	1.475(7)
C(24)-C(241)	1.499(4)	C(26)-C(27)	1.407(5)
C(26)-C(210)	1.409(4)	C(26)-C(261)	1.474(5)
C(27)-C(28)	1.401(5)	C(28)-C(29)	1.391(5)
C(29)-C(210)	1.394(4)	C(141)-C(142)	1.388(4)
C(141)-C(146)	1.384(4)	C(142)-C(143)	1.387(5)
C(143)-C(144)	1.377(5)	C(144)-C(145)	1.382(5)
C(145)-C(146)	1.387(4)	C(221)-C(224)	1.571(12)
C(221)-C(226)	1.441(13)	C(222)-C(225)	1.550(12)
C(222)-C(226)	1.354(13)	C(223)-C(224)	1.364(12)

C(223)-C(225)	1.399(12)	C(241)-C(242)	1.388(4)
C(241)-C(246)	1.386(4)	C(242)-C(243)	1.387(5)
C(243)-C(244)	1.375(6)	C(244)-C(245)	1.381(5)
C(245)-C(246)	1.385(4)		

		$Cp_{(cent)}$-Ti(1)-N(11)	124.7
$Cp_{(cent)}$-Ti(1)-N(13)	118.6	$Cp_{(cent)}$-Ti(1)-N(15)	119.7
N(11)-Ti(1)-N(13)	105.6(1)	N(11)-Ti(1)-N(15)	107.8(1)
N(13)-Ti(1)-N(15)	65.04(8)	N(11)-Ti(1)-C(14)	107.4(1)
N(13)-Ti(1)-C(14)	32.52(8)	N(15)-Ti(1)-C(14)	32.70(8)
N(11)-Ti(1)-C(16)	152.59(11)	N(13)-Ti(1)-C(16)	100.1(1)
N(15)-Ti(1)-C(16)	91.4(1)	C(14)-Ti(1)-C(16)	99.32(9)
N(11)-Ti(1)-C(17)	135.23(13)	N(13)-Ti(1)-C(17)	90.2(1)
N(15)-Ti(1)-C(17)	116.80(12)	C(14)-Ti(1)-C(17)	107.88(11)
C(16)-Ti(1)-C(17)	34.15(13)	N(11)-Ti(1)-C(18)	103.14(12)
N(13)-Ti(1)-C(18)	113.66(11)	N(15)-Ti(1)-C(18)	148.11(11)
C(14)-Ti(1)-C(18)	139.73(11)	C(16)-Ti(1)-C(18)	56.85(12)
N(11)-Ti(1)-C(19)	96.19(11)	N(13)-Ti(1)-C(19)	145.75(11)
N(15)-Ti(1)-C(19)	132.45(11)	C(14)-Ti(1)-C(19)	155.3(1)
C(16)-Ti(1)-C(19)	56.57(11)	N(11)-Ti(1)-C(110)	121.37(11)
N(13)-Ti(1)-C(110)	132.98(9)	N(15)-Ti(1)-C(110)	99.8(1)
C(14)-Ti(1)-C(110)	122.49(9)	C(16)-Ti(1)-C(110)	33.42(11)
C(17)-Ti(1)-C(18)	33.88(13)	C(17)-Ti(1)-C(19)	56.10(12)
C(18)-Ti(1)-C(19)	33.99(13)	C(17)-Ti(1)-C(110)	55.64(11)
C(18)-Ti(1)-C(110)	56.25(11)	C(19)-Ti(1)-C(110)	34.04(11)
N(21)-Ti(2)-N(23)	108.5(1)	N(21)-Ti(2)-N(25)	105.8(1)
N(23)-Ti(2)-N(25)	65.08(8)	N(21)-Ti(2)-C(24)	108.0(1)
N(23)-Ti(2)-C(24)	32.77(8)	N(25)-Ti(2)-C(24)	32.48(8)
N(21)-Ti(2)-C(26)	152.5(1)	N(23)-Ti(2)-C(26)	90.72(9)
N(25)-Ti(2)-C(26)	99.96(9)	C(24)-Ti(2)-C(26)	98.79(9)
N(21)-Ti(2)-C(27)	136.90(11)	N(23)-Ti(2)-C(27)	114.4(1)
N(25)-Ti(2)-C(27)	88.6(1)	C(24)-Ti(2)-C(27)	105.5(1)
C(26)-Ti(2)-C(27)	33.50(11)	N(21)-Ti(2)-C(28)	104.29(11)
N(23)-Ti(2)-C(28)	146.7(1)	N(25)-Ti(2)-C(28)	111.27(11)
C(24)-Ti(2)-C(28)	137.1(1)	C(26)-Ti(2)-C(28)	56.48(11)
N(21)-Ti(2)-C(29)	96.43(11)	N(23)-Ti(2)-C(29)	133.4(1)
N(25)-Ti(2)-C(29)	144.0(1)	C(24)-Ti(2)-C(29)	155.0(1)
C(26)-Ti(2)-C(29)	56.4(1)	N(21)-Ti(2)-C(210)	120.8(1)
N(23)-Ti(2)-C(210)	100.30(9)	N(25)-Ti(2)-C(210)	133.2(1)
C(24)-Ti(2)-C(210)	122.96(9)	C(26)-Ti(2)-C(210)	33.6(1)

C(27)-Ti(2)-C(28)	34.12(12)	C(27)-Ti(2)-C(29)	56.40(11)
C(28)-Ti(2)-C(29)	34.30(12)	C(27)-Ti(2)-C(210)	55.8(1)
C(28)-Ti(2)-C(210)	56.51(11)	C(29)-Ti(2)-C(210)	34.0(1)
N(13)-Si(13)-C(131)	104.90(14)	N(13)-Si(13)-C(132)	111.88(15)
C(131)-Si(13)-C(132)	109.6(2)	N(13)-Si(13)-C(133)	111.15(13)
C(131)-Si(13)-C(133)	109.06(16)	C(132)-Si(13)-C(133)	110.1(2)
N(15)-Si(15)-C(151)	106.88(13)	N(15)-Si(15)-C(152)	112.60(13)
C(151)-Si(15)-C(152)	107.77(16)	N(15)-Si(15)-C(153)	109.56(13)
C(151)-Si(15)-C(153)	107.97(18)	C(152)-Si(15)-C(153)	111.82(17)
N(23)-Si(23)-C(231)	106.87(13)	N(23)-Si(23)-C(232)	109.35(13)
C(231)-Si(23)-C(232)	108.00(17)	N(23)-Si(23)-C(233)	112.87(12)
C(231)-Si(23)-C(233)	107.85(16)	C(232)-Si(23)-C(233)	111.67(17)
N(25)-Si(25)-C(251)	105.71(13)	N(25)-Si(25)-C(252)	112.09(14)
C(251)-Si(25)-C(252)	108.8(2)	N(25)-Si(25)-C(253)	110.80(13)
C(251)-Si(25)-C(253)	109.35(16)	C(252)-Si(25)-C(253)	109.93(17)
Ti(1)-N(11)-C(12)	174.28(19)	Ti(1)-N(13)-Si(13)	135.55(12)
Ti(1)-N(13)-C(14)	89.37(15)	Si(13)-N(13)-C(14)	131.63(19)
Ti(1)-N(15)-Si(15)	139.81(13)	Ti(1)-N(15)-C(14)	88.65(15)
Si(15)-N(15)-C(14)	130.30(19)	Ti(2)-N(21)-C(22)	173.1(2)
Ti(2)-N(23)-Si(23)	139.88(12)	Ti(2)-N(23)-C(24)	88.42(15)
Si(23)-N(23)-C(24)	130.40(18)	Ti(2)-N(25)-Si(25)	137.34(12)
Ti(2)-N(25)-C(24)	89.28(15)	Si(25)-N(25)-C(24)	131.46(18)
N(11)-C(12)-C(121)	110.0(2)	N(11)-C(12)-C(122)	109.7(2)
C(121)-C(12)-C(122)	109.4(3)	N(11)-C(12)-C(123)	107.9(2)
C(121)-C(12)-C(123)	109.5(3)	C(122)-C(12)-C(123)	110.2(3)
Ti(1)-C(14)-N(13)	58.11(13)	Ti(1)-C(14)-N(15)	58.65(13)
N(13)-C(14)-N(15)	116.3(2)	Ti(1)-C(14)-C(141)	171.01(18)
N(13)-C(14)-C(141)	122.1(2)	N(15)-C(14)-C(141)	121.5(2)
Ti(1)-C(16)-C(17)	71.28(17)	Ti(1)-C(16)-C(110)	71.57(17)
C(17)-C(16)-C(110)	105.4(3)	Ti(1)-C(16)-C(161)	121.2(2)
C(17)-C(16)-C(161)	125.7(3)	C(110)-C(16)-C(161)	128.9(4)
Ti(1)-C(17)-C(16)	74.57(17)	Ti(1)-C(17)-C(18)	70.91(19)
C(16)-C(17)-C(18)	108.7(3)	Ti(1)-C(18)-C(17)	75.20(19)
Ti(1)-C(18)-C(19)	73.28(18)	C(17)-C(18)-C(19)	108.3(3)
Ti(1)-C(19)-C(18)	72.73(18)	Ti(1)-C(19)-C(110)	74.80(17)
C(18)-C(19)-C(110)	108.0(3)	N(21)-C(22)-C(221)	109.3(3)
N(21)-C(22)-C(222)	108.5(3)	C(221)-C(22)-C(222)	108.3(3)
N(21)-C(22)-C(223)	111.0(3)	C(221)-C(22)-C(223)	110.6(3)
C(222)-C(22)-C(223)	109.1(3)	N(21)-C(22)-C(224)	107.3(5)
C(221)-C(22)-C(224)	61.7(5)	C(222)-C(22)-C(224)	144.0(6)

C(223)-C(22)-C(224)	53.6(5)	N(21)-C(22)-C(225)	105.2(5)
C(221)-C(22)-C(225)	145.5(5)	C(222)-C(22)-C(225)	59.9(5)
C(223)-C(22)-C(225)	54.3(5)	C(224)-C(22)-C(225)	107.2(6)
N(21)-C(22)-C(226)	110.6(5)	C(221)-C(22)-C(226)	57.1(5)
C(222)-C(22)-C(226)	53.3(5)	C(223)-C(22)-C(226)	138.2(6)
C(224)-C(22)-C(226)	115.2(6)	C(225)-C(22)-C(226)	110.7(6)
Ti(2)-C(24)-N(23)	58.81(13)	Ti(2)-C(24)-N(25)	58.24(13)
N(23)-C(24)-N(25)	116.6(2)	Ti(2)-C(24)-C(241)	170.83(18)
N(23)-C(24)-C(241)	122.1(2)	N(25)-C(24)-C(241)	121.2(2)
Ti(2)-C(26)-C(27)	71.39(17)	Ti(2)-C(26)-C(210)	70.86(16)
C(27)-C(26)-C(210)	106.3(3)	Ti(2)-C(26)-C(261)	121.6(2)
C(27)-C(26)-C(261)	125.3(3)	C(210)-C(26)-C(261)	128.3(3)
Ti(2)-C(27)-C(26)	75.11(17)	Ti(2)-C(27)-C(28)	70.66(18)
C(26)-C(27)-C(28)	108.8(3)	Ti(2)-C(28)-C(27)	75.22(17)
Ti(2)-C(28)-C(29)	72.97(17)	C(27)-C(28)-C(29)	107.9(3)
Ti(2)-C(29)-C(28)	72.74(17)	Ti(2)-C(29)-C(210)	74.71(16)
C(28)-C(29)-C(210)	108.1(3)	Ti(1)-C(110)-C(16)	75.01(17)
Ti(1)-C(110)-C(19)	71.16(17)	C(16)-C(110)-C(19)	109.5(3)
C(14)-C(141)-C(142)	119.3(2)	C(14)-C(141)-C(146)	120.6(2)
C(142)-C(141)-C(146)	120.0(3)	C(141)-C(142)-C(143)	119.8(3)
C(142)-C(143)-C(144)	120.4(3)	C(143)-C(144)-C(145)	119.8(3)
C(144)-C(145)-C(146)	120.4(3)	C(141)-C(146)-C(145)	119.6(3)
Ti(2)-C(210)-C(26)	75.50(16)	Ti(2)-C(210)-C(29)	71.29(16)
C(26)-C(210)-C(29)	108.9(3)	C(22)-C(221)-C(224)	58.7(4)
C(22)-C(221)-C(226)	59.2(4)	C(224)-C(221)-C(226)	114.4(5)
C(22)-C(222)-C(225)	60.7(4)	C(22)-C(222)-C(226)	60.8(4)
C(225)-C(222)-C(226)	118.6(6)	C(22)-C(223)-C(224)	64.1(4)
C(22)-C(223)-C(225)	65.1(4)	C(224)-C(223)-C(225)	128.2(6)
C(22)-C(224)-C(221)	59.6(4)	C(22)-C(224)-C(223)	62.3(4)
C(221)-C(224)-C(223)	116.6(6)	C(22)-C(225)-C(222)	59.4(4)
C(22)-C(225)-C(223)	60.6(4)	C(222)-C(225)-C(223)	114.3(6)
C(22)-C(226)-C(221)	63.7(4)	C(22)-C(226)-C(222)	65.9(4)
C(221)-C(226)-C(222)	126.6(6)	C(24)-C(241)-C(242)	119.0(2)
C(24)-C(241)-C(246)	121.5(2)	C(242)-C(241)-C(246)	119.5(3)
C(241)-C(242)-C(243)	120.1(3)	C(242)-C(243)-C(244)	120.0(3)
C(243)-C(244)-C(245)	120.2(3)	C(244)-C(245)-C(246)	120.1(3)
C(241)-C(246)-C(245)	120.0(3)		

$Cp_{(cent)}$ refers to the computed C_5H_4Me ring carbon centroid

A.3 Atomic coordinates ($\times 10^4$) and isotropic or equivalent isotropic displacement parameters ($Å^2 \times 10^3$). $U_{(eq)}$ is defined as one third of the trace of the orthogonalised U_{ij} tensor

	x	y	z	$U_{(eq)}$
Ti(1)	1029(1)	-1654(1)	3843(1)	23
Ti(2)	4028(1)	1609(1)	1495(1)	22
Si(13)	2513(1)	-1375(1)	2006(1)	27
Si(15)	2730(1)	-1308(1)	5601(1)	28
Si(23)	2280(1)	1278(1)	3187(1)	26
Si(25)	2550(1)	1339(1)	-404(1)	28
N(11)	278(2)	-1132(1)	3761(1)	27
N(13)	2304(2)	-1501(1)	3090(1)	24
N(15)	2351(2)	-1453(1)	4548(1)	25
N(21)	4797(2)	1093(1)	1459(2)	28
N(23)	2688(2)	1414(1)	2147(1)	23
N(25)	2777(2)	1444(1)	690(1)	25
C(12)	-441(2)	-726(1)	3683(2)	28
C(14)	2813(2)	-1369(1)	3800(2)	22
C(16)	1309(2)	-2548(1)	4149(2)	39
C(17)	959(3)	-2497(1)	3277(2)	45
C(18)	-15(3)	-2296(1)	3278(2)	44
C(19)	-298(2)	-2226(1)	4123(2)	42
C(22)	5528(2)	693(1)	1367(2)	44
C(24)	2251(2)	1321(1)	1381(2)	22
C(26)	3714(2)	2507(1)	1769(2)	35
C(27)	4029(2)	2451(1)	910(2)	38
C(28)	5021(2)	2261(1)	915(2)	40
C(29)	5330(2)	2200(1)	1770(2)	36
C(110)	509(2)	-2379(1)	4656(2)	36
C(121)	-1112(3)	-709(1)	4474(2)	50
C(122)	-1100(3)	-801(2)	2877(2)	54
C(123)	158(3)	-235(1)	3616(3)	55
C(131)	1285(3)	-1524(2)	1449(2)	56
C(132)	2838(5)	-706(2)	1824(3)	74
C(133)	3522(2)	-1787(1)	1571(2)	43
C(141)	3831(2)	-1114(1)	3767(2)	24
C(142)	3897(2)	-602(1)	3928(2)	34

C(143)	4834(3)	-365(1)	3915(2)	45
C(144)	5700(3)	-636(1)	3750(3)	48
C(145)	5634(2)	-1146(1)	3589(2)	44
C(146)	4699(2)	-1387(1)	3594(2)	32
C(151)	1981(3)	-1720(1)	6331(2)	46
C(152)	4103(2)	-1439(1)	5808(2)	43
C(153)	2400(3)	-643(1)	5843(2)	50
C(161)	2309(3)	-2734(2)	4423(3)	63
C(210)	4530(2)	2344(1)	2295(2)	33
C(221)	6097(3)	762(2)	514(3)	44
C(222)	4953(3)	189(2)	1327(3)	47
C(223)	6262(3)	683(2)	2117(3)	46
C(224)	6581(7)	931(4)	1400(8)	45
C(225)	5420(10)	366(4)	2198(6)	45
C(226)	5300(10)	393(4)	587(6)	45
C(231)	2976(3)	1716(1)	3938(2)	46
C(232)	2649(3)	624(1)	3473(2)	46
C(233)	893(2)	1385(1)	3323(2)	45
C(241)	1243(2)	1063(1)	1298(2)	24
C(242)	1202(2)	543(1)	1364(2)	39
C(243)	282(3)	294(1)	1264(3)	50
C(244)	-594(3)	563(1)	1114(3)	52
C(245)	-561(2)	1081(1)	1059(2)	43
C(246)	356(2)	1331(1)	1145(2)	32
C(251)	3756(3)	1494(2)	-949(2)	53
C(252)	2224(4)	671(1)	-633(2)	56
C(253)	1521(2)	1758(1)	-821(2)	40
C(261)	2710(3)	2692(1)	2036(3)	58

A.4 Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic 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)	22(1)	22(1)	26(1)	1(1)	1(1)	-2(1)
Ti(2)	20(1)	22(1)	24(1)	-2(1)	-1(1)	-2(1)
Si(13)	29(1)	30(1)	23(1)	1(1)	2(1)	3(1)
Si(15)	28(1)	30(1)	24(1)	-1(1)	-4(1)	7(1)
Si(23)	26(1)	29(1)	23(1)	2(1)	3(1)	5(1)
Si(25)	28(1)	33(1)	22(1)	0(1)	-3(1)	0(1)
N(11)	25(1)	30(1)	27(1)	-1(1)	0(1)	-1(1)
N(13)	23(1)	24(1)	26(1)	1(1)	1(1)	-1(1)
N(15)	24(1)	24(1)	27(1)	2(1)	-3(1)	1(1)
N(21)	28(1)	26(1)	30(1)	-3(1)	0(1)	-3(1)
N(23)	22(1)	23(1)	25(1)	-1(1)	1(1)	-2(1)
N(25)	22(1)	31(1)	23(1)	-1(1)	-3(1)	-4(1)
C(12)	30(1)	26(2)	26(1)	1(1)	1(1)	4(1)
C(14)	22(1)	16(1)	28(1)	2(1)	0(1)	4(1)
C(16)	39(2)	17(2)	60(2)	4(1)	8(1)	-2(1)
C(17)	67(2)	23(2)	45(2)	-9(1)	16(2)	-13(1)
C(18)	41(2)	40(2)	49(2)	2(1)	-7(1)	-13(1)
C(19)	26(1)	39(2)	61(2)	10(1)	1(1)	-8(1)
C(22)	45(1)	38(1)	49(1)	-6(1)	1(1)	12(1)
C(24)	24(1)	17(1)	25(1)	1(1)	-1(1)	2(1)
C(26)	31(1)	18(2)	55(2)	-4(1)	-5(1)	-3(1)
C(27)	44(2)	28(2)	43(2)	7(1)	-10(1)	-10(1)
C(28)	37(2)	34(2)	48(2)	-1(1)	10(1)	-13(1)
C(29)	24(1)	31(2)	52(2)	-6(1)	-2(1)	-7(1)
C(110)	34(2)	31(2)	43(2)	8(1)	6(1)	-6(1)
C(121)	57(2)	48(2)	45(2)	7(2)	16(2)	19(2)
C(122)	50(2)	65(2)	46(2)	-6(2)	-13(2)	22(2)
C(123)	59(2)	36(2)	70(3)	6(2)	8(2)	0(2)
C(131)	36(2)	100(3)	32(2)	-6(2)	-4(1)	14(2)
C(132)	148(5)	34(2)	40(2)	13(2)	11(2)	-4(2)
C(133)	35(2)	59(2)	35(2)	-6(1)	6(1)	9(1)
C(141)	26(1)	22(1)	24(1)	2(1)	-3(1)	0(1)

C(142)	33(2)	22(2)	48(2)	0(1)	2(1)	2(1)
C(143)	45(2)	28(2)	63(2)	-3(1)	-1(2)	-9(1)
C(144)	31(2)	47(2)	68(2)	-6(2)	0(2)	-12(1)
C(145)	25(1)	40(2)	68(2)	-8(2)	1(1)	1(1)
C(146)	27(1)	29(2)	41(2)	-3(1)	-2(1)	2(1)
C(151)	52(2)	60(2)	27(2)	4(1)	2(1)	-3(2)
C(152)	35(2)	62(2)	32(2)	-3(1)	-9(1)	16(1)
C(153)	63(2)	42(2)	43(2)	-12(1)	-13(2)	21(2)
C(161)	44(2)	49(2)	95(3)	10(2)	3(2)	5(2)
C(210)	31(1)	28(2)	39(2)	-6(1)	-5(1)	-5(1)
C(221)	45(1)	39(1)	49(1)	-5(1)	4(1)	13(1)
C(222)	48(1)	39(1)	54(1)	-6(1)	2(1)	9(1)
C(223)	47(1)	42(1)	50(1)	-7(1)	-2(1)	14(1)
C(224)	45(2)	39(2)	51(2)	-6(1)	1(1)	12(1)
C(225)	45(2)	38(2)	50(2)	-6(1)	1(1)	12(1)
C(226)	45(2)	39(2)	50(2)	-6(1)	0(1)	12(1)
C(231)	54(2)	56(2)	29(2)	-7(1)	0(1)	-6(2)
C(232)	59(2)	38(2)	40(2)	9(1)	9(2)	14(2)
C(233)	33(2)	69(2)	35(2)	9(2)	10(1)	16(2)
C(241)	24(1)	24(1)	24(1)	2(1)	0(1)	-2(1)
C(242)	38(2)	24(2)	55(2)	5(1)	-5(1)	-3(1)
C(243)	51(2)	26(2)	71(2)	6(2)	-6(2)	-16(1)
C(244)	36(2)	53(2)	67(2)	8(2)	-4(2)	-24(2)
C(245)	25(1)	49(2)	55(2)	9(2)	-4(1)	-3(1)
C(246)	27(1)	29(2)	39(2)	4(1)	-3(1)	0(1)
C(251)	35(2)	93(3)	31(2)	4(2)	4(1)	1(2)
C(252)	89(3)	39(2)	39(2)	-11(1)	-12(2)	-2(2)
C(253)	39(2)	49(2)	32(2)	5(1)	-6(1)	7(1)
C(261)	40(2)	46(2)	89(3)	-6(2)	0(2)	7(2)

A.5 Hydrogen coordinates (× 10^4) and isotropic displacement parameters (Å^2 × 10^3)

	x	y	z	$U_{(eq)}$
H(171)	1347	-2584	2757	60
H(181)	-435	-2219	2761	60
H(191)	-957	-2091	4316	60
H(271)	3615	2532	391	60
H(281)	5430	2188	397	60
H(291)	6002	2079	1971	60
H(1101)	506	-2369	5292	60
H(1211)	-1597	-430	4414	60
H(1212)	-674	-656	4993	60
H(1213)	-1477	-1031	4528	60
H(1221)	-1587	-524	2824	60
H(1222)	-1463	-1126	2921	60
H(1223)	-654	-809	2365	60
H(1231)	-315	52	3561	60
H(1232)	588	-191	4143	60
H(1233)	602	-247	3104	60
H(1311)	1350	-1458	825	60
H(1312)	1111	-1878	1547	60
H(1313)	745	-1305	1686	60
H(1321)	2949	-651	1199	60
H(1322)	3459	-621	2153	60
H(1323)	2268	-492	2015	60
H(1331)	3626	-1707	956	60
H(1332)	4162	-1729	1900	60
H(1333)	3316	-2142	1630	60
H(1421)	3276	-407	4043	60
H(1431)	4876	1	4013	60
H(1441)	6367	-465	3752	60
H(1451)	6259	-1341	3476	60
H(1461)	4654	-1752	3470	60
H(1511)	2179	-1650	6938	60
H(1512)	2128	-2077	6197	60
H(1513)	1251	-1653	6243	60
H(1521)	4277	-1349	6412	60

H(1522)	4238	-1799	5711	60
H(1523)	4514	-1234	5410	60
H(1531)	2622	-566	6445	60
H(1532)	1661	-599	5787	60
H(1533)	2755	-421	5439	60
H(1611)	2337	-2730	5076	60
H(1612)	2398	-3080	4225	60
H(1613)	2838	-2513	4205	60
H(2101)	4537	2333	2933	60
H(2211)	6599	489	451	60
H(2212)	6454	1091	524	60
H(2213)	5608	755	26	60
H(2221)	5448	-89	1264	60
H(2222)	4569	141	1864	60
H(2223)	4479	189	826	60
H(2231)	6755	412	2042	60
H(2232)	6629	1013	2144	60
H(2233)	5887	637	2659	60
H(2241)	7099	673	1339	60
H(2242)	6669	1111	1959	60
H(2243)	6630	1181	923	60
H(2251)	5896	81	2175	60
H(2252)	5559	573	2712	60
H(2253)	4710	234	2222	60
H(2261)	5809	121	527	60
H(2262)	5331	613	64	60
H(2263)	4614	245	619	60
H(2311)	2760	1650	4535	60
H(2312)	3712	1659	3888	60
H(2313)	2808	2066	3777	60
H(2321)	2411	548	4061	60
H(2322)	3390	591	3448	60
H(2323)	2321	390	3056	60
H(2331)	703	1303	3919	60
H(2332)	733	1742	3199	60
H(2333)	510	1168	2913	60
H(2421)	1829	349	1474	60
H(2431)	254	-78	1299	60
H(2441)	-1247	386	1049	60
H(2451)	-1196	1272	950	60

H(2461)	378	1703	1102	60
H(2511)	3671	1440	-1580	60
H(2512)	3935	1848	-837	60
H(2513)	4303	1272	-726	60
H(2521)	2104	631	-1265	60
H(2522)	2798	454	-452	60
H(2523)	1609	578	-321	60
H(2531)	1403	1690	-1443	60
H(2532)	1718	2112	-737	60
H(2533)	886	1688	-502	60
H(2611)	2689	2691	2683	60
H(2612)	2604	3035	1825	60
H(2613)	2175	2465	1813	60

APPENDIX B – X-RAY STRUCTURE ANALYSIS OF Ti(η-C_5Me_5) (N-2,6-$C_6H_3Me_2$){$MeC(N^iPr)_2$} (7)

B.1 Crystal data, data collection and refinement

Empirical formula	$C_{26}H_{41}N_3Ti_1$
Formula weight	443.53
Crystal description	greenish-brown plate
Crystal size	0.20 x 0.20 x 0.05 mm
Temperature	150 K
Crystal system	tetragonal
Space group	I 41 c d
Unit cell dimensions	a = 20.5223(4) Å α = 90 °
	b = 20.5223(4) Å β = 90 °
	c = 24.3873(6) Å γ = 90 °
Reflections for cell refinement	33295
Range in theta	0 to 27.5 °.
Volume, Z	10271.1 $Å^3$, 16
Density (calculated)	1.15 Mg/m^3
Absorption coefficient	0.35 mm^{-1}
F(000)	3844.33
Diffractometer type	Nonius KappaCCD
Wavelength	0.71073 Å
Scan type	\ w/2 \ q
Index ranges	0<=h<=18, 0<=k<=25, -31<=l<=31
Reflections collected	33295
Independent reflections	5910 [R(merge) = 0.6]
Observed reflections	4139 [I>3sigma(I)]

Absorption correction	multi-scan
Tmin, Tmax	0.93, 0.98
Structure solution by	direct methods and Fourier difference maps
Hydrogen atom location	geometric
Hydrogen atom treatment	none
Refinement method	Full-matrix least-squares on F
Weighting scheme	Chebychev polynomial
Data / restraints / parameters	4139 / 0 / 272
Goodness-of-fit on F	1.0434
Final R indices [I>3sigma(I)]	R1 = 0.0396, Rw = 0.0418
Final maximum delta/sigma	0.0011
Largest diff. peak and hole	0.53 and -0.50 e.A^{-3}

B.2 Bond lengths (Å) and angles (°)

Ti(1)-N(1)	2.094(2)	Ti(1)-N(2)	2.099(2)
Ti(1)-N(3)	1.738(2)	Ti(1)-C(17)	2.360(3)
Ti(1)-C(18)	2.388(3)	Ti(1)-C(19)	2.446(3)
Ti(1)-C(20)	2.457(3)	Ti(1)-C(21)	2.389(3)
Ti(1)-$Cp_{(cent)}$	2.085	N(1)-C(1)	1.335(4)
N(1)-C(3)	1.462(4)	N(2)-C(1)	1.339(4)
N(2)-C(6)	1.460(4)	N(3)-C(9)	1.382(4)
C(1)-C(2)	1.500(4)	C(3)-C(4)	1.513(6)
C(3)-C(5)	1.529(5)	C(6)-C(7)	1.520(5)
C(6)-C(8)	1.527(5)	C(9)-C(10)	1.419(4)
C(9)-C(14)	1.419(4)	C(10)-C(11)	1.396(4)
C(10)-C(15)	1.489(5)	C(11)-C(12)	1.377(5)
C(12)-C(13)	1.376(5)	C(13)-C(14)	1.396(4)
C(14)-C(16)	1.504(5)	C(17)-C(18)	1.416(4)
C(17)-C(21)	1.407(4)	C(17)-C(22)	1.502(4)
C(18)-C(19)	1.420(4)	C(18)-C(23)	1.517(4)
C(19)-C(20)	1.411(4)	C(19)-C(24)	1.502(4)
C(20)-C(21)	1.433(4)	C(20)-C(25)	1.498(4)

C(21)-C(26)	1.509(4)		
N(1)-Ti(1)-N(2)	64.45(9)	N(1)-Ti(1)-N(3)	109.2(1)
N(2)-Ti(1)-N(3)	109.74(11)	N(1)-Ti(1)-C(1)	32.23(9)
N(2)-Ti(1)-C(1)	32.33(9)	N(3)-Ti(1)-C(1)	111.2(1)
N(1)-Ti(1)-C(17)	140.5(1)	N(2)-Ti(1)-C(17)	140.74(9)
N(3)-Ti(1)-C(17)	90.76(11)	C(1)-Ti(1)-C(17)	158.0(1)
N(1)-Ti(1)-C(18)	105.8(1)	N(2)-Ti(1)-C(18)	142.0(1)
N(3)-Ti(1)-C(18)	108.1(1)	C(1)-Ti(1)-C(18)	130.3(1)
C(17)-Ti(1)-C(18)	34.7(1)	N(1)-Ti(1)-C(19)	89.7(1)
N(2)-Ti(1)-C(19)	107.9(1)	N(3)-Ti(1)-C(19)	142.3(1)
C(1)-Ti(1)-C(19)	102.2(1)	C(17)-Ti(1)-C(19)	57.0(1)
N(1)-Ti(1)-C(20)	107.46(9)	N(2)-Ti(1)-C(20)	89.93(9)
N(3)-Ti(1)-C(20)	143.0(1)	C(1)-Ti(1)-C(20)	102.11(9)
C(17)-Ti(1)-C(20)	57.05(9)	N(1)-Ti(1)-C(21)	141.8(1)
N(2)-Ti(1)-C(21)	106.28(9)	N(3)-Ti(1)-C(21)	108.71(11)
C(1)-Ti(1)-C(21)	130.66(9)	C(17)-Ti(1)-C(21)	34.5(1)
C(18)-Ti(1)-C(19)	34.13(9)	C(18)-Ti(1)-C(20)	56.57(9)
C(19)-Ti(1)-C(20)	33.45(9)	C(18)-Ti(1)-C(21)	57.2(1)
C(19)-Ti(1)-C(21)	56.5(1)	C(20)-Ti(1)-C(21)	34.4(1)
$Cp_{(cent)}$-Ti(1)-N(1)	119.1	$Cp_{(cent)}$-Ti(1)-N(2)	119.5
$Cp_{(cent)}$-Ti(1)-N(3)	121.4	Ti(1)-N(1)-C(1)	91.0(2)
Ti(1)-N(1)-C(3)	143.0(2)	C(1)-N(1)-C(3)	121.0(3)
Ti(1)-N(2)-C(1)	90.7(2)	Ti(1)-N(2)-C(6)	144.3(2)
C(1)-N(2)-C(6)	121.2(2)	Ti(1)-N(3)-C(9)	168.9(2)
Ti(1)-C(1)-N(1)	56.77(14)	Ti(1)-C(1)-N(2)	57.01(13)
N(1)-C(1)-N(2)	113.5(2)	N(1)-C(3)-C(4)	109.5(3)
N(1)-C(3)-C(5)	110.6(3)	C(4)-C(3)-C(5)	110.7(3)
N(2)-C(6)-C(7)	109.4(2)	N(2)-C(6)-C(8)	111.5(3)
C(7)-C(6)-C(8)	110.3(3)	N(3)-C(9)-C(10)	121.1(3)
N(3)-C(9)-C(14)	119.6(3)	C(10)-C(9)-C(14)	119.3(3)
C(9)-C(10)-C(11)	119.0(3)	C(9)-C(10)-C(15)	120.8(3)
C(11)-C(10)-C(15)	120.2(3)	C(10)-C(11)-C(12)	121.4(3)
C(11)-C(12)-C(13)	119.8(3)	C(12)-C(13)-C(14)	121.5(3)
C(9)-C(14)-C(13)	118.9(3)	C(9)-C(14)-C(16)	120.8(3)
C(13)-C(14)-C(16)	120.2(3)	Ti(1)-C(17)-C(18)	73.7(2)
Ti(1)-C(17)-C(21)	73.9(2)	C(18)-C(17)-C(21)	108.1(3)
Ti(1)-C(17)-C(22)	120.9(2)	C(18)-C(17)-C(22)	125.4(3)
C(21)-C(17)-C(22)	126.4(3)	Ti(1)-C(18)-C(17)	71.6(2)
Ti(1)-C(18)-C(19)	75.2(2)	C(17)-C(18)-C(19)	107.9(3)

Ti(1)-C(18)-C(23)	124.7(2)	C(17)-C(18)-C(23)	125.1(3)
C(19)-C(18)-C(23)	126.6(3)	Ti(1)-C(19)-C(18)	70.7(2)
Ti(1)-C(19)-C(20)	73.7(2)	C(18)-C(19)-C(20)	108.4(3)
Ti(1)-C(19)-C(24)	125.9(2)	C(18)-C(19)-C(24)	127.7(3)
C(20)-C(19)-C(24)	123.7(3)	Ti(1)-C(20)-C(19)	72.9(2)
Ti(1)-C(20)-C(21)	70.21(14)	C(19)-C(20)-C(21)	107.3(2)
Ti(1)-C(20)-C(25)	126.1(2)	C(19)-C(20)-C(25)	124.6(3)
C(21)-C(20)-C(25)	127.9(3)	Ti(1)-C(21)-C(17)	71.7(2)
Ti(1)-C(21)-C(20)	75.4(2)	C(17)-C(21)-C(20)	108.3(3)
Ti(1)-C(21)-C(26)	124.8(2)	C(17)-C(21)-C(26)	125.5(3)
C(20)-C(21)-C(26)	125.8(3)		

$Cp_{(cent)}$ refers to the computed C_5Me_5 ring carbon centroid

B.3 Atomic coordinates ($\times 10^4$) and isotropic or equivalent isotropic displacement parameters ($Å^2 \times 10^3$). $U_{(eq)}$ is defined as one third of the trace of the orthogonalised U_{ij} tensor

	x	y	z	$U_{(eq)}$
Ti(1)	2575(1)	-486(1)	1377(1)	13
N(1)	3302(1)	-946(1)	1839(1)	21
N(2)	2497(1)	-1504(1)	1437(1)	18
N(3)	2890(1)	-277(1)	739(1)	19
C(1)	3057(1)	-1531(1)	1717(1)	21
C(2)	3378(2)	-2159(2)	1881(2)	36
C(3)	3973(1)	-875(2)	2031(1)	33
C(4)	4051(2)	-223(2)	2313(2)	55
C(5)	4451(2)	-938(2)	1554(2)	48
C(6)	2220(2)	-2084(1)	1182(1)	27
C(7)	1518(2)	-1950(2)	1020(2)	39
C(8)	2614(2)	-2294(2)	681(2)	47
C(9)	3050(1)	-14(1)	235(1)	20
C(10)	3574(2)	433(2)	179(1)	28
C(11)	3743(2)	653(2)	-344(1)	37
C(12)	3407(2)	454(2)	-802(1)	40

C(13)	2889(2)	32(2)	-749(1)	32
C(14)	2698(1)	-208(1)	-239(1)	22
C(15)	3942(2)	663(2)	668(2)	46
C(16)	2131(2)	-671(2)	-195(1)	35
C(17)	1922(1)	460(1)	1383(1)	23
C(18)	2320(1)	495(1)	1857(1)	22
C(19)	2128(1)	-13(1)	2217(1)	21
C(20)	1615(1)	-364(1)	1970(1)	20
C(21)	1492(1)	-69(1)	1447(1)	22
C(22)	1937(2)	931(2)	912(1)	36
C(23)	2803(2)	1035(2)	1979(2)	37
C(24)	2368(2)	-140(2)	2789(1)	34
C(25)	1245(2)	-905(2)	2239(1)	32
C(26)	940(2)	-238(2)	1064(1)	35

B.4 Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic 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)	12(1)	14(1)	11(1)	1(1)	0(1)	-2(1)
N(1)	15(1)	26(1)	21(1)	4(1)	-4(1)	-2(1)
N(2)	18(1)	17(1)	20(1)	1(1)	-2(1)	-2(1)
N(3)	19(1)	23(1)	14(1)	2(1)	5(1)	0(1)
C(1)	19(1)	26(1)	18(1)	8(1)	2(1)	-1(1)
C(2)	34(2)	32(2)	41(2)	14(2)	-5(2)	11(1)
C(3)	16(1)	52(2)	30(2)	16(2)	-10(1)	-5(1)
C(4)	29(2)	80(3)	55(3)	-12(2)	-11(2)	-24(2)
C(5)	23(2)	58(2)	64(3)	10(2)	8(2)	3(2)
C(6)	38(2)	14(1)	29(2)	1(1)	-4(1)	-5(1)
C(7)	29(2)	45(2)	41(2)	-6(2)	-5(2)	-16(2)
C(8)	61(2)	34(2)	45(2)	-14(2)	-3(2)	17(2)
C(9)	25(1)	16(1)	19(1)	5(1)	5(1)	7(1)

C(10)	30(2)	25(2)	29(2)	7(1)	10(1)	1(1)
C(11)	38(2)	32(2)	40(2)	16(2)	19(2)	2(1)
C(12)	55(2)	36(2)	29(2)	17(2)	22(2)	16(2)
C(13)	50(2)	28(2)	18(1)	2(1)	5(1)	20(2)
C(14)	29(2)	16(1)	20(1)	1(1)	3(1)	9(1)
C(15)	44(2)	52(2)	43(2)	10(2)	-1(2)	-22(2)
C(16)	41(2)	33(2)	30(2)	-1(1)	-7(1)	-1(1)
C(17)	28(1)	21(1)	19(1)	1(1)	6(1)	6(1)
C(18)	32(2)	16(1)	19(1)	-5(1)	6(1)	0(1)
C(19)	25(2)	20(1)	18(1)	-3(1)	6(1)	0(1)
C(20)	20(1)	23(1)	17(1)	-2(1)	7(1)	-1(1)
C(21)	19(1)	28(1)	19(2)	0(1)	1(1)	6(1)
C(22)	50(2)	29(2)	30(2)	15(1)	6(2)	12(1)
C(23)	55(2)	22(2)	33(2)	-5(1)	3(2)	-13(2)
C(24)	47(2)	42(2)	14(2)	-3(1)	2(1)	-4(2)
C(25)	29(2)	36(2)	31(2)	1(1)	12(1)	-10(1)
C(26)	18(2)	49(2)	37(2)	-1(2)	-5(1)	6(1)

B.5 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$)

	x	y	z	$U_{(iso)}$
H(21)	3111	-2534	1746	43
H(22)	3413	-2179	2289	43
H(23)	3823	-2181	1716	43
H(31)	4071	-1231	2299	39
H(41)	4510	-175	2445	65
H(42)	3747	-198	2633	65
H(43)	3948	134	2049	65
H(51)	4907	-889	1693	58
H(52)	4400	-1376	1379	58
H(53)	4359	-591	1277	58
H(61)	2235	-2449	1453	32
H(71)	1327	-2347	845	46

H(72)	1260	-1836	1355	46
H(73)	1503	-1579	755	46
H(81)	2413	-2692	516	56
H(82)	3072	-2394	794	56
H(83)	2616	-1934	404	56
H(111)	4117	961	-386	44
H(121)	3537	616	-1173	48
H(131)	2645	-106	-1085	39
H(151)	4290	973	550	56
H(152)	4145	281	857	56
H(153)	3637	888	926	56
H(161)	1945	-750	-568	41
H(162)	2283	-1093	-34	41
H(163)	1789	-476	47	41
H(221)	1630	1299	987	43
H(222)	2388	1105	866	43
H(223)	1801	702	568	43
H(231)	2578	1393	2184	44
H(232)	3167	859	2207	44
H(233)	2981	1211	1627	44
H(241)	2100	115	3056	41
H(242)	2835	-3	2819	41
H(243)	2330	-615	2873	41
H(251)	876	-719	2457	39
H(252)	1543	-1152	2488	39
H(253)	1069	-1205	1952	39
H(261)	537	-1	1180	42
H(262)	859	-719	1077	42
H(263)	1058	-108	682	42

APPENDIX C – X-RAY STRUCTURE ANALYSIS OF Ti(η-C_5Me_5) (N-2,6-$C_6H_3Me_2$)Cl(py) (13)

C.1 Crystal data, data collection and refinement

Empirical formula	$C_{23}H_{29}ClN_2Ti$
Formula weight	416.85
Crystal description	brown block
Crystal size	0.30 x 0.25 x 0.20 mm
Temperature	190 K
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 8.6260(6) Å α = 74.772(4) °
	b = 9.8500(8) Å β = 81.227(4) °
	c = 14.215(1) Å γ = 67.901(4) °
Reflections for cell refinement	7979
Range in theta	0 to 27 °.
Volume, Z	1077.8 $Å^3$
Density (calculated)	1.28 Mg/m^3
Absorption coefficient	0.53 mm^{-1}
F(000)	440
Diffractometer type	Enraf-nonius DIP2000
Wavelength	0.71069 A
Scan type	omega
Theta range for data collection	1.49 to 25.94 deg.
Index ranges	0<=h<=10, -10<=k<=12, -16<=l<=17
Reflections collected	7979
Independent reflections	3892 [R(merge) = 0.037]

Observed reflections	2826 [I>3sigma(I)]
Absorption correction	multi-scan
Tmin, Tmax	0.876, 0.899
Decay correction	not measured
Structure solution	by direct methods and Fourier difference maps
Hydrogen atom location	geometric
Hydrogen atom treatment	riding model
Refinement method	Full-matrix least-squares on F
Weighting scheme	Chebychev polynomial
Data / restraints / parameters	2826 / 0 / 245
Goodness-of-fit on F	1.1120
Final R indices [I>3sigma(I)]	R1 = 0.0591, Rw = 0.0574
Extinction coefficient	none required
Final maximum delta/sigma	0.002
Largest diff. peak and hole	-0.436 and 0.519 e.A^{-3}

C.2 Bond lengths (Å) and angles (°)

Ti(1)-Cl(1)	2.345(1)	Ti(1)-N(1)	1.754(3)
Ti(1)-N(2)	2.177(3)	$Cp_{(cent)}$ – Ti(1)	2.062
Ti(1)-C(9)	2.434(4)	Ti(1)-C(10)	2.376(4)
Ti(1)-C(11)	2.342(4)	Ti(1)-C(12)	2.348(4)
Ti(1)-C(13)	2.434(4)	N(1)-C(1)	1.363(4)
N(2)-C(19)	1.342(5)	N(2)-C(23)	1.348(5)
C(1)-C(2)	1.417(5)	C(1)-C(6)	1.417(5)
C(2)-C(3)	1.387(5)	C(2)-C(7)	1.514(5)
C(3)-C(4)	1.379(6)	C(4)-C(5)	1.378(6)
C(5)-C(6)	1.394(5)	C(6)-C(8)	1.501(5)
C(9)-C(10)	1.417(5)	C(9)-C(13)	1.406(5)
C(9)-C(14)	1.501(5)	C(10)-C(11)	1.413(5)
C(10)-C(15)	1.509(5)	C(11)-C(12)	1.413(5)
C(11)-C(16)	1.506(5)	C(12)-C(13)	1.417(5)

C(12)-C(17)	1.505(5)	C(13)-C(18)	1.501(5)
C(19)-C(20)	1.377(5)	C(20)-C(21)	1.384(7)
C(21)-C(22)	1.372(7)	C(22)-C(23)	1.378(6)

$Cp_{(cent)}$–Ti(1)–Cl(1)	115.9	$Cp_{(cent)}$-Ti(1)-N(1)	121.8
$Cp_{(cent)}$-Ti(1)-N(2)	110.2	Cl(1)-Ti(1)-N(1)	105.4(1)
Cl(1)-Ti(1)-N(2)	96.35(9)	N(1)-Ti(1)-N(2)	103.7(1)
Cl(1)-Ti(1)-C(9)	111.5(1)	N(1)-Ti(1)-C(9)	141.8(1)
N(2)-Ti(1)-C(9)	82.4(1)	Cl(1)-Ti(1)-C(10)	143.6(1)
N(1)-Ti(1)-C(10)	107.5(1)	N(2)-Ti(1)-C(10)	90.5(1)
C(9)-Ti(1)-C(10)	34.2(1)	Cl(1)-Ti(1)-C(11)	131.1(1)
N(1)-Ti(1)-C(11)	90.8(1)	N(2)-Ti(1)-C(11)	124.7(1)
C(9)-Ti(1)-C(11)	57.2(1)	C(10)-Ti(1)-C(11)	34.9(1)
Cl(1)-Ti(1)-C(12)	96.6(1)	N(1)-Ti(1)-C(12)	109.8(1)
N(2)-Ti(1)-C(12)	139.2(1)	C(9)-Ti(1)-C(12)	56.9(1)
C(10)-Ti(1)-C(12)	57.7(1)	Cl(1)-Ti(1)-C(13)	87.2(1)
N(1)-Ti(1)-C(13)	144.1(1)	N(2)-Ti(1)-C(13)	108.2(1)
C(9)-Ti(1)-C(13)	33.6(1)	C(10)-Ti(1)-C(13)	56.8(1)
C(11)-Ti(1)-C(12)	35.1(1)	C(11)-Ti(1)-C(13)	57.5(1)
C(12)-Ti(1)-C(13)	34.4(1)	Ti(1)-N(1)-C(1)	167.2(2)
Ti(1)-N(2)-C(19)	123.7(2)	Ti(1)-N(2)-C(23)	119.1(3)
C(19)-N(2)-C(23)	117.2(3)	N(1)-C(1)-C(2)	122.3(3)
N(1)-C(1)-C(6)	119.7(3)	C(2)-C(1)-C(6)	118.0(3)
C(1)-C(2)-C(3)	120.0(3)	C(1)-C(2)-C(7)	119.7(3)
C(3)-C(2)-C(7)	120.3(3)	C(2)-C(3)-C(4)	121.3(4)
C(3)-C(4)-C(5)	119.7(3)	C(4)-C(5)-C(6)	120.8(4)
C(1)-C(6)-C(5)	120.2(3)	C(1)-C(6)-C(8)	119.7(3)
C(5)-C(6)-C(8)	120.1(3)	Ti(1)-C(9)-C(10)	70.6(2)
Ti(1)-C(9)-C(13)	73.2(2)	C(10)-C(9)-C(13)	108.4(3)
Ti(1)-C(9)-C(14)	128.6(3)	C(10)-C(9)-C(14)	125.3(4)
C(13)-C(9)-C(14)	125.7(4)	Ti(1)-C(10)-C(9)	75.1(2)
Ti(1)-C(10)-C(11)	71.3(2)	C(9)-C(10)-C(11)	108.0(3)
Ti(1)-C(10)-C(15)	124.3(3)	C(9)-C(10)-C(15)	125.6(4)
C(11)-C(10)-C(15)	126.1(4)	Ti(1)-C(11)-C(10)	73.9(2)
Ti(1)-C(11)-C(12)	72.7(2)	C(10)-C(11)-C(12)	107.6(3)
Ti(1)-C(11)-C(16)	123.0(3)	C(10)-C(11)-C(16)	125.9(4)
C(12)-C(11)-C(16)	126.4(3)	Ti(1)-C(12)-C(11)	72.2(2)
Ti(1)-C(12)-C(13)	76.1(2)	C(11)-C(12)-C(13)	108.5(3)
Ti(1)-C(12)-C(17)	121.7(3)	C(11)-C(12)-C(17)	125.4(3)
C(13)-C(12)-C(17)	125.9(3)	Ti(1)-C(13)-C(9)	73.2(2)

Ti(1)-C(13)-C(12)	69.5(2)	C(9)-C(13)-C(12)	107.5(3)
Ti(1)-C(13)-C(18)	123.9(3)	C(9)-C(13)-C(18)	126.1(4)
C(12)-C(13)-C(18)	126.4(4)	N(2)-C(19)-C(20)	123.4(4)
C(19)-C(20)-C(21)	118.8(4)	C(20)-C(21)-C(22)	118.5(4)
C(21)-C(22)-C(23)	119.8(4)	N(2)-C(23)-C(22)	122.4(4)

$Cp_{(cent)}$ refers to the computed C_5Me_5 ring carbon centroid

C.3 Atomic coordinates ($\times 10^4$) and isotropic or equivalent isotropic displacement parameters ($Å^2 \times 10^3$). $U_{(eq)}$ is defined as one third of the trace of the orthogonalised U_{ij} tensor

	x	y	z	$U_{(eq)}$
Ti(1)	-3126(1)	6553(1)	7046(1)	19
Cl(1)	-5196(1)	7322(1)	5929(1)	38
N(1)	-2754(4)	4636(3)	7536(2)	23
N(2)	-1051(4)	6560(3)	5962(2)	26
C(1)	-2749(4)	3262(4)	8063(2)	22
C(2)	-1287(5)	2125(4)	8477(3)	26
C(3)	-1338(5)	729(4)	8980(3)	30
C(4)	-2803(6)	428(4)	9112(3)	35
C(5)	-4240(5)	1517(4)	8717(3)	33
C(6)	-4235(5)	2923(4)	8186(3)	27
C(7)	325(5)	2443(5)	8369(3)	37
C(8)	-5802(5)	4083(5)	7739(3)	40
C(9)	-2650(5)	8692(4)	7332(3)	30
C(10)	-1950(4)	7409(4)	8079(3)	27
C(11)	-3274(5)	6970(4)	8610(3)	25
C(12)	-4778(4)	7963(4)	8173(3)	26
C(13)	-4396(5)	9046(4)	7394(3)	31
C(14)	-1715(6)	9637(5)	6682(3)	47
C(15)	-136(5)	6738(5)	8328(4)	43
C(16)	-3118(6)	5749(4)	9526(3)	37
C(17)	-6505(5)	7946(5)	8534(3)	42
C(18)	-5631(6)	10358(5)	6764(3)	50
C(19)	512(5)	5556(5)	6077(3)	32
C(20)	1822(5)	5575(5)	5393(3)	40

C(21)	1516(6)	6663(5)	4530(3)	43
C(22)	-79(6)	7692(5)	4401(3)	40
C(23)	-1327(5)	7622(5)	5123(3)	35

C.4 Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic 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)	18(1)	21(1)	17(1)	-1(1)	0(1)	-9(1)
Cl(1)	35(1)	47(1)	34(1)	2(1)	-15(1)	-18(1)
N(1)	21(1)	26(2)	24(1)	-5(1)	0(1)	-10(1)
N(2)	30(2)	34(2)	21(1)	-6(1)	4(1)	-20(1)
C(1)	26(2)	24(2)	19(2)	-9(1)	2(1)	-10(1)
C(2)	29(2)	27(2)	24(2)	-7(1)	1(2)	-11(1)
C(3)	38(2)	22(2)	24(2)	-7(1)	-3(2)	-3(2)
C(4)	54(3)	23(2)	29(2)	-7(2)	3(2)	-18(2)
C(5)	35(2)	36(2)	34(2)	-9(2)	5(2)	-21(2)
C(6)	29(2)	26(2)	27(2)	-8(1)	4(2)	-11(1)
C(7)	25(2)	34(2)	50(2)	-6(2)	-8(2)	-8(2)
C(8)	25(2)	38(2)	55(3)	-5(2)	-1(2)	-15(2)
C(9)	38(2)	29(2)	26(2)	-7(1)	7(2)	-19(2)
C(10)	24(2)	29(2)	32(2)	-11(2)	-1(2)	-12(1)
C(11)	29(2)	22(2)	23(2)	-5(1)	-3(1)	-8(1)
C(12)	22(2)	30(2)	28(2)	-12(1)	2(1)	-8(1)
C(13)	33(2)	25(2)	28(2)	-3(1)	-4(2)	-5(2)
C(14)	66(3)	43(3)	48(3)	-15(2)	12(2)	-38(2)
C(15)	28(2)	49(3)	61(3)	-25(2)	-11(2)	-13(2)
C(16)	53(3)	32(2)	23(2)	0(2)	-3(2)	-15(2)
C(17)	27(2)	46(2)	51(3)	-21(2)	12(2)	-10(2)
C(18)	58(3)	31(2)	45(3)	-1(2)	-18(2)	2(2)
C(19)	33(2)	41(2)	26(2)	-7(2)	1(2)	-18(2)
C(20)	31(2)	58(3)	39(2)	-21(2)	8(2)	-21(2)
C(21)	50(3)	65(3)	30(2)	-21(2)	15(2)	-39(2)
C(22)	54(3)	58(3)	21(2)	-2(2)	2(2)	-40(2)
C(23)	38(2)	40(2)	27(2)	0(2)	-3(2)	-21(2)

C.5 Hydrogen coordinates (× 10^4) and isotropic displacement parameters (Å^2 × 10^3)

	x	y	z	$U_{(eq)}$
H(31)	-328(5)	-41(4)	9235(3)	37
H(41)	-2820(6)	-536(4)	9480(3)	47
H(51)	-5261(5)	1308(4)	8806(3)	49
H(71)	1190(5)	1566(5)	8688(3)	49
H(72)	152(5)	3266(5)	8663(3)	49
H(73)	653(5)	2700(5)	7689(3)	49
H(81)	-6688(5)	3680(5)	7887(3)	51
H(82)	-6121(5)	4963(5)	7998(3)	51
H(83)	-5598(5)	4345(5)	7044(3)	51
H(141)	-2459(6)	10439(5)	6234(3)	75
H(142)	-1273(6)	10049(5)	7074(3)	75
H(143)	-811(6)	9020(5)	6324(3)	75
H(151)	22(5)	5877(5)	8863(4)	58
H(152)	166(5)	7475(5)	8509(4)	58
H(153)	557(5)	6439(5)	7769(4)	58
H(161)	-4199(6)	5674(4)	9741(3)	47
H(162)	-2702(6)	5991(4)	10026(3)	47
H(163)	-2357(6)	4807(4)	9395(3)	47
H(171)	-7313(5)	8732(5)	8113(3)	56
H(172)	-6746(5)	8102(5)	9187(3)	56
H(173)	-6558(5)	6992(5)	8528(3)	56
H(181)	-6743(6)	10350(5)	6960(3)	58
H(182)	-5565(6)	11278(5)	6833(3)	58
H(183)	-5372(6)	10282(5)	6094(3)	58
H(191)	719(5)	4786(5)	6668(3)	46
H(201)	2925(5)	4845(5)	5512(3)	59
H(211)	2396(6)	6698(5)	4032(3)	62
H(221)	-321(6)	8458(5)	3810(3)	57
H(231)	-2435(5)	8352(5)	5026(3)	49

APPENDIX D – X-RAY STRUCTURE ANALYSIS OF Ti(η-C_5Me_5) (N-2,6-$C_6H_3Me_2$){PhC($NSiMe_3$)$_2$} (14)

D.1 Crystal data, data collection and refinement

Empirical formula	C_{31} H_{47} N_3 Si_2 Ti_1
Formula weight	565.81
Crystal description	red fragment
Crystal size	0.60 x 0.30 x 0.20 mm
Temperature	150 K
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 11.672(5) Å alpha = 90 deg. b = 15.361(2) Å beta = 100.92(4) deg. c = 18.018(7) Å gamma = 90 deg.
Reflections for cell refinement	32
Range in theta	5 to 28 deg.
Volume, Z	3172(1) $Å^3$, 4
Density (calculated)	1.18 Mg/m^3
Absorption coefficient	0.37 mm^{-1}
F(000)	1217.66
Diffractometer type	Nonius KappaCCD
Wavelength	0.71073 Å
Scan type	CCD
Theta range for data collection	4.08 to 27.48 deg.
Index ranges	-15<=h<=14, 0<=k<=19, 0<=l<=21
Reflections collected	18449
Independent reflections	6434 [R(merge) = 0.04]
Observed reflections	4392 [I>3sigma(I)]
Absorption correction	Multi-scan (Tmin = 0.90, Tmax = 0.93)
Structure solution by	direct methods and Fourier difference maps
Hydrogen atom location	geometric
Hydrogen atom treatment	riding model
Refinement method	Full-matrix least-squares on F
Weighting scheme	Chebychev polynomial
Data / restraints / parameters	4392 / 0 / 335
Goodness-of-fit on F	1.0617

Final R indices [I>3sigma(I)]	R1 = 0.0401, Rw = 0.0489
Extinction coefficient	none
Final maximum delta/sigma	0.0008
Largest diff. peak and hole	0.51 and -0.40 e.Å^{-3}

Comments:

The crystals of Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){PhC($NSiMe_3$)$_2$} were found to be twinned. The twinning was interpreted and resolved using EvalCCD (Nonius, 2001). Otherwise structure solution and refinement proceeded normally.

D.2 Bond lengths (Å) and angles (°)

Ti(1)-N(1)	2.134(2)	Ti(1)-N(2)	2.107(2)
Ti(1)-N(3)	1.748(2)	Ti(1)-$Cp_{(cent)}$	2.079
Ti(1)-C(1)	2.488(3)	Ti(1)-C(22)	2.378(3)
Ti(1)-C(23)	2.375(3)	Ti(1)-C(24)	2.415(3)
Ti(1)-C(25)	2.435(3)	Ti(1)-C(26)	2.420(3)
N(1)-Si(1)	1.767(2)	N(1)-C(1)	1.327(4)
N(2)-Si(2)	1.745(2)	N(2)-C(1)	1.346(4)
N(3)-C(14)	1.386(3)	Si(1)-C(8)	1.855(4)
Si(1)-C(9)	1.863(3)	Si(1)-C(10)	1.872(3)
Si(2)-C(11)	1.874(3)	Si(2)-C(12)	1.867(3)
Si(2)-C(13)	1.877(3)	C(1)-C(2)	1.492(4)
C(2)-C(3)	1.395(4)	C(2)-C(7)	1.392(4)
C(3)-C(4)	1.396(4)	C(4)-C(5)	1.373(6)
C(5)-C(6)	1.385(5)	C(6)-C(7)	1.405(5)
C(14)-C(15)	1.405(4)	C(14)-C(19)	1.425(4)
C(15)-C(16)	1.400(5)	C(15)-C(20)	1.511(5)
C(16)-C(17)	1.385(6)	C(17)-C(18)	1.373(5)
C(18)-C(19)	1.387(5)	C(19)-C(21)	1.500(5)
C(22)-C(23)	1.420(4)	C(22)-C(26)	1.417(4)
C(22)-C(27)	1.512(4)	C(23)-C(24)	1.430(4)
C(23)-C(28)	1.503(4)	C(24)-C(25)	1.401(4)
C(24)-C(29)	1.503(4)	C(25)-C(26)	1.434(4)
C(25)-C(30)	1.510(4)	C(26)-C(31)	1.497(4)

N(1)-Ti(1)-N(2)	64.94(8)	N(1)-Ti(1)-N(3)	108.4(1)
N(2)-Ti(1)-N(3)	108.0(1)	N(1)-Ti(1)-C(1)	32.23(9)
N(2)-Ti(1)-C(1)	32.77(9)	N(3)-Ti(1)-C(1)	110.26(9)
$Cp_{(cent)}$-Ti(1)-N(1)	120.5	$Cp_{(cent)}$-Ti(1)-N(2)	119.6
$Cp_{(cent)}$-Ti(1)-N(3)	121.8	N(1)-Ti(1)-C(22)	141.1(1)
N(2)-Ti(1)-C(22)	140.8(1)	N(3)-Ti(1)-C(22)	91.3(1)
C(1)-Ti(1)-C(22)	158.48(9)	N(1)-Ti(1)-C(23)	106.3(1)
N(2)-Ti(1)-C(23)	142.2(1)	N(3)-Ti(1)-C(23)	109.52(11)
C(1)-Ti(1)-C(23)	130.4(1)	C(22)-Ti(1)-C(23)	34.77(11)
N(1)-Ti(1)-C(24)	90.36(9)	N(2)-Ti(1)-C(24)	107.52(9)
N(3)-Ti(1)-C(24)	144.19(11)	C(1)-Ti(1)-C(24)	101.86(9)
C(22)-Ti(1)-C(24)	57.6(1)	N(1)-Ti(1)-C(25)	109.1(1)
N(2)-Ti(1)-C(25)	90.12(9)	N(3)-Ti(1)-C(25)	142.4(1)
C(1)-Ti(1)-C(25)	102.78(9)	C(22)-Ti(1)-C(25)	57.0(1)
N(1)-Ti(1)-C(26)	143.40(9)	N(2)-Ti(1)-C(26)	106.5(1)
N(3)-Ti(1)-C(26)	108.0(1)	C(1)-Ti(1)-C(26)	131.4(1)
C(22)-Ti(1)-C(26)	34.3(1)	C(23)-Ti(1)-C(24)	34.7(1)
C(23)-Ti(1)-C(25)	56.7(1)	C(24)-Ti(1)-C(25)	33.58(9)
C(23)-Ti(1)-C(26)	57.2(1)	C(24)-Ti(1)-C(26)	57.0(1)
C(25)-Ti(1)-C(26)	34.4(1)	Ti(1)-N(1)-Si(1)	144.68(13)
Ti(1)-N(1)-C(1)	88.7(2)	Si(1)-N(1)-C(1)	126.2(2)
Ti(1)-N(2)-Si(2)	144.39(13)	Ti(1)-N(2)-C(1)	89.3(2)
Si(2)-N(2)-C(1)	126.1(2)	Ti(1)-N(3)-C(14)	165.9(2)
N(1)-Si(1)-C(8)	106.02(14)	N(1)-Si(1)-C(9)	114.22(14)
C(8)-Si(1)-C(9)	108.8(2)	N(1)-Si(1)-C(10)	112.88(14)
C(8)-Si(1)-C(10)	107.8(2)	C(9)-Si(1)-C(10)	106.9(2)
N(2)-Si(2)-C(11)	107.68(13)	N(2)-Si(2)-C(12)	112.74(13)
C(11)-Si(2)-C(12)	105.1(2)	N(2)-Si(2)-C(13)	112.64(13)
C(11)-Si(2)-C(13)	108.5(2)	C(12)-Si(2)-C(13)	109.8(2)
Ti(1)-C(1)-N(1)	59.05(14)	Ti(1)-C(1)-N(2)	57.88(13)
N(1)-C(1)-N(2)	116.8(2)	Ti(1)-C(1)-C(2)	173.7(2)
N(1)-C(1)-C(2)	121.5(2)	N(2)-C(1)-C(2)	121.7(2)
C(1)-C(2)-C(3)	119.3(2)	C(1)-C(2)-C(7)	121.5(2)
C(3)-C(2)-C(7)	119.2(3)	C(2)-C(3)-C(4)	120.2(3)
C(3)-C(4)-C(5)	120.2(3)	C(4)-C(5)-C(6)	120.7(3)
C(5)-C(6)-C(7)	119.4(3)	C(2)-C(7)-C(6)	120.3(3)
N(3)-C(14)-C(15)	121.3(3)	N(3)-C(14)-C(19)	120.0(3)
C(15)-C(14)-C(19)	118.7(3)	C(14)-C(15)-C(16)	119.3(3)
C(14)-C(15)-C(20)	119.8(3)	C(16)-C(15)-C(20)	120.9(3)
C(15)-C(16)-C(17)	121.5(3)	C(16)-C(17)-C(18)	119.3(3)

C(17)-C(18)-C(19)	121.5(3)	C(14)-C(19)-C(18)	119.8(3)
C(14)-C(19)-C(21)	119.8(3)	C(18)-C(19)-C(21)	120.5(3)
Ti(1)-C(22)-C(23)	72.5(2)	Ti(1)-C(22)-C(26)	74.4(2)
C(23)-C(22)-C(26)	108.2(2)	Ti(1)-C(22)-C(27)	122.5(2)
C(23)-C(22)-C(27)	126.6(3)	C(26)-C(22)-C(27)	125.0(3)
Ti(1)-C(23)-C(22)	72.7(2)	Ti(1)-C(23)-C(24)	74.2(2)
C(22)-C(23)-C(24)	108.2(3)	Ti(1)-C(23)-C(28)	125.1(2)
C(22)-C(23)-C(28)	124.4(3)	C(24)-C(23)-C(28)	127.0(3)
Ti(1)-C(24)-C(23)	71.1(2)	Ti(1)-C(24)-C(25)	74.0(2)
C(23)-C(24)-C(25)	107.6(3)	Ti(1)-C(24)-C(29)	122.7(2)
C(23)-C(24)-C(29)	128.5(3)	C(25)-C(24)-C(29)	123.9(3)
Ti(1)-C(25)-C(24)	72.4(2)	Ti(1)-C(25)-C(26)	72.2(2)
C(24)-C(25)-C(26)	108.9(3)	Ti(1)-C(25)-C(30)	125.5(2)
C(24)-C(25)-C(30)	122.1(3)	C(26)-C(25)-C(30)	128.8(3)
Ti(1)-C(26)-C(22)	71.2(2)	Ti(1)-C(26)-C(25)	73.4(2)
C(22)-C(26)-C(25)	107.2(3)	Ti(1)-C(26)-C(31)	127.1(2)
C(22)-C(26)-C(31)	124.4(3)	C(25)-C(26)-C(31)	127.9(3)

$Cp_{(cent)}$ refers to the computed C_5Me_5 ring carbon centroid

D.3 Atomic coordinates ($\times 10^4$) and isotropic or equivalent isotropic displacement parameters ($Å^2 \times 10^3$). $U_{(eq)}$ is defined as one third of the trace of the orthogonalised U_{ij} tensor

	x	y	z	$U_{(eq)}$
Ti(1)	1882(1)	1479(1)	7748(1)	17
N(1)	3702(2)	1230(2)	7840(1)	19
N(2)	2429(2)	1257(1)	6714(1)	18
N(3)	1213(2)	530(1)	7990(1)	23
Si(1)	5034(1)	1068(1)	8478(1)	24
Si(2)	1958(1)	1161(1)	5739(1)	22
C(1)	3518(2)	1110(2)	7098(2)	19
C(2)	4460(2)	786(2)	6712(2)	21
C(3)	4502(3)	-98(2)	6538(2)	28
C(4)	5362(3)	-411(2)	6165(2)	38
C(5)	6175(3)	147(3)	5971(2)	44
C(6)	6162(3)	1024(3)	6147(2)	40

C(7)	5294(3)	1345(2)	6520(2)	28
C(8)	4674(3)	1098(3)	9437(2)	43
C(9)	5763(3)	13(2)	8355(2)	44
C(10)	6126(3)	1948(2)	8425(2)	41
C(11)	460(3)	1647(2)	5496(2)	34
C(12)	1777(3)	5(2)	5420(2)	32
C(13)	2933(3)	1748(2)	5188(2)	35
C(14)	470(2)	-81(2)	8210(2)	23
C(15)	685(3)	-432(2)	8943(2)	29
C(16)	-97(3)	-1040(2)	9143(2)	38
C(17)	-1077(3)	-1306(2)	8634(2)	42
C(18)	-1273(3)	-979(2)	7912(2)	35
C(19)	-521(3)	-379(2)	7684(2)	27
C(20)	1750(3)	-150(2)	9505(2)	38
C(21)	-750(3)	-35(2)	6891(2)	36
C(22)	572(3)	2361(2)	8282(2)	26
C(23)	1723(3)	2589(2)	8640(2)	27
C(24)	2291(3)	2984(2)	8088(2)	24
C(25)	1492(3)	2997(2)	7402(2)	24
C(26)	418(3)	2612(2)	7513(2)	26
C(27)	-368(3)	1979(2)	8657(2)	42
C(28)	2179(3)	2527(2)	9476(2)	40
C(29)	3497(3)	3365(2)	8194(2)	32
C(30)	1763(3)	3434(2)	6704(2)	34
C(31)	-723(3)	2582(2)	6969(2)	36

D.4 Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic 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)	15(1)	18(1)	17(1)	-1(1)	4(1)	0(1)
N(1)	16(1)	24(1)	18(1)	-4(1)	3(1)	-2(1)
N(2)	19(1)	20(1)	16(1)	-1(1)	2(1)	1(1)
N(3)	22(1)	21(1)	26(1)	1(1)	5(1)	-1(1)

Si(1)	18(1)	28(1)	24(1)	-2(1)	-3(1)	-1(1)
Si(2)	26(1)	23(1)	15(1)	1(1)	1(1)	-3(1)
C(1)	21(1)	14(1)	20(1)	0(1)	3(1)	-4(1)
C(2)	18(1)	30(1)	14(1)	1(1)	0(1)	2(1)
C(3)	27(2)	30(2)	27(2)	-4(1)	6(1)	2(1)
C(4)	35(2)	44(2)	35(2)	-11(2)	8(1)	11(2)
C(5)	27(2)	71(3)	37(2)	-5(2)	14(1)	14(2)
C(6)	22(2)	66(2)	35(2)	8(2)	13(1)	-6(2)
C(7)	24(2)	34(1)	27(2)	3(1)	7(1)	-3(1)
C(8)	37(2)	66(2)	22(2)	1(2)	-6(1)	5(2)
C(9)	34(2)	41(2)	50(2)	-3(2)	-10(2)	11(2)
C(10)	27(2)	43(2)	49(2)	-2(2)	-6(2)	-13(2)
C(11)	26(2)	39(2)	32(2)	-2(1)	-8(1)	2(1)
C(12)	43(2)	26(1)	25(2)	-3(1)	4(1)	-6(1)
C(13)	44(2)	40(2)	19(2)	6(1)	1(1)	-11(2)
C(14)	21(1)	19(1)	30(2)	1(1)	10(1)	2(1)
C(15)	34(2)	25(2)	31(2)	2(1)	14(1)	3(1)
C(16)	47(2)	35(2)	37(2)	7(1)	21(2)	4(2)
C(17)	38(2)	30(2)	64(3)	5(2)	26(2)	-8(1)
C(18)	26(2)	29(2)	52(2)	-1(1)	11(2)	-6(1)
C(19)	21(1)	23(1)	38(2)	0(1)	10(1)	2(1)
C(20)	47(2)	43(2)	23(2)	2(1)	4(1)	3(2)
C(21)	28(2)	40(2)	39(2)	5(1)	2(1)	1(1)
C(22)	26(2)	24(1)	32(2)	-2(1)	14(1)	2(1)
C(23)	34(2)	23(1)	28(1)	-7(1)	12(1)	1(1)
C(24)	29(2)	19(1)	25(2)	-7(1)	10(1)	1(1)
C(25)	27(2)	18(1)	29(2)	-2(1)	10(1)	2(1)
C(26)	23(1)	17(1)	39(2)	-1(1)	10(1)	5(1)
C(27)	37(2)	37(2)	61(2)	0(2)	29(2)	1(1)
C(28)	52(2)	43(2)	26(2)	-10(2)	13(1)	3(2)
C(29)	30(2)	27(2)	39(2)	-9(1)	4(1)	-9(1)
C(30)	41(2)	24(2)	37(2)	5(1)	10(1)	-4(1)
C(31)	24(2)	32(2)	50(2)	4(2)	4(1)	6(1)

D.5 Hydrogen coordinates (× 10^4) and isotropic displacement parameters (Å^2 × 10^3)

	x	y	z	$U_{(eq)}$
H(31)	3915(3)	-507(2)	6682(2)	34
H(41)	5387(3)	-1043(2)	6036(2)	46
H(51)	6787(3)	-81(3)	5701(2)	53
H(61)	6763(3)	1426(3)	6010(2)	48
H(71)	5278(3)	1978(2)	6648(2)	34
H(81)	5401(3)	1008(3)	9824(2)	51
H(82)	4324(3)	1676(3)	9521(2)	51
H(83)	4102(3)	626(3)	9484(2)	51
H(91)	6507(3)	-31(2)	8735(2)	49
H(92)	5235(3)	-479(2)	8431(2)	49
H(93)	5939(3)	-18(2)	7834(2)	49
H(101)	6860(3)	1824(2)	8797(2)	48
H(102)	5801(3)	2521(2)	8547(2)	48
H(103)	6301(3)	1967(2)	7903(2)	48
H(111)	169(3)	1601(2)	4939(2)	39
H(112)	492(3)	2274(2)	5649(2)	39
H(113)	-79(3)	1326(2)	5770(2)	39
H(121)	1506(3)	-12(2)	4859(2)	38
H(122)	1187(3)	-287(2)	5671(2)	38
H(123)	2541(3)	-305(2)	5557(2)	38
H(131)	2626(3)	1674(2)	4635(2)	42
H(132)	2955(3)	2381(2)	5319(2)	42
H(133)	3739(3)	1501(2)	5318(2)	42
H(161)	52(3)	-1286(2)	9667(2)	49
H(171)	-1634(3)	-1732(2)	8791(2)	53
H(181)	-1970(3)	-1181(2)	7540(2)	43
H(201)	1771(3)	-462(2)	9994(2)	46
H(202)	1716(3)	492(2)	9589(2)	46
H(203)	2469(3)	-294(2)	9303(2)	46
H(211)	-1475(3)	-311(2)	6601(2)	46
H(212)	-854(3)	610(2)	6898(2)	46
H(213)	-75(3)	-180(2)	6644(2)	46
H(271)	-1092(3)	1883(2)	8269(2)	55
H(272)	-539(3)	2391(2)	9051(2)	55

H(273)	-94(3)	1411(2)	8898(2)	55
H(281)	3011(3)	2722(2)	9593(2)	49
H(282)	1699(3)	2908(2)	9748(2)	49
H(283)	2127(3)	1910(2)	9644(2)	49
H(291)	3637(3)	3592(2)	7699(2)	38
H(292)	3568(3)	3853(2)	8568(2)	38
H(293)	4087(3)	2906(2)	8385(2)	38
H(301)	1083(3)	3369(2)	6278(2)	41
H(302)	1918(3)	4067(2)	6811(2)	41
H(303)	2468(3)	3158(2)	6563(2)	41
H(311)	-610(3)	2792(2)	6462(2)	43
H(312)	-1299(3)	2965(2)	7157(2)	43
H(313)	-1023(3)	1971(2)	6923(2)	43

APPENDIX E – X-RAY STRUCTURE ANALYSIS OF [Ti(η-C_5Me_5)(μ-O){MeC(N^iPr)$_2$}]$_2$ (22)

E.1 Crystal data, data collection and refinement

Empirical formula	$C_{36}H_{64}N_4O_2Ti_2$
Formula weight	680.71
Crystal description	Amber block
Crystal size	0.45 x 0.40 x 0.30 mm
Temperature	175 K
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 9.7810(4) Å α = 90 deg.
	b = 15.4630(4) Å β = 92.625(2) deg.
	c = 12.0930(5) Å γ = 90 deg.
Reflections for cell refinement	9980
Range in theta	0 to 27 deg.
Volume, Z	1827.07 $Å^3$, 2
Density (calculated)	1.237 Mg/m^3
Absorption coefficient	0.47 mm^{-1}
F(000)	736
Diffractometer type	Enraf-nonius DIP2000
Wavelength	0.71069 A
Scan type	\w
Theta range for data collection	1.69 to 26.45 deg.
Index ranges	0<=h<=12, 0<=k<=19, -15<=l<=15
Reflections collected	9980
Independent reflections	3890 [R(merge) = 0.07]
Observed reflections	2403 [I>3sigma(I)]
Absorption correction	Multi-scan
Tmin, Tmax	0.829, 0.868
Decay correction	not measured
Structure solution	by direct methods and
	Fourier difference maps
Hydrogen atom location	geometric
Hydrogen atom treatment	riding model
Refinement method	Full-matrix least-squares on F

Weighting scheme	Chebychev polynomial
Data / restraints / parameters	2403 / 0 / 199
Goodness-of-fit on F	1.0710
Final R indices [I>3sigma(I)]	R1 = 0.0523, Rw = 0.0395
Extinction coefficient	none
Final maximum delta/sigma	0.0002
Largest diff. peak and hole	0.63 and -0.52 e.Å^{-3}

E.2 Bond lengths (Å) and angles (°)

Ti(1)...Ti(1B)	2.823(1)	Ti(1)-O(1)	1.855(2)
Ti(1)-O(1B)	1.869(2)	Ti(1)-N(1)	2.188(3)
Ti(1)-N(2)	2.168(3)	Ti(1)-C(9)	2.427(3)
Ti(1)-C(10)	2.369(3)	Ti(1)-C(11)	2.438(3)
Ti(1)-C(12)	2.505(3)	Ti(1)-C(13)	2.491(3)
Ti(1)-Cp$_{(cent)}$	2.13	N(1)-C(1)	1.328(4)
N(1)-C(3)	1.466(4)	N(2)-C(1)	1.327(4)
N(2)-C(6)	1.478(4)	C(1)-C(2)	1.510(4)
C(3)-C(4)	1.527(5)	C(3)-C(5)	1.516(5)
C(6)-C(7)	1.536(5)	C(6)-C(8)	1.510(5)
C(9)-C(10)	1.428(4)	C(9)-C(13)	1.414(5)
C(9)-C(14)	1.491(5)	C(10)-C(11)	1.413(4)
C(10)-C(15)	1.489(5)	C(11)-C(12)	1.400(4)
C(11)-C(16)	1.500(4)	C(12)-C(13)	1.420(5)
C(12)-C(17)	1.497(4)	C(13)-C(18)	1.502(4)

O(1)-Ti(1)-O(1B)	81.41(9)	O(1)-Ti(1)-N(1)	89.9(1)
O(1B)- -Ti(1)-N(1)	132.56(9)	O(1)-Ti(1)-N(2)	130.1(1)
O(1B)- Ti(1)-N(2)	90.3(1)	N(1)-Ti(1)-N(2)	60.7(1)
O(1)-Ti(1)-C(9)	90.2(1)	O(1B)-Ti(1)-C(9)	126.6(1)
N(1)-Ti(1)-C(9)	99.8(1)	N(2)-Ti(1)-C(9)	131.2(1)
O(1)-Ti(1)-C(10)	95.7(1)	O(1B) -Ti(1)-C(10)	93.6(1)
N(1)-Ti(1)-C(10)	133.7(1)	N(2)-Ti(1)-C(10)	134.0(1)
O(1)-Ti(1)-C(11)	128.3(1)	O(1B) -Ti(1)-C(11)	88.9(1)
N(1)-Ti(1)-C(11)	130.2(1)	N(2)-Ti(1)-C(11)	100.3(1)
O(1)-Ti(1)-C(12)	145.7(1)	O(1B) -Ti(1)-C(12)	115.7(1)
N(1)-Ti(1)-C(12)	97.4(1)	N(2)-Ti(1)-C(12)	81.4(1)

O(1)-Ti(1)-C(13)	117.4(1)	O(1B) -Ti(1)-C(13)	143.9(1)
N(1)-Ti(1)-C(13)	80.7(1)	N(2)-Ti(1)-C(13)	97.8(1)
C(9)-Ti(1)-C(10)	34.6(1)	C(9)-Ti(1)-C(11)	56.4(1)
C(10)-Ti(1)-C(11)	34.2(1)	C(9)-Ti(1)-C(12)	55.6(1)
C(10)-Ti(1)-C(12)	55.8(1)	C(11)-Ti(1)-C(12)	32.9(1)
C(9)-Ti(1)-C(13)	33.4(1)	C(10)-Ti(1)-C(13)	56.1(1)
C(11)-Ti(1)-C(13)	55.1(1)	C(12)-Ti(1)-C(13)	33.0(1)
O(1)-Ti(1)-$Cp_{(cent)}$	117.8	O(1B)-Ti(1)-$Cp_{(cent)}$	115.9
N(1)-Ti(1)-$Cp_{(cent)}$	109.4	N(2)-Ti(1)-$Cp_{(cent)}$	110.0
Ti(1)-O(1)-Ti(1B)	98.59(9)	Ti(1)-N(1)-C(1)	91.7(2)
Ti(1)-N(1)-C(3)	139.6(2)	C(1)-N(1)-C(3)	122.2(3)
Ti(1)-N(2)-C(1)	92.6(2)	Ti(1)-N(2)-C(6)	140.8(2)
C(1)-N(2)-C(6)	121.7(3)	N(1)-C(1)-N(2)	112.1(3)
N(1)-C(1)-C(2)	123.9(3)	N(2)-C(1)-C(2)	123.9(3)
N(1)-C(3)-C(4)	113.0(3)	N(1)-C(3)-C(5)	110.3(3)
C(4)-C(3)-C(5)	108.9(3)	N(2)-C(6)-C(7)	112.4(3)
N(2)-C(6)-C(8)	109.9(3)	C(7)-C(6)-C(8)	110.0(3)
Ti(1)-C(9)-C(10)	70.5(2)	Ti(1)-C(9)-C(13)	75.8(2)
C(10)-C(9)-C(13)	107.1(3)	Ti(1)-C(9)-C(14)	123.6(2)
C(10)-C(9)-C(14)	124.8(3)	C(13)-C(9)-C(14)	127.8(3)
Ti(1)-C(10)-C(9)	74.9(2)	Ti(1)-C(10)-C(11)	75.6(2)
C(9)-C(10)-C(11)	107.9(3)	Ti(1)-C(10)-C(15)	124.3(2)
C(9)-C(10)-C(15)	125.5(3)	C(11)-C(10)-C(15)	125.6(3)
Ti(1)-C(11)-C(10)	70.3(2)	Ti(1)-C(11)-C(12)	76.2(2)
C(10)-C(11)-C(12)	108.6(3)	Ti(1)-C(11)-C(16)	121.6(2)
C(10)-C(11)-C(16)	123.7(3)	C(12)-C(11)-C(16)	127.6(3)
Ti(1)-C(12)-C(11)	70.9(2)	Ti(1)-C(12)-C(13)	72.9(2)
C(11)-C(12)-C(13)	107.8(3)	Ti(1)-C(12)-C(17)	126.4(2)
C(11)-C(12)-C(17)	128.3(3)	C(13)-C(12)-C(17)	123.7(3)
Ti(1)-C(13)-C(9)	70.8(2)	Ti(1)-C(13)-C(12)	74.0(2)
C(9)-C(13)-C(12)	108.5(3)	Ti(1)-C(13)-C(18)	126.3(2)
C(9)-C(13)-C(18)	127.4(3)	C(12)-C(13)-C(18)	123.8(3)

(i) Symmetry transformations used to generate equivalent atoms carrying the suffix 'B': -x,-y,-z+1.

(ii) $Cp_{(cent)}$ refers to the computed centroid for the C_5Me_5 ligand

E.3 Atomic coordinates ($\times 10^4$) and isotropic or equivalent isotropic displacement parameters ($Å^2 \times 10^3$). $U_{(eq)}$ is defined as one third of the trace of the orthogonalised U_{ij} tensor

	x	y	z	$U_{(eq)}$
Ti(1)	398(1)	-342(1)	6048(1)	14
O(1)	-1180(2)	-185(1)	5162(2)	19
N(1)	-649(3)	175(2)	7465(2)	21
N(2)	1475(3)	548(2)	7165(2)	18
C(1)	346(3)	743(2)	7680(3)	21
C(2)	190(4)	1540(2)	8384(3)	29
C(3)	-2043(3)	306(2)	7830(3)	27
C(4)	-2143(4)	227(3)	9082(3)	40
C(5)	-3014(3)	-339(3)	7269(3)	34
C(6)	2689(3)	1118(2)	7223(3)	24
C(7)	3430(4)	1108(2)	8371(3)	36
C(8)	3665(3)	860(2)	6350(3)	31
C(9)	-138(3)	-1866(2)	6239(3)	22
C(10)	852(3)	-1760(2)	5418(3)	20
C(11)	2093(3)	-1493(2)	5958(3)	20
C(12)	1886(3)	-1412(2)	7092(3)	19
C(13)	508(3)	-1640(2)	7269(3)	23
C(14)	-1536(4)	-2232(2)	6028(3)	35
C(15)	684(4)	-2042(2)	4242(3)	34
C(16)	3403(3)	-1369(2)	5380(3)	28
C(17)	2920(4)	-1212(2)	8007(3)	29
C(18)	-72(4)	-1715(2)	8394(3)	33

E.4 Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic 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)	15(1)	12(1)	14(1)	1(1)	1(1)	1(1)
O(1)	16(1)	21(1)	18(1)	5(1)	0(1)	-1(1)
N(1)	23(1)	21(1)	19(1)	-1(1)	6(1)	0(1)
N(2)	18(1)	15(1)	21(1)	-2(1)	1(1)	-2(1)
C(1)	27(2)	19(2)	16(1)	3(1)	0(1)	3(1)
C(2)	34(2)	27(2)	25(2)	-6(1)	2(1)	0(2)
C(3)	26(2)	28(2)	28(2)	2(2)	6(1)	6(2)
C(4)	36(2)	55(3)	30(2)	-2(2)	13(2)	4(2)
C(5)	22(2)	46(2)	35(2)	5(2)	7(1)	2(2)
C(6)	24(2)	14(1)	34(2)	2(1)	-3(1)	-2(1)
C(7)	38(2)	29(2)	38(2)	0(2)	-11(2)	-10(2)
C(8)	19(2)	33(2)	42(2)	3(2)	-3(1)	-8(1)
C(9)	25(2)	13(1)	29(2)	2(1)	-1(1)	1(1)
C(10)	24(2)	13(1)	22(2)	3(1)	-2(1)	3(1)
C(11)	23(2)	11(1)	27(2)	2(1)	1(1)	5(1)
C(12)	24(2)	11(1)	23(2)	2(1)	-2(1)	4(1)
C(13)	31(2)	11(1)	25(2)	3(1)	3(1)	5(1)
C(14)	31(2)	24(2)	51(2)	1(2)	-1(2)	-6(2)
C(15)	50(2)	22(2)	29(2)	-2(1)	-4(2)	8(2)
C(16)	25(2)	26(2)	34(2)	2(1)	9(1)	5(1)
C(17)	35(2)	21(2)	31(2)	2(1)	-12(2)	1(1)
C(18)	38(2)	30(2)	31(2)	13(2)	11(2)	7(2)

E.5 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$)

	x	y	z	$U_{(eq)}$
H(21)	1041(4)	1850(2)	8424(3)	40
H(22)	-51(4)	1377(2)	9116(3)	40
H(23)	-514(4)	1903(2)	8055(3)	40
H(31)	-2277(3)	884(2)	7603(3)	37
H(41)	-3069(4)	321(3)	9286(3)	53
H(42)	-1556(4)	649(3)	9440(3)	53
H(43)	-1855(4)	-342(3)	9309(3)	53
H(51)	-3924(3)	-246(3)	7508(3)	44
H(52)	-2725(3)	-916(3)	7460(3)	44
H(53)	-3003(3)	-265(3)	6481(3)	44
H(61)	2325(3)	1688(2)	7092(3)	33
H(71)	4200(4)	1493(2)	8371(3)	48
H(72)	2817(4)	1291(2)	8923(3)	48
H(73)	3742(4)	531(2)	8534(3)	48
H(81)	4450(3)	1234(2)	6391(3)	37
H(82)	3953(3)	273(2)	6478(3)	37
H(83)	3217(3)	905(2)	5630(3)	37
H(141)	-2014(4)	-2238(2)	6704(3)	46
H(142)	-1466(4)	-2812(2)	5752(3)	46
H(143)	-2029(4)	-1881(2)	5490(3)	46
H(151)	1497(4)	-1898(2)	3868(3)	43
H(152)	536(4)	-2655(2)	4207(3)	43
H(153)	-86(4)	-1749(2)	3893(3)	43
H(161)	4112(3)	-1184(2)	5901(3)	40
H(162)	3661(3)	-1907(2)	5052(3)	40
H(163)	3271(3)	-940(2)	4811(3)	40
H(171)	2483(4)	-1200(2)	8701(3)	41
H(172)	3619(4)	-1648(2)	8030(3)	41
H(173)	3324(4)	-658(2)	7873(3)	41
H(181)	593(4)	-1518(2)	8946(3)	44
H(182)	-299(4)	-2308(2)	8536(3)	44
H(183)	-881(4)	-1366(2)	8419(3)	44

APPENDIX F – X-RAY STRUCTURE ANALYSIS OF [Ti(η-C_5H_4Me)(μ-O){PhC($NSiMe_3$)}]$_2$ (24)

F.1 Crystal data, data collection and refinement

Empirical formula	C_{50} H_{72} N_4 O_2 Si_4 Ti_2
Formula weight	969.30
Crystal description	pale yellow block
Crystal size	0.40 x 0.40 x 0.40 mm
Temperature	150 K
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 10.1320(4) Å α = 92.248(4) deg.
	b = 10.4210(7) Å β = 104.045(5) deg.
	c = 15.3100(11) Å γ = 118.207(4) deg.
Reflections for cell refinement	22600
Range in theta	0 to 27 deg.
Volume,	Z 1359.4(2) $Å^3$, 1
Density (calculated)	1.184 Mg/m^3
Absorption coefficient	0.421 mm^{-1}
F(000)	516.836
Diffractometer type	DIP2000
Wavelength	0.71073 Å
Scan type	\w
Theta range for data collection	0.00 to 26.57 deg.
Index ranges	-12<=h<=12, -12<=k<=13, 0<=l<=19
Reflections collected	22600
Independent reflections	5134 [R(merge) = 0.020]
Observed reflections	5007 [I>3sigma(I)]
Absorption correction	Multi-scan (Tmin = 0.84, Tmax = 0.85)
Structure solution	by direct and Fourier difference maps
Hydrogen atom location	Geometrical
Hydrogen atom treatment	Riding model
Refinement method	Full-matrix least-squares on F
Data / restraints / parameters	5007 / 0/ 280
Goodness-of-fit on F	1.0253
Final R indices [I>3sigma(I)]	R1 = 0.0694, Rw = 0.0432

Final maximum delta/sigma	0.019533
Largest diff. peak and hole	0.57 and -0.47 e.A^-3

F.2 Bond lengths (Å) and angles (°)

Ti(1)---Ti(1B)	2.7718(6)	$Cp_{(cent)}$-Ti(1)	2.087
Ti(1)-N(1)	2.155(2)	Ti(1)-N(2)	2.165(2)
Ti(1)-O(1)	1.8429(13)	Ti(1)-O(1B)	1.8604(12)
Ti(1)-C(15)	2.483(2)	Ti(1)-C(16)	2.401(2)
Ti(1)-C(17)	2.323(2)	Ti(1)-C(18)	2.370(2)
Ti(1)-C(19)	2.454(2)	Si(1)-N(1)	1.739(2)
Si(1)-C(8)	1.870(2)	Si(1)-C(9)	1.864(2)
Si(1)-C(10)	1.863(2)	Si(2)-N(2)	1.739(2)
Si(2)-C(11)	1.867(3)	Si(2)-C(12)	1.872(2)
Si(2)-C(13)	1.863(2)	N(1)-C(1)	1.328(2)
N(2)-C(1)	1.317(2)	C(1)-C(2)	1.500(2)
C(2)-C(3)	1.385(3)	C(2)-C(7)	1.394(3)
C(3)-C(4)	1.392(3)	C(4)-C(5)	1.386(4)
C(5)-C(6)	1.380(4)	C(6)-C(7)	1.382(3)
C(14)-C(15)	1.502(3)	C(15)-C(16)	1.409(3)
C(15)-C(19)	1.405(3)	C(16)-C(17)	1.408(3)
C(17)-C(18)	1.408(3)	C(18)-C(19)	1.408(3)
C(20)-C(21)	1.354(6)	C(20)-C(25)	1.348(7)
C(21)-C(22)	1.338(7)	C(22)-C(23)	1.321(6)
C(23)-C(24)	1.359(7)	C(24)-C(25)	1.372(7)
Ti(1B)-Ti(1)-N(1)	114.01(4)	Ti(1B)-Ti(1)-N(2)	115.96(5)
$Cp_{(cent)}$-Ti(1)-O(1)	117.7	$Cp_{(cent)}$-Ti(1)-O(1B)	115.5
$Cp_{(cent)}$-Ti(1)-N(1)	111.2	$Cp_{(cent)}$-Ti(1)-N(2)	109.2
N(1)-Ti(1)-N(2)	62.14(6)	Ti(1B) -Ti(1)-O(1)	41.78(4)
N(1)-Ti(1)-O(1)	129.13(6)	N(2)-Ti(1)-O(1)	88.14(6)
Ti(1B) -Ti(1)-O(1B)	41.30(4)	N(1)-Ti(1)-O(1B)	88.91(6)
N(2)-Ti(1)-O(1B)	133.19(6)	O(1)-Ti(1)-O(1B)	83.09(6)
Ti(1B) -Ti(1)-C(15)	147.39(5)	N(1)-Ti(1)-C(15)	82.30(6)
N(2)-Ti(1)-C(15)	96.56(7)	O(1)-Ti(1)-C(15)	145.10(7)
O(1B) -Ti(1)-C(15)	116.27(7)	Ti(1B) -Ti(1)-C(16)	113.92(6)
N(1)-Ti(1)-C(16)	100.21(7)	N(2)-Ti(1)-C(16)	130.00(7)
O(1)-Ti(1)-C(16)	129.50(7)	O(1B)- Ti(1)-C(16)	88.50(7)

Ti(1B) -Ti(1)-C(17)	95.78(5)	N(1)-Ti(1)-C(17)	134.64(7)
N(2)-Ti(1)-C(17)	134.03(7)	O(1)-Ti(1)-C(17)	95.99(7)
O(1B) -Ti(1)-C(17)	92.68(7)	Ti(1B) -Ti(1)-C(18)	112.40(6)
N(1)-Ti(1)-C(18)	133.48(7)	N(2)-Ti(1)-C(18)	99.80(7)
O(1)-Ti(1)-C(18)	89.03(7)	O(1B) -Ti(1)-C(18)	125.78(7)
Ti(1B) -Ti(1)-C(19)	146.29(5)	N(1)-Ti(1)-C(19)	99.68(7)
N(2)-Ti(1)-C(19)	80.18(6)	O(1)-Ti(1)-C(19)	115.69(7)
O(1B) -Ti(1)-C(19)	144.10(7)	C(15)-Ti(1)-C(16)	33.48(7)
C(15)-Ti(1)-C(17)	56.63(7)	C(16)-Ti(1)-C(17)	34.64(8)
C(15)-Ti(1)-C(18)	56.08(8)	C(16)-Ti(1)-C(18)	57.00(8)
C(17)-Ti(1)-C(18)	34.90(8)	C(15)-Ti(1)-C(19)	33.07(8)
C(16)-Ti(1)-C(19)	55.75(8)	C(17)-Ti(1)-C(19)	56.81(7)
C(18)-Ti(1)-C(19)	33.90(7)	N(1)-Si(1)-C(8)	113.0(1)
N(1)-Si(1)-C(9)	110.3(1)	C(8)-Si(1)-C(9)	107.60(12)
N(1)-Si(1)-C(10)	107.73(9)	C(8)-Si(1)-C(10)	108.99(12)
C(9)-Si(1)-C(10)	109.26(12)	N(2)-Si(2)-C(11)	109.7(1)
N(2)-Si(2)-C(12)	113.3(1)	C(11)-Si(2)-C(12)	108.40(12)
N(2)-Si(2)-C(13)	107.6(1)	C(11)-Si(2)-C(13)	108.55(14)
C(12)-Si(2)-C(13)	109.16(11)	Ti(1)-N(1)-Si(1)	136.28(8)
Ti(1)-N(1)-C(1)	91.43(11)	Si(1)-N(1)-C(1)	129.94(13)
Ti(1)-N(2)-Si(2)	135.21(8)	Ti(1)-N(2)-C(1)	91.29(11)
Si(2)-N(2)-C(1)	131.24(13)	Ti(1)-O(1)-Ti(1B)	96.91(6)
N(1)-C(1)-N(2)	114.9(2)	N(1)-C(1)-C(2)	123.1(2)
N(2)-C(1)-C(2)	122.0(2)	C(1)-C(2)-C(3)	121.2(2)
C(1)-C(2)-C(7)	119.2(2)	C(3)-C(2)-C(7)	119.5(2)
C(2)-C(3)-C(4)	119.9(2)	C(3)-C(4)-C(5)	120.1(2)
C(4)-C(5)-C(6)	120.0(2)	C(5)-C(6)-C(7)	120.1(2)
C(2)-C(7)-C(6)	120.3(2)	Ti(1)-C(15)-C(14)	126.0(2)
Ti(1)-C(15)-C(16)	70.05(11)	C(14)-C(15)-C(16)	126.5(2)
Ti(1)-C(15)-C(19)	72.31(11)	C(14)-C(15)-C(19)	125.8(2)
C(16)-C(15)-C(19)	107.5(2)	Ti(1)-C(16)-C(15)	76.47(12)
Ti(1)-C(16)-C(17)	69.66(11)	C(15)-C(16)-C(17)	108.3(2)
Ti(1)-C(17)-C(16)	75.70(11)	Ti(1)-C(17)-C(18)	74.38(11)
C(16)-C(17)-C(18)	107.9(2)	Ti(1)-C(18)-C(17)	70.72(11)
Ti(1)-C(18)-C(19)	76.30(11)	C(17)-C(18)-C(19)	107.8(2)
Ti(1)-C(19)-C(15)	74.62(11)	Ti(1)-C(19)-C(18)	69.80(11)
C(15)-C(19)-C(18)	108.5(2)	C(21)-C(20)-C(25)	119.3(4)
C(20)-C(21)-C(22)	120.8(4)	C(21)-C(22)-C(23)	120.6(4)
C(22)-C(23)-C(24)	120.2(4)	C(23)-C(24)-C(25)	119.5(4)
C(20)-C(25)-C(24)	119.6(4)		

(i) Symmetry transformations used to generate equivalent atoms carrying the suffix 'B': -x+2, -y,-z+1.

(ii) $Cp_{(cent)}$ refers to the computed centroid for the C_5H_4Me ligand

F.3 Atomic coordinates ($\times 10^4$) and isotropic or equivalent isotropic displacement parameters ($Å^2 \times 10^3$). $U_{(eq)}$ is defined as one third of the trace of the orthogonalised U_{ij} tensor

	x	y	z	$U_{(eq)}$
Ti(1)	9616(1)	964(1)	4554(1)	21
Si(1)	5804(1)	-1508(1)	2949(1)	30
Si(2)	11944(1)	2127(1)	2988(1)	34
N(1)	7744(2)	-83(2)	3287(1)	25
N(2)	10214(2)	1377(2)	3290(1)	27
O(1)	11355(2)	752(1)	4977(1)	26
C(1)	8748(2)	475(2)	2803(1)	24
C(2)	8260(2)	140(2)	1777(1)	27
C(3)	8324(3)	-991(2)	1318(1)	35
C(4)	7943(3)	-1225(3)	367(2)	49
C(5)	7482(3)	-340(3)	-121(1)	55
C(6)	7407(3)	781(3)	336(2)	52
C(7)	7794(3)	1025(3)	1280(1)	39
C(8)	4544(3)	-1228(3)	1949(2)	50
C(9)	5693(3)	-3306(3)	2622(2)	47
C(10)	5017(3)	-1601(3)	3940(2)	47
C(11)	12523(3)	690(3)	2863(2)	54
C(12)	11795(3)	2865(3)	1895(2)	47
C(13)	13500(3)	3659(3)	3936(2)	52
C(14)	7176(4)	2569(3)	3865(2)	62
C(15)	8558(3)	2678(2)	4576(1)	38
C(16)	8523(3)	2036(2)	5369(2)	40
C(17)	10075(3)	2478(2)	5876(1)	40
C(18)	11078(3)	3411(2)	5402(1)	39

C(19)	10136(3)	3520(2)	4597(1)	37
C(20)	6570(5)	4185(5)	414(3)	91
C(21)	6741(6)	4189(4)	1319(4)	99
C(22)	8151(7)	4994(4)	1939(2)	90
C(23)	9406(5)	5803(4)	1679(3)	86
C(24)	9281(7)	5824(5)	777(4)	107
C(25)	7841(8)	4995(5)	138(3)	100

F.4 Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic 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)	25(1)	22(1)	16(1)	2(1)	4(1)	12(1)
Si(1)	24(1)	36(1)	27(1)	4(1)	4(1)	13(1)
Si(2)	29(1)	38(1)	24(1)	6(1)	8(1)	8(1)
N(1)	25(1)	29(1)	19(1)	4(1)	4(1)	13(1)
N(2)	28(1)	29(1)	17(1)	5(1)	4(1)	10(1)
O(1)	26(1)	28(1)	24(1)	7(1)	7(1)	14(1)
C(1)	29(1)	24(1)	21(1)	5(1)	5(1)	16(1)
C(2)	27(1)	31(1)	19(1)	3(1)	3(1)	12(1)
C(3)	40(1)	37(1)	28(1)	2(1)	9(1)	19(1)
C(4)	63(2)	52(1)	29(1)	-3(1)	14(1)	26(1)
C(5)	61(2)	70(2)	21(1)	5(1)	5(1)	24(1)
C(6)	56(2)	67(2)	29(1)	17(1)	3(1)	31(1)
C(7)	48(2)	45(1)	29(1)	12(1)	7(1)	29(1)
C(8)	37(2)	65(2)	40(1)	6(1)	-1(1)	26(1)
C(9)	38(2)	35(1)	54(1)	4(1)	11(1)	9(1)
C(10)	32(1)	63(2)	41(1)	7(1)	14(1)	18(1)
C(11)	40(2)	71(2)	59(2)	17(1)	22(1)	30(1)
C(12)	48(2)	47(1)	30(1)	12(1)	14(1)	10(1)
C(13)	38(2)	57(1)	32(1)	6(1)	8(1)	1(1)
C(14)	72(2)	52(2)	67(2)	2(1)	0(1)	45(2)
C(15)	47(1)	31(1)	39(1)	-2(1)	6(1)	26(1)
C(16)	52(2)	39(1)	40(1)	2(1)	20(1)	29(1)
C(17)	59(2)	40(1)	24(1)	-4(1)	8(1)	30(1)

C(18)	39(1)	29(1)	37(1)	-8(1)	0(1)	15(1)
C(19)	51(2)	25(1)	38(1)	3(1)	11(1)	21(1)
C(20)	88(3)	84(3)	96(3)	-1(2)	1(2)	51(2)
C(21)	112(4)	60(2)	139(4)	4(2)	82(3)	33(2)
C(22)	165(5)	53(2)	60(2)	6(2)	45(2)	57(3)
C(23)	89(3)	69(2)	93(3)	-8(2)	6(2)	45(2)
C(24)	116(4)	71(2)	155(5)	26(3)	91(4)	40(3)
C(25)	179(6)	84(3)	59(2)	28(2)	42(3)	77(3)

F.5 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$)

	x	y	z	$U_{(eq)}$
H(31)	8649	-1629	1667	60
H(41)	8001	-2027	39	60
H(51)	7205	-515	-796	60
H(61)	7076	1412	-13	60
H(71)	7743	1833	1602	60
H(81)	3464	-2061	1786	60
H(82)	4968	-1165	1421	60
H(83)	4560	-289	2111	60
H(91)	4586	-4111	2431	60
H(92)	6296	-3519	3153	60
H(93)	6145	-3252	2109	60
H(101)	3913	-2406	3766	60
H(102)	5648	-1803	4461	60
H(103)	5082	-647	4118	60
H(111)	13511	1124	2693	60
H(112)	12694	349	3456	60
H(113)	11687	-155	2386	60
H(121)	12814	3277	1762	60
H(122)	11531	3660	1961	60
H(123)	10968	2060	1390	60
H(131)	14494	4110	3785	60
H(132)	13617	3259	4508	60
H(133)	13183	4414	4019	60

H(141)	7537	3123	3383	60
H(142)	6660	2992	4155	60
H(143)	6420	1515	3591	60
H(161)	7563	1387	5542	60
H(171)	10409	2178	6458	60
H(181)	12237	3905	5601	60
H(191)	10524	4096	4125	60
H(201)	5513	3595	-35	60
H(211)	5804	3586	1519	60
H(221)	8234	4976	2600	60
H(231)	10437	6382	2145	60
H(241)	10222	6424	583	60
H(251)	7732	5002	-523	60

APPENDIX G – X-RAY STRUCTURE ANALYSIS OF Ti(η-C_5Me_5) {OC(O)N(2,6-$C_6H_3Me_2$)C(O)O}{MeC(N^{i}Pr)$_2$} (31)

G.1 Crystal data, data collection and refinement

Empirical formula	$C_{28}\ H_{41}\ N_3\ O_4\ Ti_1\ .\ 0.5(C_6H_6)$
Formula weight	570.61
Crystal description	red prism
Crystal size	0.30 x 0.10 x 0.10 mm
Temperature	150 K
Crystal system	Orthorhombic
Space group	P b c a
Unit cell dimensions	a = 14.4250(2) Å α = 90 deg.
	b = 17.2619(3) Å β = 90 deg.
	c = 24.3318(4) Å γ = 90 deg.
Reflections for cell refinement	19617
Range in theta	0 to 28 deg.
Volume, Z	6058.7 Å^3, 8
Density (calculated)	1.25 Mg/m^3
Absorption coefficient	0.32 mm^{-1}
F(000)	2442.45
Diffractometer type	Nonius Kappa CCD
Wavelength	0.71073 A
Scan type	\w
Index ranges	0<=h<=18, 0<=k<=22, 0<=l<=31
Reflections collected	19617
Independent reflections	6916 [R(merge) = 0.055]
Observed reflections	4551 [I>3sigma(I)]
Absorption correction	Multi-scan
Tmin, Tmax	0.91, 0.97
Structure solution	by Direct methods and
	Fourier difference maps
Hydrogen atom location	geometric
Hydrogen atom treatment	No refinement
Refinement method	Full-matrix least-squares on F
Weighting scheme	Chebychev
Data / restraints / parameters	4551 / 0 / 352

Goodness-of-fit on F	0.9955
Final R indices [I>3sigma(I)]	R1 = 0.0463, Rw = 0.0534
Final maximum delta/sigma	0.0003
Largest diff. peak and hole	0.58 and -0.54 e. $Å^{-3}$

G.2 Bond lengths (Å) and angles (°)

Ti(1)-O(1)	1.932(2)	Ti(1)-O(3)	1.931(2)
Ti(1)-N(2)	2.064(2)	Ti(1)-N(3)	2.071(2)
Ti(1)-C(11)	2.485(2)	Ti(1)-C(19)	2.394(2)
Ti(1)-C(20)	2.388(2)	Ti(1)-C(21)	2.376(2)
Ti(1)-C(22)	2.349(2)	Ti(1)-C(23)	2.375(2)
Ti(1)-$Cp_{(cent)}$	2.046	O(1)-C(1)	1.299(3)
O(2)-C(1)	1.213(3)	O(3)-C(2)	1.300(3)
O(4)-C(2)	1.210(3)	N(1)-C(1)	1.410(3)
N(1)-C(2)	1.417(3)	N(1)-C(3)	1.446(3)
N(2)-C(11)	1.333(3)	N(2)-C(13)	1.474(3)
N(3)-C(11)	1.325(3)	N(3)-C(16)	1.474(3)
C(3)-C(4)	1.397(3)	C(3)-C(8)	1.390(3)
C(4)-C(5)	1.397(4)	C(4)-C(9)	1.500(4)
C(5)-C(6)	1.374(4)	C(6)-C(7)	1.387(4)
C(7)-C(8)	1.399(4)	C(8)-C(10)	1.502(4)
C(11)-C(12)	1.501(3)	C(13)-C(14)	1.516(4)
C(13)-C(15)	1.530(3)	C(16)-C(17)	1.528(4)
C(16)-C(18)	1.532(4)	C(19)-C(20)	1.422(4)
C(19)-C(23)	1.411(4)	C(19)-C(24)	1.498(4)
C(20)-C(21)	1.427(3)	C(20)-C(25)	1.499(4)
C(21)-C(22)	1.427(3)	C(21)-C(26)	1.498(3)
C(22)-C(23)	1.420(3)	C(22)-C(27)	1.495(4)
C(23)-C(28)	1.503(4)	C(29)-C(30)	1.382(4)
C(29)-C(31B)	1.384(4)	C(30)-C(31)	1.381(4)

O(1)-Ti(1)-O(3)	83.38(6)	O(1)-Ti(1)-N(2)	88.70(7)
O(3)-Ti(1)-N(2)	127.65(7)	O(1)-Ti(1)-N(3)	136.68(7)
O(3)-Ti(1)-N(3)	87.71(7)	N(2)-Ti(1)-N(3)	64.09(7)
O(1)-Ti(1)-C(11)	111.83(7)	O(3)-Ti(1)-C(11)	106.22(7)
N(2)-Ti(1)-C(11)	32.43(7)	N(3)-Ti(1)-C(11)	32.21(7)
O(1)-Ti(1)-C(19)	139.98(8)	O(3)-Ti(1)-C(19)	114.52(8)

N(2)-Ti(1)-C(19)	104.40(8)	N(3)-Ti(1)-C(19)	81.75(8)
C(11)-Ti(1)-C(19)	97.63(8)	O(1)-Ti(1)-C(20)	110.65(8)
O(3)-Ti(1)-C(20)	142.36(8)	N(2)-Ti(1)-C(20)	88.52(8)
N(3)-Ti(1)-C(20)	102.10(8)	C(11)-Ti(1)-C(20)	100.57(8)
O(1)-Ti(1)-C(21)	82.39(7)	O(3)-Ti(1)-C(21)	121.55(8)
N(2)-Ti(1)-C(21)	108.33(8)	N(3)-Ti(1)-C(21)	136.36(8)
C(11)-Ti(1)-C(21)	131.66(8)	O(1)-Ti(1)-C(22)	89.29(8)
O(3)-Ti(1)-C(22)	88.49(8)	N(2)-Ti(1)-C(22)	143.23(8)
N(3)-Ti(1)-C(22)	132.87(8)	C(11)-Ti(1)-C(22)	155.16(8)
O(1)-Ti(1)-C(23)	123.24(8)	O(3)-Ti(1)-C(23)	85.05(8)
N(2)-Ti(1)-C(23)	138.77(8)	N(3)-Ti(1)-C(23)	97.90(8)
C(11)-Ti(1)-C(23)	124.76(8)	C(19)-Ti(1)-C(20)	34.58(9)
C(19)-Ti(1)-C(21)	57.63(8)	C(20)-Ti(1)-C(21)	34.85(8)
C(19)-Ti(1)-C(22)	57.68(8)	C(20)-Ti(1)-C(22)	58.16(8)
C(21)-Ti(1)-C(22)	35.16(8)	C(19)-Ti(1)-C(23)	34.41(9)
C(20)-Ti(1)-C(23)	57.79(8)	C(21)-Ti(1)-C(23)	58.09(8)
C(22)-Ti(1)-C(23)	34.98(8)	$Cp_{(cent)}$-Ti(1)-O(1)	110.8
$Cp_{(cent)}$-Ti(1)-O(3)	112.2	$Cp_{(cent)}$-Ti(1)-N(2)	118.9
$Cp_{(cent)}$-Ti(1)-N(3)	111.8	Ti(1)-O(1)-C(1)	135.72(13)
Ti(1)-O(3)-C(2)	136.45(14)	C(1)-N(1)-C(2)	127.6(2)
C(1)-N(1)-C(3)	115.9(2)	C(2)-N(1)-C(3)	116.4(2)
Ti(1)-N(2)-C(11)	91.44(13)	Ti(1)-N(2)-C(13)	140.9(2)
C(11)-N(2)-C(13)	122.1(2)	Ti(1)-N(3)-C(11)	91.40(13)
Ti(1)-N(3)-C(16)	134.0(2)	C(11)-N(3)-C(16)	127.6(2)
O(1)-C(1)-O(2)	123.5(2)	O(1)-C(1)-N(1)	117.0(2)
O(2)-C(1)-N(1)	119.5(2)	O(3)-C(2)-O(4)	123.9(2)
O(3)-C(2)-N(1)	116.6(2)	O(4)-C(2)-N(1)	119.5(2)
N(1)-C(3)-C(4)	119.0(2)	N(1)-C(3)-C(8)	118.6(2)
C(4)-C(3)-C(8)	122.5(2)	C(3)-C(4)-C(5)	118.0(2)
C(3)-C(4)-C(9)	120.3(2)	C(5)-C(4)-C(9)	121.7(2)
C(4)-C(5)-C(6)	120.6(3)	C(5)-C(6)-C(7)	120.5(2)
C(6)-C(7)-C(8)	120.8(2)	C(3)-C(8)-C(7)	117.7(2)
C(3)-C(8)-C(10)	120.6(2)	C(7)-C(8)-C(10)	121.8(2)
Ti(1)-C(11)-N(2)	56.12(11)	Ti(1)-C(11)-N(3)	56.39(11)
N(2)-C(11)-N(3)	111.2(2)	Ti(1)-C(11)-C(12)	170.6(2)
N(2)-C(11)-C(12)	123.9(2)	N(3)-C(11)-C(12)	124.9(2)
N(2)-C(13)-C(14)	110.6(2)	N(2)-C(13)-C(15)	111.2(2)
C(14)-C(13)-C(15)	110.1(2)	N(3)-C(16)-C(17)	112.5(2)
N(3)-C(16)-C(18)	113.8(2)	C(17)-C(16)-C(18)	112.1(2)
Ti(1)-C(19)-C(20)	72.47(13)	Ti(1)-C(19)-C(23)	72.04(13)

C(20)-C(19)-C(23)	108.7(2)	Ti(1)-C(19)-C(24)	126.5(2)
C(20)-C(19)-C(24)	124.4(3)	C(23)-C(19)-C(24)	126.6(3)
Ti(1)-C(20)-C(19)	72.94(13)	Ti(1)-C(20)-C(21)	72.11(12)
C(19)-C(20)-C(21)	107.6(2)	Ti(1)-C(20)-C(25)	125.8(2)
C(19)-C(20)-C(25)	124.3(2)	C(21)-C(20)-C(25)	127.7(2)
Ti(1)-C(21)-C(20)	73.04(12)	Ti(1)-C(21)-C(22)	71.39(12)
C(20)-C(21)-C(22)	107.6(2)	Ti(1)-C(21)-C(26)	121.4(2)
C(20)-C(21)-C(26)	127.7(2)	C(22)-C(21)-C(26)	124.8(2)
Ti(1)-C(22)-C(21)	73.46(12)	Ti(1)-C(22)-C(23)	73.50(13)
C(21)-C(22)-C(23)	108.2(2)	Ti(1)-C(22)-C(27)	120.0(2)
C(21)-C(22)-C(27)	125.7(2)	C(23)-C(22)-C(27)	126.1(2)
Ti(1)-C(23)-C(19)	73.55(13)	Ti(1)-C(23)-C(22)	71.51(13)
C(19)-C(23)-C(22)	107.9(2)	Ti(1)-C(23)-C(28)	120.7(2)
C(19)-C(23)-C(28)	127.3(2)	C(22)-C(23)-C(28)	124.8(2)
C(30)-C(29)-C(31B)	120.2(3)	C(29)-C(30)-C(31)	119.5(3)
C(29B)-C(31)-C(30)	120.3(3)		

i) Symmetry transformations used to generate equivalent atoms carrying the suffix 'B': -x+1,-y+1,-z. $Cp_{(cent)}$ refers to the centroid for the C_5Me_5 ring.

G.3 Atomic coordinates ($\times 10^4$) and isotropic or equivalent isotropic displacement parameters ($Å^2 \times 10^3$). $U_{(eq)}$ is defined as one third of the trace of the orthogonalised U_{ij} tensor

	x	y	z	$U_{(eq)}$
Ti(1)	3611(1)	1222(1)	1531(1)	15
O(1)	4862(1)	1256(1)	1813(1)	21
O(2)	6280(1)	1671(1)	2000(1)	30
O(3)	4166(1)	1695(1)	892(1)	21
O(4)	5092(1)	2372(1)	347(1)	32
N(1)	5627(1)	2045(1)	1194(1)	19
N(2)	3170(1)	1763(1)	2241(1)	19
N(3)	2520(1)	1991(1)	1443(1)	20
C(1)	5610(1)	1644(1)	1699(1)	18

C(2)	4939(2)	2048(1)	779(1)	19
C(3)	6457(2)	2488(1)	1083(1)	22
C(4)	7195(2)	2129(2)	812(1)	27
C(5)	7989(2)	2568(2)	708(1)	36
C(6)	8049(2)	3323(2)	884(1)	40
C(7)	7311(2)	3668(2)	1155(1)	36
C(8)	6494(2)	3255(1)	1256(1)	28
C(9)	7127(2)	1294(2)	646(1)	37
C(10)	5675(2)	3621(1)	1535(1)	36
C(11)	2614(2)	2231(1)	1957(1)	20
C(12)	2143(2)	2929(1)	2197(1)	30
C(13)	3492(2)	1955(1)	2800(1)	24
C(14)	3851(2)	1238(2)	3090(1)	39
C(15)	4244(2)	2581(2)	2786(1)	36
C(16)	2134(2)	2426(2)	974(1)	31
C(17)	2677(2)	3165(2)	850(1)	45
C(18)	1090(2)	2577(2)	1018(1)	47
C(19)	2415(2)	302(1)	1331(1)	27
C(20)	2838(2)	74(1)	1833(1)	24
C(21)	3779(2)	-123(1)	1716(1)	23
C(22)	3928(2)	4(1)	1144(1)	24
C(23)	3082(2)	260(1)	908(1)	26
C(24)	1403(2)	472(2)	1265(2)	47
C(25)	2329(2)	-21(2)	2366(1)	39
C(26)	4497(2)	-416(1)	2110(1)	34
C(27)	4819(2)	-128(2)	843(1)	36
C(28)	2946(2)	448(2)	310(1)	42
C(29)	5702(2)	5011(2)	385(1)	38
C(30)	5383(2)	4311(2)	186(1)	34
C(31)	4679(2)	4302(2)	-199(1)	38

G.4 Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic 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)	14(1)	13(1)	17(1)	0(1)	0(1)	0(1)
O(1)	17(1)	25(1)	21(1)	8(1)	-2(1)	-4(1)
O(2)	21(1)	40(1)	28(1)	10(1)	-6(1)	-8(1)
O(3)	19(1)	26(1)	18(1)	4(1)	-2(1)	-4(1)
O(4)	32(1)	42(1)	21(1)	11(1)	-3(1)	-11(1)
N(1)	17(1)	21(1)	18(1)	2(1)	0(1)	-4(1)
N(2)	19(1)	19(1)	18(1)	-2(1)	-1(1)	-1(1)
N(3)	22(1)	19(1)	20(1)	2(1)	-1(1)	4(1)
C(1)	17(1)	18(1)	19(1)	1(1)	0(1)	-1(1)
C(2)	20(1)	20(1)	16(1)	0(1)	0(1)	0(1)
C(3)	22(1)	23(1)	19(1)	5(1)	0(1)	-7(1)
C(4)	21(1)	35(1)	25(1)	6(1)	1(1)	-2(1)
C(5)	22(1)	48(2)	39(1)	13(1)	1(1)	-5(1)
C(6)	31(1)	51(2)	39(2)	19(1)	-9(1)	-20(1)
C(7)	44(2)	32(1)	33(1)	8(1)	-11(1)	-20(1)
C(8)	35(1)	26(1)	22(1)	2(1)	-4(1)	-8(1)
C(9)	29(1)	39(2)	44(2)	-3(1)	11(1)	2(1)
C(10)	55(2)	23(1)	31(1)	-3(1)	7(1)	-1(1)
C(11)	19(1)	17(1)	25(1)	1(1)	6(1)	-2(1)
C(12)	35(1)	24(1)	31(1)	-1(1)	7(1)	6(1)
C(13)	23(1)	30(1)	20(1)	-4(1)	2(1)	-5(1)
C(14)	46(2)	45(2)	25(1)	4(1)	-7(1)	5(1)
C(15)	33(1)	48(2)	26(1)	-8(1)	-3(1)	-14(1)
C(16)	39(1)	30(1)	24(1)	2(1)	-4(1)	14(1)
C(17)	58(2)	33(2)	43(2)	20(1)	14(1)	15(1)
C(18)	44(2)	51(2)	47(2)	2(1)	-14(1)	18(2)
C(19)	22(1)	17(1)	44(1)	-4(1)	-5(1)	-4(1)
C(20)	27(1)	11(1)	35(1)	1(1)	6(1)	-5(1)
C(21)	24(1)	12(1)	32(1)	4(1)	2(1)	0(1)
C(22)	27(1)	14(1)	29(1)	-3(1)	-1(1)	1(1)
C(23)	32(1)	16(1)	31(1)	-5(1)	-8(1)	-3(1)

C(24)	22(1)	33(1)	86(2)	-1(2)	-11(2)	-6(1)
C(25)	43(2)	24(1)	50(2)	-1(1)	21(1)	-8(1)
C(26)	43(2)	21(1)	37(1)	10(1)	-6(1)	5(1)
C(27)	37(2)	30(1)	42(2)	-4(1)	14(1)	6(1)
C(28)	57(2)	37(2)	32(1)	-7(1)	-16(1)	-4(1)
C(29)	28(1)	49(2)	37(1)	6(1)	-2(1)	-3(1)
C(30)	28(1)	36(1)	37(1)	11(1)	7(1)	1(1)
C(31)	31(1)	38(1)	44(2)	1(1)	3(1)	-6(1)

G.5 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$)

	x	y	z	$U_{(eq)}$
H(51)	8519	2331	504	43
H(61)	8628	3626	815	48
H(71)	7363	4218	1280	44
H(91)	7713	1134	458	45
H(92)	7031	966	980	45
H(93)	6592	1224	389	45
H(101)	5826	4171	1630	43
H(102)	5527	3328	1878	43
H(103)	5129	3609	1283	43
H(121)	1763	3189	1907	36
H(122)	2622	3299	2337	36
H(123)	1732	2764	2506	36
H(131)	2950	2163	3010	29
H(141)	4066	1380	3468	46
H(142)	4381	1016	2877	46
H(143)	3343	846	3117	46
H(151)	4449	2700	3169	43
H(152)	4785	2391	2567	43
H(153)	3989	3061	2612	43
H(161)	2211	2075	650	37
H(171)	2389	3438	530	54
H(172)	2664	3512	1179	54

H(173)	3333	3030	760	54
H(181)	876	2872	688	57
H(182)	960	2885	1357	57
H(183)	752	2072	1038	57
H(241)	1063	-20	1183	56
H(242)	1157	703	1612	56
H(243)	1313	846	955	56
H(251)	2071	-558	2389	47
H(252)	2765	68	2679	47
H(253)	1810	363	2384	47
H(261)	4459	-993	2132	41
H(262)	5127	-261	1977	41
H(263)	4385	-188	2482	41
H(271)	4840	-674	706	44
H(272)	5352	-36	1098	44
H(273)	4860	237	525	44
H(281)	2722	-24	112	50
H(282)	3548	621	148	50
H(283)	2477	871	273	50
H(291)	6211	5021	664	46
H(301)	5659	3814	320	41
H(311)	4445	3796	-344	45

APPENDIX H – X-RAY STRUCTURE ANALYSIS OF Ti(η-C_5H_4Me) {OC(O)N(2,6-$C_6H_3Me_2$)C(O)O}{PhC($NSiMe_3$)$_2$} (32)

H.1 Crystal data, data collection and refinement

Empirical formula	$C_{29}\ H_{39}\ N_3\ O_4\ Si_2\ Ti_1$
Formula weight	597.72
Crystal description	yellow block
Crystal size	0.20 x 0.20 x 0.20 mm
Temperature	150 K
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 10.7126(2) Å α = 90 deg.
	b = 17.2231(4) Å β = 90.704 deg.
	c = 16.6483(4) Å γ = 90 deg.
Reflections for cell refinement	6533
Range in theta	2.91 to 27.85 deg.
Volume, Z	3071.5 $Å^3$, 4
Density (calculated)	1.29 Mg/m^3
Absorption coefficient	0.39 mm^{-1}
F(000)	1264
Diffractometer type	Nonius KappaCCD
Wavelength	0.71073 A
Scan type	omega / 2 theta
Theta range for data collection	3.04 to 27.49 deg.
Index ranges	-13<=h<=13, -19<=k<=22, -21<=l<=21
Reflections collected	11752
Independent reflections	7025 [R(merge) = 0.05]
Observed reflections	4207 [I>3sigma(I)]
Absorption correction	Multi-scan
Tmin, Tmax	0.925, 0.925
Structure solution	by direct methods and
	Fourier difference maps
Hydrogen atom location	geometric
Hydrogen atom treatment	riding model
Refinement method	Full-matrix least-squares on F

Weighting scheme	Unit weights
Data / restraints / parameters	4207 / 0 / 353
Goodness-of-fit on F	0.3819
Final R indices [I>3sigma(I)]	R1 = 0.0396, Rw = 0.0478
Extinction coefficient	193(13)
Final maximum delta/sigma	0.004
Largest diff. peak and hole	0.30 and -0.28 e. $Å^{-3}$

H.2 Bond lengths (Å) and angles (°)

$Cp_{(cent)}$-Ti(1)	2.026	Ti(1)-O(1)	1.925(2)
Ti(1)-O(3)	1.915(2)	Ti(1)-N(2)	2.079(3)
Ti(1)-N(3)	2.095(3)	Ti(1)-C(11)	2.454(3)
Ti(1)-C(24)	2.366(3)	Ti(1)-C(25)	2.352(3)
Ti(1)-C(26)	2.348(3)	Ti(1)-C(27)	2.347(3)
Ti(1)-C(28)	2.362(3)	O(1)-C(1)	1.309(4)
O(2)-C(1)	1.211(4)	O(3)-C(2)	1.304(4)
O(4)-C(2)	1.206(4)	N(1)-C(1)	1.402(4)
N(1)-C(2)	1.408(4)	N(1)-C(3)	1.450(4)
N(2)-Si(1)	1.767(3)	N(2)-C(11)	1.328(4)
N(3)-Si(2)	1.763(3)	N(3)-C(11)	1.337(4)
Si(1)-C(18)	1.847(4)	Si(1)-C(19)	1.855(4)
Si(1)-C(20)	1.854(4)	Si(2)-C(21)	1.845(4)
Si(2)-C(22)	1.858(4)	Si(2)-C(23)	1.854(4)
C(3)-C(4)	1.392(5)	C(3)-C(8)	1.387(5)
C(4)-C(5)	1.390(5)	C(4)-C(9)	1.500(5)
C(5)-C(6)	1.373(6)	C(6)-C(7)	1.376(6)
C(7)-C(8)	1.400(5)	C(8)-C(10)	1.499(6)
C(11)-C(12)	1.500(5)	C(12)-C(13)	1.382(5)
C(12)-C(17)	1.395(5)	C(13)-C(14)	1.387(6)
C(14)-C(15)	1.377(7)	C(15)-C(16)	1.374(7)
C(16)-C(17)	1.377(6)	C(24)-C(25)	1.416(5)
C(24)-C(28)	1.413(5)	C(24)-C(29)	1.503(5)
C(25)-C(26)	1.412(5)	C(26)-C(27)	1.402(5)
C(27)-C(28)	1.421(5)		

$Cp_{(cent)}$-Ti(1)-O(1)	110.9	$Cp_{(cent)}$-Ti(1)-O(3)	113.1
$Cp_{(cent)}$-Ti(1)-N(2)	117.2	$Cp_{(cent)}$-Ti(1)-N(3)	115.7

O(1)-Ti(1)-O(3)	83.6(1)	O(1)-Ti(1)-N(2)	86.6(1)
O(3)-Ti(1)-N(2)	128.9(1)	O(1)-Ti(1)-N(3)	132.6(1)
O(3)-Ti(1)-N(3)	86.3(1)	N(2)-Ti(1)-N(3)	64.9(1)
O(1)-Ti(1)-C(11)	107.5(1)	O(3)-Ti(1)-C(11)	105.4(1)
N(2)-Ti(1)-C(11)	32.8(1)	N(3)-Ti(1)-C(11)	33.0(1)
O(1)-Ti(1)-C(24)	90.5(1)	O(3)-Ti(1)-C(24)	88.8(1)
N(2)-Ti(1)-C(24)	141.4(1)	N(3)-Ti(1)-C(24)	135.5(1)
C(11)-Ti(1)-C(24)	158.0(1)	O(1)-Ti(1)-C(25)	82.1(1)
O(3)-Ti(1)-C(25)	121.1(1)	N(2)-Ti(1)-C(25)	106.8(1)
N(3)-Ti(1)-C(25)	140.4(1)	C(11)-Ti(1)-C(25)	133.4(1)
O(1)-Ti(1)-C(26)	109.2(1)	O(3)-Ti(1)-C(26)	143.8(1)
N(2)-Ti(1)-C(26)	86.5(1)	N(3)-Ti(1)-C(26)	106.0(1)
C(11)-Ti(1)-C(26)	102.7(1)	O(1)-Ti(1)-C(27)	140.0(1)
O(3)-Ti(1)-C(27)	116.8(1)	N(2)-Ti(1)-C(27)	102.4(1)
N(3)-Ti(1)-C(27)	85.1(1)	C(11)-Ti(1)-C(27)	99.9(1)
O(1)-Ti(1)-C(28)	124.5(1)	O(3)-Ti(1)-C(28)	86.5(1)
N(2)-Ti(1)-C(28)	137.6(1)	N(3)-Ti(1)-C(28)	100.8(1)
C(11)-Ti(1)-C(28)	127.7(1)	C(24)-Ti(1)-C(25)	34.9(1)
C(24)-Ti(1)-C(26)	58.3(1)	C(25)-Ti(1)-C(26)	35.0(1)
C(24)-Ti(1)-C(27)	58.3(1)	C(25)-Ti(1)-C(27)	57.9(1)
C(26)-Ti(1)-C(27)	34.7(1)	C(24)-Ti(1)-C(28)	34.8(1)
C(25)-Ti(1)-C(28)	57.8(1)	C(26)-Ti(1)-C(28)	58.0(1)
C(27)-Ti(1)-C(28)	35.1(1)	Ti(1)-O(1)-C(1)	134.8(2)
Ti(1)-O(3)-C(2)	136.6(2)	C(1)-N(1)-C(2)	126.9(3)
C(1)-N(1)-C(3)	116.5(3)	C(2)-N(1)-C(3)	116.6(3)
Ti(1)-N(2)-Si(1)	135.9(2)	Ti(1)-N(2)-C(11)	89.3(2)
Si(1)-N(2)-C(11)	130.4(2)	Ti(1)-N(3)-Si(2)	135.6(1)
Ti(1)-N(3)-C(11)	88.4(2)	Si(2)-N(3)-C(11)	130.4(2)
N(2)-Si(1)-C(18)	106.1(2)	N(2)-Si(1)-C(19)	111.4(2)
C(18)-Si(1)-C(19)	108.8(2)	N(2)-Si(1)-C(20)	110.9(2)
C(18)-Si(1)-C(20)	110.9(2)	C(19)-Si(1)-C(20)	108.6(2)
N(3)-Si(2)-C(21)	106.3(2)	N(3)-Si(2)-C(22)	110.8(2)
C(21)-Si(2)-C(22)	109.7(2)	N(3)-Si(2)-C(23)	111.8(2)
C(21)-Si(2)-C(23)	108.1(2)	C(22)-Si(2)-C(23)	110.1(2)
O(1)-C(1)-O(2)	122.8(3)	O(1)-C(1)-N(1)	116.8(3)
O(2)-C(1)-N(1)	120.4(3)	O(3)-C(2)-O(4)	123.2(3)
O(3)-C(2)-N(1)	117.0(3)	O(4)-C(2)-N(1)	119.8(3)
N(1)-C(3)-C(4)	119.2(3)	N(1)-C(3)-C(8)	117.7(3)
C(4)-C(3)-C(8)	123.1(3)	C(3)-C(4)-C(5)	117.4(4)
C(3)-C(4)-C(9)	121.6(3)	C(5)-C(4)-C(9)	121.0(4)

C(4)-C(5)-C(6)	120.8(4)	C(5)-C(6)-C(7)	120.9(4)
C(6)-C(7)-C(8)	120.4(4)	C(3)-C(8)-C(7)	117.4(4)
C(3)-C(8)-C(10)	121.3(3)	C(7)-C(8)-C(10)	121.3(4)
Ti(1)-C(11)-N(2)	57.9(2)	Ti(1)-C(11)-N(3)	58.6(2)
N(2)-C(11)-N(3)	114.3(3)	Ti(1)-C(11)-C(12)	162.5(2)
N(2)-C(11)-C(12)	122.7(3)	N(3)-C(11)-C(12)	122.8(3)
C(11)-C(12)-C(13)	122.3(3)	C(11)-C(12)-C(17)	118.1(3)
C(13)-C(12)-C(17)	119.6(3)	C(12)-C(13)-C(14)	119.9(4)
C(13)-C(14)-C(15)	119.9(4)	C(14)-C(15)-C(16)	120.5(4)
C(15)-C(16)-C(17)	120.1(5)	C(12)-C(17)-C(16)	119.9(4)
Ti(1)-C(24)-C(25)	72.0(2)	Ti(1)-C(24)-C(28)	72.5(2)
C(25)-C(24)-C(28)	107.3(3)	Ti(1)-C(24)-C(29)	119.7(2)
C(25)-C(24)-C(29)	126.6(3)	C(28)-C(24)-C(29)	126.1(3)
Ti(1)-C(25)-C(24)	73.1(2)	Ti(1)-C(25)-C(26)	72.3(2)
C(24)-C(25)-C(26)	108.5(3)	Ti(1)-C(26)-C(25)	72.7(2)
Ti(1)-C(26)-C(27)	72.6(2)	C(25)-C(26)-C(27)	108.0(3)
Ti(1)-C(27)-C(26)	72.6(2)	Ti(1)-C(27)-C(28)	73.0(2)
C(26)-C(27)-C(28)	108.0(3)	Ti(1)-C(28)-C(24)	72.8(2)
Ti(1)-C(28)-C(27)	71.9(2)	C(24)-C(28)-C(27)	108.2(3)

H.3 Atomic coordinates ($\times 10^4$) and isotropic or equivalent isotropic displacement parameters ($Å^2 \times 10^3$). $U_{(eq)}$ is defined as one third of the trace of the orthogonalised U_{ij} tensor

	x	y	z	$U_{(eq)}$
Ti(1)	7388(1)	2354(1)	7597(1)	19
O(1)	7745(2)	3449(1)	7582(1)	25
O(2)	8431(2)	4586(1)	8024(2)	34
O(3)	6660(2)	2587(1)	8614(1)	26
O(4)	5952(2)	3201(2)	9679(2)	36
N(1)	7263(3)	3855(2)	8864(2)	22
N(2)	9257(2)	2187(2)	7322(2)	21
N(3)	8249(2)	1413(2)	8178(2)	21
Si(1)	10425(1)	2727(1)	6833(1)	23
Si(2)	7899(1)	818(1)	9007(1)	24

C(1)	7857(3)	3989(2)	8131(2)	23
C(2)	6570(3)	3193(2)	9079(2)	23
C(3)	7362(3)	4465(2)	9461(2)	24
C(4)	6533(3)	5088(2)	9425(2)	28
C(5)	6614(4)	5639(2)	10033(3)	39
C(6)	7494(4)	5573(3)	10636(3)	47
C(7)	8332(4)	4967(3)	10646(2)	44
C(8)	8273(4)	4390(2)	10055(2)	33
C(9)	5604(4)	5172(2)	8749(2)	35
C(10)	9173(4)	3724(3)	10055(3)	44
C(11)	9346(3)	1675(2)	7916(2)	20
C(12)	10570(3)	1452(2)	8298(2)	25
C(13)	11229(4)	802(2)	8064(3)	39
C(14)	12366(4)	630(3)	8429(3)	53
C(15)	12834(4)	1107(4)	9024(3)	58
C(16)	12192(4)	1758(4)	9253(3)	57
C(17)	11059(3)	1934(3)	8897(2)	38
C(18)	9675(4)	3146(2)	5926(2)	35
C(19)	11016(4)	3530(2)	7476(3)	40
C(20)	11758(3)	2097(2)	6560(2)	31
C(21)	6210(4)	616(2)	8940(3)	40
C(22)	8264(4)	1325(2)	9967(2)	39
C(23)	8742(4)	-121(2)	8968(3)	39
C(24)	5421(3)	2581(2)	6979(2)	28
C(25)	6348(3)	2660(2)	6385(2)	26
C(26)	6938(3)	1934(2)	6283(2)	28
C(27)	6386(3)	1404(2)	6810(2)	32
C(28)	5441(3)	1800(2)	7239(2)	32
C(29)	4591(4)	3213(2)	7293(3)	40

H.4 Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic 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)	18(1)	17(1)	22(1)	0(1)	-2(1)	0(1)
O(1)	35(1)	18(1)	22(1)	-1(1)	3(1)	-3(1)
O(2)	43(2)	22(1)	37(1)	-4(1)	13(1)	-10(1)
O(3)	32(1)	19(1)	28(1)	-1(1)	9(1)	-4(1)
O(4)	45(2)	30(1)	33(1)	0(1)	16(1)	-4(1)
N(1)	26(1)	18(1)	21(1)	-1(1)	3(1)	1(1)
N(2)	20(1)	23(2)	21(1)	1(1)	-2(1)	-1(1)
N(3)	19(1)	20(1)	24(1)	1(1)	-2(1)	1(1)
Si(1)	21(1)	25(1)	23(1)	2(1)	1(1)	-3(1)
Si(2)	26(1)	21(1)	25(1)	3(1)	3(1)	2(1)
C(1)	26(2)	20(2)	24(2)	0(1)	0(1)	3(1)
C(2)	22(2)	21(2)	24(2)	3(1)	1(1)	1(1)
C(3)	27(2)	23(2)	21(2)	0(1)	5(1)	-2(1)
C(4)	31(2)	24(2)	29(2)	1(1)	8(2)	-3(1)
C(5)	48(2)	24(2)	46(2)	-8(2)	23(2)	-4(2)
C(6)	58(3)	45(3)	38(2)	-19(2)	11(2)	-20(2)
C(7)	45(2)	54(3)	33(2)	-10(2)	-5(2)	-15(2)
C(8)	32(2)	37(2)	30(2)	-2(2)	-2(2)	-8(2)
C(9)	33(2)	35(2)	39(2)	8(2)	6(2)	9(2)
C(10)	38(2)	51(3)	42(2)	6(2)	-10(2)	2(2)
C(11)	22(2)	20(2)	19(2)	-3(1)	-1(1)	0(1)
C(12)	21(2)	31(2)	23(2)	7(1)	1(1)	1(1)
C(13)	31(2)	37(2)	50(2)	6(2)	-1(2)	10(2)
C(14)	38(2)	53(3)	69(3)	20(3)	8(2)	19(2)
C(15)	22(2)	105(4)	45(3)	29(3)	-4(2)	8(2)
C(16)	30(2)	104(4)	36(2)	-1(3)	-13(2)	0(3)
C(17)	27(2)	59(3)	28(2)	-4(2)	-4(2)	3(2)
C(18)	32(2)	40(2)	34(2)	10(2)	4(2)	0(2)
C(19)	35(2)	35(2)	49(3)	-9(2)	6(2)	-10(2)
C(20)	26(2)	38(2)	30(2)	3(2)	2(2)	-1(2)

C(21)	34(2)	37(2)	47(2)	14(2)	8(2)	-5(2)
C(22)	55(3)	36(2)	26(2)	3(2)	5(2)	-1(2)
C(23)	47(2)	25(2)	45(2)	7(2)	7(2)	9(2)
C(24)	20(2)	28(2)	35(2)	1(2)	-8(1)	-1(1)
C(25)	27(2)	22(2)	27(2)	2(1)	-11(1)	1(1)
C(26)	30(2)	30(2)	25(2)	-8(1)	-8(1)	2(2)
C(27)	35(2)	17(2)	45(2)	-2(2)	-19(2)	-1(1)
C(28)	26(2)	28(2)	40(2)	7(2)	-10(2)	-9(2)
C(29)	24(2)	39(2)	57(3)	-3(2)	-5(2)	8(2)

H.5 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$)

	x	y	z	$U_{(eq)}$
H(51)	6047(4)	6071(2)	10030(3)	49
H(61)	7529(4)	5955(3)	11055(3)	61
H(71)	8958(4)	4936(3)	11063(2)	55
H(91)	5117(4)	5633(2)	8829(2)	46
H(92)	6038(4)	5211(2)	8249(2)	46
H(93)	5064(4)	4727(2)	8735(2)	46
H(101)	9732(4)	3766(3)	10508(3)	55
H(102)	9644(4)	3733(3)	9568(3)	55
H(103)	8719(4)	3244(3)	10088(3)	55
H(131)	10891(4)	471(2)	7651(3)	51
H(141)	12831(4)	180(3)	8270(3)	67
H(151)	13623(4)	990(4)	9276(3)	62
H(161)	12527(4)	2088(4)	9667(3)	63
H(171)	10603(3)	2386(3)	9059(2)	46
H(181)	10272(4)	3448(2)	5636(2)	45
H(182)	8991(4)	3472(2)	6081(2)	45
H(183)	9369(4)	2732(2)	5591(2)	45
H(191)	11648(4)	3814(2)	7197(3)	51
H(192)	11363(4)	3318(2)	7963(3)	51
H(193)	10338(4)	3871(2)	7602(3)	51
H(201)	12382(3)	2401(2)	6295(2)	40

H(202)	12111(3)	1869(2)	7037(2)	40
H(203)	11469(3)	1693(2)	6206(2)	40
H(211)	5968(4)	290(2)	9379(3)	50
H(212)	5754(4)	1095(2)	8959(3)	50
H(213)	6029(4)	356(2)	8441(3)	50
H(221)	8068(4)	993(2)	10411(2)	47
H(222)	9137(4)	1453(2)	9985(2)	47
H(223)	7780(4)	1793(2)	9998(2)	47
H(231)	8531(4)	-431(2)	9425(3)	49
H(232)	9626(4)	-27(2)	8970(3)	49
H(233)	8506(4)	-391(2)	8485(3)	49
H(251)	6541(3)	3128(2)	6100(2)	34
H(261)	7601(3)	1822(2)	5918(2)	38
H(271)	6605(3)	866(2)	6867(2)	40
H(281)	4912(3)	1579(2)	7639(2)	41
H(291)	4049(4)	3001(2)	7692(3)	49
H(292)	5098(4)	3614(2)	7530(3)	49
H(293)	4100(4)	3427(2)	6861(3)	49

APPENDIX I – DATA FROM RATES STUDIES OF INSERTION OF CO_2 INTO $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}4\text{-}C_6H_4X)C(O)O\}\{MeC(N^iPr)_2\}$ ($X = CF_3$, Me, NMe_2)

I.1 Reaction of $Ti(\eta\text{-}C_5Me_5)\{N\text{-}4\text{-}C_6H_4CF_3)C(O)O\}\{MeC(N^iPr)_2\}$

1st run

Time (min)	Time (sec)	I(s) CF_3	I(p) CF_3	I/Io CF_3	- ln (I/Io) CF_3
0	0				
2.5	150	4.17	0.83	0.834	0.181522
5	300	3.77	1.41	0.727799	0.31773
7.5	450	3.41	1.83	0.650763	0.429609
10	600	3.03	2.16	0.583815	0.538171
12.5	750	2.68	2.46	0.521401	0.651236
15	900	2.34	2.77	0.457926	0.781048
17.5	1050	2.22	2.97	0.427746	0.849227
20	1200	1.98	3.13	0.387476	0.948103
22.5	1350	1.79	3.23	0.356574	1.031214
25	1500	1.53	3.5	0.304175	1.190152
27.5	1650	1.52	3.56	0.299213	1.206601
30	1800	1.38	3.6	0.277108	1.283346
32.5	1950	1.33	3.72	0.263366	1.334209
35	2100	1.12	3.83	0.226263	1.486059
37.5	2250	1.16	3.94	0.227451	1.480821
40	2400	1.04	4	0.206349	1.578185
42.5	2550	0.97	4.02	0.194389	1.637895
45	2700	0.92	4.08	0.184	1.69282
50	3000	0.81	4.21	0.161355	1.824151
55	3300	0.74	4.29	0.147117	1.916525
60	3600	0.71	4.32	0.141153	1.95791
70	4200	0.51	4.45	0.102823	2.27475
80	4800	0.52	4.57	0.102161	2.281204
90	5400	0.42	4.5	0.085366	2.460809

2nd run

Time (min)	Time (sec)	I(s) CF_3	I(p) CF_3	I/Io CF_3	-ln (I/Io) CF_3
2.166667	130	115	12	0.905512	0.099255
3	180	96	15	0.864865	0.145182
4	240	99.2	22	0.818482	0.200304
5	300	82.5	22	0.789474	0.236389
6	360	72	24	0.75	0.287682
7	420	78	33	0.702703	0.352821
8	480	73	37.5	0.660633	0.414556
9	540	75	43	0.635593	0.453197
10	600	66	44	0.6	0.510826
11	660	60.5	48	0.557604	0.584107
12	720	60	54.5	0.524017	0.64623
13	780	59.5	60	0.497908	0.69734
14	840	48	54	0.470588	0.753772
15	900	54	64	0.457627	0.781701
16	960	50	67.5	0.425532	0.854415
17	1020	45.5	66	0.408072	0.896312
18	1080	44.5	69.5	0.390351	0.940709
19	1140	39	72	0.351351	1.045969
20	1200	40	81	0.330579	1.106911
22	1320	29	72.5	0.285714	1.252763
24	1440	27.5	79.5	0.257009	1.358643
26	1560	24	79.5	0.231884	1.461518
28	1680	21.5	80.5	0.210784	1.55692
30	1800	22.5	101	0.182186	1.702726
32	1920	18.5	92.5	0.166667	1.791759
34	2040	17	94	0.153153	1.876317
36	2160	15	94	0.137615	1.983298
38	2280	13	89.5	0.126829	2.064913
40	2400	12	93	0.114286	2.169054
43	2580	11	107	0.09322	2.372789
46	2760	8	96.5	0.076555	2.569746
50	3000	8	112	0.066667	2.70805
55	3300	6.5	120	0.051383	2.96844
60	3600	4.5	117	0.037037	3.295837
65	3900	4	119	0.03252	3.42589
70	4200	3.5	119	0.028571	3.555348
75	4500	3	116.5	0.025105	3.684704

80	4800	3	118	0.024793	3.697178
90	5400	1.5	105	0.014085	4.26268

I.2 Reaction of Ti(η-C_5Me_5){N-4-C_6H_4Me)C(O)O}{MeC(N^iPr)$_2$}

1st run

Time (min)	Time (sec)	I(s) Me	I(p) Me	I/Io Me	- ln (I/Io) Me
0	0				
2.5	150	2.36	0.94	0.715152	0.335261
5	300	2.25	1.45	0.608108	0.497403
7.5	450	2.38	1.86	0.561321	0.577463
10	600	1.86	1.95	0.488189	0.717053
15	900	1.6	2.18	0.42328	0.85972
20	1200	1.58	2.39	0.397985	0.921341
25	1500	1.6	2.5	0.390244	0.940983
30	1800	1.11	2.5	0.307479	1.179348
35	2100	1.1	2.67	0.291777	1.231765
40	2400	1.16	2.98	0.280193	1.272276
45	2700	0.74	2.78	0.210227	1.559566
50	3000	0.89	2.93	0.232984	1.456784
55	3300	0.71	2.88	0.197772	1.620643
60	3600	0.56	2.82	0.16568	1.797694

2nd run

Time (min)	Time (sec)	I(s) Me	I(p) Me	I/Io Me	-ln (I/Io) Me
2.666667	160	61.5	11	0.848276	0.164549
3.5	210	39.5	10	0.79798	0.225672
4.25	255	72.5	22	0.767196	0.265013
5	300	40	15.5	0.720721	0.327504
6	360	55.5	27	0.672727	0.396415
7.5	450	41	23.5	0.635659	0.453093
8.5	510	36	25	0.590164	0.527355
10	600	41.5	34	0.549669	0.598439
11.5	690	25	24.5	0.505051	0.683097
12.5	750	32	36.5	0.467153	0.761098
13.5	810	29.5	37	0.443609	0.812812

15	900	26.5	40.5	0.395522	0.927548
16	960	21.5	39	0.355372	1.03459
17.5	1050	25	45	0.357143	1.029619
18.5	1110	24	48	0.333333	1.098612
20	1200	20	45	0.307692	1.178655
21	1260	20	47	0.298507	1.20896
22.5	1350	21	54	0.28	1.272966
23.5	1410	17	53.5	0.241135	1.422399
25	1500	14	46	0.233333	1.455287
26	1560	21	69	0.233333	1.455287
27.5	1650	15.5	56.5	0.215278	1.535826
28.5	1710	13	53.5	0.195489	1.632253
30	1800	13	59	0.180556	1.711717
31	1860	12.5	56	0.182482	1.701105
32.5	1950	13.5	72.5	0.156977	1.851658
33.5	2010	11	59	0.157143	1.8506
35	2100	12	73	0.141176	1.957745
37.5	2250	11	71.5	0.133333	2.014903
40	2400	9	76.5	0.105263	2.251292
42.5	2550	7.5	75	0.090909	2.397895
45	2700	6	70.5	0.078431	2.545531
47.5	2850	5.5	66	0.076923	2.564949
50	3000	5	73	0.064103	2.747271
55	3300	3	59.5	0.048	3.036554
60	3600	3	63	0.045455	3.091042

I.3 Reaction of Ti(η-C_5Me_5){N-4-$C_6H_4NMe_2$)C(O)O}{MeC(N^iPr)$_2$}

1st run

Time (min)	Time (sec)	I(s) NMe_2	I(p) NMe_2	I/Io NMe_2	-ln(I/Io) NMe_2
0	0			0	1
2.5	150	4.39	1.28	0.77425	0.25586
5	300	3.53	1.93	0.64652	0.436151
7.5	450	3.21	2.45	0.567138	0.567153
10	600	2.8	2.8	0.5	0.693147
12.5	750	2.26	3.1	0.421642	0.863599
15	900	1.91	3.4	0.359699	1.022489
17.5	1050	1.72	3.7	0.317343	1.147772

20	1200	1.44	3.85	0.272212	1.301175
22.5	1350	1.34	4.07	0.247689	1.395579
25	1500	1.2	4.2	0.222222	1.504077
27.5	1650	1.1	4.31	0.203327	1.592939
30	1800	0.84	4.33	0.162476	1.817226
35	2100	0.7	4.65	0.130841	2.033772
40	2400	0.6	4.84	0.110294	2.204605
45	2700	0.51	4.93	0.09375	2.367124
50	3000	0.43	5.04	0.078611	2.543249
55	3300	0.37	5.11	0.067518	2.695357
60	3600	0.07	4.61	0.014957	4.202558

2nd run

Time (min)	Time (sec)	I(s) NMe_2	I(p) NMe_2	I/Io NMe_2	-ln(I/Io) NMe_2
2.5	150	75.5	21	0.782383	0.24541
4	240	59	26	0.694118	0.365114
5	300	47.5	26.5	0.641892	0.443335
6	360	37.5	26	0.590551	0.526699
7.5	450	52.5	50	0.512195	0.66905
8.5	510	47	53	0.47	0.755023
10	600	41.5	58.5	0.415	0.879477
11	660	43.5	71	0.379913	0.967814
12.5	750	38	73	0.342342	1.071944
13.5	810	34	75.5	0.310502	1.169564
15	900	27	73.5	0.268657	1.314321
16	960	26	79	0.247619	1.395864
17.5	1050	22	77.5	0.221106	1.509115
18.5	1110	19	74	0.204301	1.588161
20	1200	17	79.5	0.176166	1.73633
22.5	1350	14.5	82	0.150259	1.895394
25	1500	13	100.5	0.114537	2.166853
27.5	1650	10.5	98	0.096774	2.335375
30	1800	7	80	0.08046	2.519998
32.5	1950	6	90	0.0625	2.772589
35	2100	5.5	104.5	0.05	2.995732
37.5	2250	4	116	0.033333	3.401197
40	2400	3	113.5	0.025751	3.659279
42.5	2550	3.5	122	0.027888	3.579543
45	2700	2.5	114	0.021459	3.841601

Appendix I

APPENDIX J – X-RAY STRUCTURE ANALYSIS OF Ti(η-C_5Me_5) {N(2,6-$C_6H_3Me_2$)C(N-2,6-$C_6H_3Me_2$)O}{MeC(N^{i}Pr)$_2$} (41)

J.1 Crystal data, data collection and refinement

Empirical formula	$C_{35}\ H_{50}\ N_4\ O_1\ Ti_1$
Formula weight	590.71
Crystal description	brown needle
Crystal size	0.40 x 0.20 x 0.10 mm
Temperature	150 K
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 19.0867(9) Å α = 90 deg.
	b = 9.8270(4) Å β = 93.316(2) deg.
	c = 17.7637(7) Å γ = 90 deg.
Reflections for cell refinement	5007
Range in theta	2.910 to 25.350 deg.
Volume, Z	3326.3(2) A^3, 4
Density (calculated)	1.18 Mg/m^3
Absorption coefficient	0.29 mm^{-1}
F(000)	1273.15
Diffractometer type	Nonius KappaCCD
Wavelength	0.71073 A
Scan type	\w/2\q
Theta range for data collection	2.910 to 25.350
Index ranges	-22<=h<=22, 0<=k<=11, 0<=l<=20
Reflections collected	10047
Independent reflections	5557 [R(merge) = 0.03]
Observed reflections	3318 [I>3sigma(I)]
Absorption correction	Multi-scan (Tmin = 0.944, Tmax = 0.971)
Structure solution	by direct methods and
	Fourier difference maps
Hydrogen atom location	geometric
Hydrogen atom treatment	riding model
Refinement method	Full-matrix least-squares on F
Weighting scheme	Chebychev polynomial

Data / restraints / parameters	3318 / 0 / 371
Goodness-of-fit on F	1.0358
Final R indices [I>3sigma(I)]	R1 = 0.0591, Rw = 0.0608
Extinction coefficient	219(34)
Final maximum delta/sigma	0.0002
Largest diff. peak and hole	0.560 and -0.464 e. $Å^{-3}$

J.2 Bond lengths (Å) and angles (°)

Ti(1)-N(1)	2.149(3)	Ti(1)-N(2)	2.027(3)
Ti(1)-N(3)	1.995(3)	Ti(1)-O(1)	1.981(3)
Ti(1)-C(26)	2.414(4)	Ti(1)-C(27)	2.373(4)
Ti(1)-C(28)	2.426(4)	Ti(1)-C(29)	2.447(4)
Ti(1)-C(30)	2.430(4)	Ti(1)-$Cp_{(cent)}$	2.094
N(1)-C(1)	1.476(5)	N(1)-C(4)	1.328(5)
N(2)-C(4)	1.356(5)	N(2)-C(6)	1.481(5)
N(3)-C(9)	1.383(5)	N(3)-C(18)	1.435(5)
N(4)-C(9)	1.283(5)	N(4)-C(10)	1.431(5)
O(1)-C(9)	1.343(4)	C(1)-C(2)	1.525(6)
C(1)-C(3)	1.537(6)	C(4)-C(5)	1.501(6)
C(6)-C(7)	1.527(6)	C(6)-C(8)	1.520(6)
C(10)-C(11)	1.395(6)	C(10)-C(15)	1.404(6)
C(11)-C(12)	1.406(6)	C(11)-C(16)	1.512(6)
C(12)-C(13)	1.380(8)	C(13)-C(14)	1.384(8)
C(14)-C(15)	1.392(6)	C(15)-C(17)	1.495(7)
C(18)-C(19)	1.402(6)	C(18)-C(23)	1.404(6)
C(19)-C(20)	1.398(6)	C(19)-C(24)	1.497(7)
C(20)-C(21)	1.386(7)	C(21)-C(22)	1.378(7)
C(22)-C(23)	1.392(6)	C(23)-C(25)	1.505(6)
C(26)-C(27)	1.415(6)	C(26)-C(30)	1.417(6)
C(26)-C(31)	1.516(6)	C(27)-C(28)	1.418(6)
C(27)-C(32)	1.510(6)	C(28)-C(29)	1.423(6)
C(28)-C(33)	1.507(6)	C(29)-C(30)	1.431(6)
C(29)-C(34)	1.500(6)	C(30)-C(35)	1.505(6)

N(1)-Ti(1)-N(2)	63.83(13)	N(1)-Ti(1)-N(3)	88.16(13)

N(2)-Ti(1)-N(3)	109.18(13)	N(1)-Ti(1)-O(1)	143.45(12)
N(2)-Ti(1)-O(1)	98.48(13)	N(3)-Ti(1)-O(1)	66.84(12)
N(1)-Ti(1)-C(4)	31.78(13)	N(2)-Ti(1)-C(4)	32.42(13)
N(3)-Ti(1)-C(4)	103.39(13)	O(1)-Ti(1)-C(4)	126.70(12)
N(1)-Ti(1)-C(9)	118.14(12)	N(2)-Ti(1)-C(9)	106.71(13)
N(3)-Ti(1)-C(9)	34.01(13)	O(1)-Ti(1)-C(9)	32.83(11)
C(4)-Ti(1)-C(9)	120.23(12)	N(1)-Ti(1)-C(26)	99.93(13)
N(2)-Ti(1)-C(26)	135.62(14)	N(3)-Ti(1)-C(26)	111.27(14)
O(1)-Ti(1)-C(26)	113.55(13)	C(4)-Ti(1)-C(26)	118.35(14)
N(1)-Ti(1)-C(27)	134.20(14)	N(2)-Ti(1)-C(27)	138.34(14)
N(3)-Ti(1)-C(27)	108.59(14)	O(1)-Ti(1)-C(27)	80.81(13)
C(4)-Ti(1)-C(27)	144.60(14)	N(1)-Ti(1)-C(28)	135.16(13)
N(2)-Ti(1)-C(28)	104.30(13)	N(3)-Ti(1)-C(28)	134.31(14)
O(1)-Ti(1)-C(28)	78.38(12)	C(4)-Ti(1)-C(28)	121.29(13)
N(1)-Ti(1)-C(29)	101.52(13)	N(2)-Ti(1)-C(29)	85.10(13)
N(3)-Ti(1)-C(29)	165.35(14)	O(1)-Ti(1)-C(29)	108.82(13)
C(4)-Ti(1)-C(29)	90.40(13)	N(1)-Ti(1)-C(30)	82.36(13)
N(2)-Ti(1)-C(30)	101.63(14)	N(3)-Ti(1)-C(30)	139.49(14)
O(1)-Ti(1)-C(30)	133.96(13)	C(4)-Ti(1)-C(30)	88.72(13)
C(9)-Ti(1)-C(26)	116.95(13)	C(9)-Ti(1)-C(27)	95.00(13)
C(26)-Ti(1)-C(27)	34.38(14)	C(9)-Ti(1)-C(28)	106.70(13)
C(26)-Ti(1)-C(28)	56.79(14)	C(27)-Ti(1)-C(28)	34.36(14)
C(9)-Ti(1)-C(29)	139.97(13)	C(26)-Ti(1)-C(29)	56.56(14)
C(27)-Ti(1)-C(29)	56.82(14)	C(28)-Ti(1)-C(29)	33.96(14)
C(9)-Ti(1)-C(30)	150.29(13)	C(26)-Ti(1)-C(30)	34.02(14)
C(27)-Ti(1)-C(30)	56.95(14)	C(28)-Ti(1)-C(30)	56.69(14)
C(29)-Ti(1)-C(30)	34.12(14)	$Cp_{(cent)}$-Ti(1)-N(1)	112.2
$Cp_{(cent)}$-Ti(1)-N(2)	114.7	$Cp_{(cent)}$-Ti(1)-N(3)	136.1
$Cp_{(cent)}$-Ti(1)-O(1)	104.1	Ti(1)-N(1)-C(1)	147.8(3)
Ti(1)-N(1)-C(4)	89.8(2)	C(1)-N(1)-C(4)	121.8(3)
Ti(1)-N(2)-C(4)	94.3(2)	Ti(1)-N(2)-C(6)	143.5(3)
C(4)-N(2)-C(6)	122.1(3)	Ti(1)-N(3)-C(9)	92.2(2)
Ti(1)-N(3)-C(18)	147.0(3)	C(9)-N(3)-C(18)	120.2(3)
C(9)-N(4)-C(10)	119.0(3)	Ti(1)-O(1)-C(9)	94.1(2)
N(1)-C(1)-C(2)	108.8(3)	N(1)-C(1)-C(3)	111.6(3)
C(2)-C(1)-C(3)	108.2(4)	N(1)-C(4)-N(2)	110.9(3)
Ti(1)-C(4)-C(5)	168.4(3)	N(1)-C(4)-C(5)	125.8(4)
N(2)-C(4)-C(5)	123.3(4)	N(2)-C(6)-C(7)	110.9(3)
N(2)-C(6)-C(8)	109.9(3)	C(7)-C(6)-C(8)	109.8(4)
N(3)-C(9)-N(4)	126.4(3)	Ti(1)-C(9)-O(1)	53.1(2)

N(3)-C(9)-O(1)	106.9(3)	N(4)-C(9)-O(1)	126.7(4)
N(4)-C(10)-C(11)	121.4(4)	N(4)-C(10)-C(15)	117.6(4)
C(11)-C(10)-C(15)	120.7(4)	C(10)-C(11)-C(12)	118.6(4)
C(10)-C(11)-C(16)	121.0(4)	C(12)-C(11)-C(16)	120.4(4)
C(11)-C(12)-C(13)	121.3(5)	C(12)-C(13)-C(14)	119.2(4)
C(13)-C(14)-C(15)	121.4(5)	C(10)-C(15)-C(14)	118.8(4)
C(10)-C(15)-C(17)	120.2(4)	C(14)-C(15)-C(17)	121.0(4)
N(3)-C(18)-C(19)	119.8(4)	N(3)-C(18)-C(23)	119.3(4)
C(19)-C(18)-C(23)	120.9(4)	C(18)-C(19)-C(20)	118.6(4)
C(18)-C(19)-C(24)	121.2(4)	C(20)-C(19)-C(24)	120.2(4)
C(19)-C(20)-C(21)	121.0(4)	C(20)-C(21)-C(22)	119.5(4)
C(21)-C(22)-C(23)	121.8(4)	C(18)-C(23)-C(22)	118.2(4)
C(18)-C(23)-C(25)	121.1(4)	C(22)-C(23)-C(25)	120.7(4)
Ti(1)-C(26)-C(27)	71.2(2)	Ti(1)-C(26)-C(30)	73.6(2)
C(27)-C(26)-C(30)	107.9(4)	Ti(1)-C(26)-C(31)	128.6(3)
C(27)-C(26)-C(31)	125.5(4)	C(30)-C(26)-C(31)	125.8(4)
Ti(1)-C(27)-C(26)	74.4(2)	Ti(1)-C(27)-C(28)	74.9(2)
C(26)-C(27)-C(28)	108.6(4)	Ti(1)-C(27)-C(32)	119.2(3)
C(26)-C(27)-C(32)	126.8(4)	C(28)-C(27)-C(32)	124.5(4)
Ti(1)-C(28)-C(27)	70.8(2)	Ti(1)-C(28)-C(29)	73.8(2)
C(27)-C(28)-C(29)	107.7(4)	Ti(1)-C(28)-C(33)	123.7(3)
C(27)-C(28)-C(33)	124.4(4)	C(29)-C(28)-C(33)	127.8(4)
Ti(1)-C(29)-C(28)	72.2(2)	Ti(1)-C(29)-C(30)	72.3(2)
C(28)-C(29)-C(30)	107.8(4)	Ti(1)-C(29)-C(34)	126.8(3)
C(28)-C(29)-C(34)	128.7(4)	C(30)-C(29)-C(34)	123.2(4)
Ti(1)-C(30)-C(26)	72.4(2)	Ti(1)-C(30)-C(29)	73.6(2)
C(26)-C(30)-C(29)	107.9(4)	Ti(1)-C(30)-C(35)	127.7(3)
C(26)-C(30)-C(35)	127.6(4)	C(29)-C(30)-C(35)	123.7(4)

i) $Cp_{(cent)}$ refers to the computed C_5Me_5 ring carbon centroid

J.3 Atomic coordinates ($\times 10^4$) and isotropic or equivalent isotropic displacement parameters ($Å^2 \times 10^3$). $U_{(eq)}$ is defined as one third of the trace of the orthogonalised U_{ij} tensor

	x	y	z	$U_{(eq)}$
Ti(1)	2510(1)	488(1)	868(1)	24
N(1)	3390(2)	1564(3)	455(2)	29
N(2)	2287(2)	2236(3)	297(2)	27
N(3)	2878(2)	942(3)	1912(2)	27
N(4)	2062(2)	1049(3)	2874(2)	28
O(1)	1766(1)	588(3)	1599(1)	28
C(1)	4153(2)	1597(4)	359(2)	33
C(2)	4496(2)	409(5)	793(3)	40
C(3)	4486(2)	2923(5)	668(3)	42
C(4)	2952(2)	2418(4)	89(2)	27
C(5)	3144(2)	3413(4)	-506(2)	36
C(6)	1707(2)	3155(4)	39(2)	31
C(7)	995(2)	2507(5)	160(3)	40
C(8)	1770(2)	4500(5)	461(2)	36
C(9)	2215(2)	885(4)	2186(2)	23
C(10)	1347(2)	906(4)	3064(2)	30
C(11)	853(2)	1925(4)	2899(2)	34
C(12)	176(2)	1773(6)	3159(3)	46
C(13)	-2(3)	653(6)	3576(3)	54
C(14)	496(3)	-348(5)	3733(3)	47
C(15)	1173(2)	-242(4)	3485(2)	37
C(16)	1037(3)	3166(5)	2448(3)	44
C(17)	1711(3)	-1313(5)	3672(3)	48
C(18)	3463(2)	1399(4)	2389(2)	27
C(19)	3896(2)	446(5)	2776(2)	31
C(20)	4498(2)	910(5)	3183(2)	43
C(21)	4658(2)	2285(6)	3220(3)	45
C(22)	4212(2)	3209(5)	2858(3)	42
C(23)	3608(2)	2798(4)	2442(2)	32
C(24)	3710(3)	-1034(5)	2781(3)	45
C(25)	3124(3)	3829(5)	2061(3)	42
C(26)	2813(2)	-1809(4)	532(2)	31
C(27)	2147(2)	-1821(4)	842(2)	32

C(28)	1662(2)	-1137(4)	339(2)	30
C(29)	2037(2)	-651(4)	-276(2)	31
C(30)	2754(2)	-1060(4)	-150(2)	32
C(31)	3442(2)	-2648(5)	811(3)	42
C(32)	1958(3)	-2498(5)	1566(2)	41
C(33)	885(2)	-1046(5)	438(3)	40
C(34)	1756(3)	18(5)	-990(2)	40
C(35)	3297(2)	-905(5)	-726(3)	44

J.4 Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic 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)	24(1)	26(1)	23(1)	-1(1)	1(1)	0(1)
N(1)	29(2)	29(2)	29(2)	0(2)	4(2)	0(2)
N(2)	26(2)	29(2)	24(2)	0(1)	-4(1)	1(1)
N(3)	26(2)	31(2)	24(2)	-1(1)	-4(1)	-2(1)
N(4)	25(2)	34(2)	26(2)	1(2)	-1(1)	-2(2)
O(1)	27(1)	34(2)	24(1)	-3(1)	2(1)	-2(1)
C(1)	31(2)	36(2)	33(2)	2(2)	9(2)	-3(2)
C(2)	27(2)	51(3)	42(2)	4(2)	4(2)	4(2)
C(3)	33(2)	47(3)	46(3)	-2(2)	3(2)	-11(2)
C(4)	28(2)	27(2)	26(2)	-5(2)	6(2)	2(2)
C(5)	37(2)	34(2)	36(2)	3(2)	2(2)	3(2)
C(6)	31(2)	32(2)	28(2)	4(2)	-2(2)	6(2)
C(7)	33(2)	42(3)	44(3)	-1(2)	0(2)	10(2)
C(8)	37(2)	37(2)	35(2)	1(2)	1(2)	8(2)
C(9)	29(2)	18(2)	22(2)	-1(2)	-2(2)	-3(2)
C(10)	31(2)	35(2)	24(2)	-8(2)	0(2)	-6(2)
C(11)	33(2)	42(3)	25(2)	-8(2)	3(2)	0(2)
C(12)	27(2)	69(3)	42(3)	-16(3)	4(2)	8(2)
C(13)	35(3)	78(4)	50(3)	-22(3)	13(2)	-13(3)
C(14)	52(3)	50(3)	40(3)	-14(2)	17(2)	-21(3)
C(15)	46(3)	36(3)	30(2)	-9(2)	6(2)	-8(2)

C(16)	51(3)	45(3)	35(2)	3(2)	-5(2)	12(2)
C(17)	70(4)	32(3)	42(3)	4(2)	12(3)	-1(2)
C(18)	23(2)	38(2)	20(2)	-1(2)	2(2)	-2(2)
C(19)	26(2)	45(2)	23(2)	-1(2)	1(2)	5(2)
C(20)	32(2)	65(3)	30(2)	5(2)	-3(2)	5(2)
C(21)	29(2)	73(4)	34(2)	-5(2)	-2(2)	-11(2)
C(22)	39(3)	47(3)	40(2)	-5(2)	5(2)	-12(2)
C(23)	31(2)	40(2)	25(2)	-2(2)	5(2)	-5(2)
C(24)	47(3)	41(3)	47(3)	4(2)	-1(2)	11(2)
C(25)	53(3)	33(2)	40(3)	-2(2)	-2(2)	-7(2)
C(26)	27(2)	29(2)	36(2)	-6(2)	-4(2)	0(2)
C(27)	39(2)	22(2)	33(2)	-2(2)	1(2)	-2(2)
C(28)	31(2)	27(2)	30(2)	-7(2)	-1(2)	-8(2)
C(29)	34(2)	30(2)	28(2)	-9(2)	0(2)	-2(2)
C(30)	33(2)	30(2)	33(2)	-7(2)	2(2)	-5(2)
C(31)	35(2)	37(3)	53(3)	0(2)	-3(2)	4(2)
C(32)	51(3)	34(2)	36(2)	1(2)	2(2)	-5(2)
C(33)	31(2)	44(3)	44(3)	-4(2)	-3(2)	-10(2)
C(34)	48(3)	42(2)	29(2)	-6(2)	-4(2)	2(2)
C(35)	47(3)	50(3)	35(2)	-14(2)	12(2)	-1(2)

J.5 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$)

	x	y	z	$U_{(eq)}$
H(11)	4237(2)	1544(4)	-190(2)	43
H(21)	5014(2)	411(5)	738(3)	51
H(22)	4399(2)	491(5)	1338(3)	51
H(23)	4291(2)	-460(5)	587(3)	51
H(31)	5002(2)	2914(5)	594(3)	57
H(32)	4407(2)	3006(5)	1217(3)	57
H(33)	4265(2)	3713(5)	391(3)	57
H(51)	2717(2)	3937(4)	-683(2)	47
H(52)	3511(2)	4056(4)	-295(2)	47
H(53)	3330(2)	2906(4)	-940(2)	47
H(61)	1743(2)	3319(4)	-513(2)	39

H(71)	613(2)	3143(5)	-22(3)	50
H(72)	956(2)	2326(5)	710(3)	50
H(73)	950(2)	1631(5)	-125(3)	50
H(81)	1380(2)	5119(5)	280(2)	48
H(82)	2231(2)	4934(5)	368(2)	48
H(83)	1740(2)	4329(5)	1013(2)	48
H(121)	-184(2)	2491(6)	3034(3)	60
H(131)	-482(3)	575(6)	3769(3)	65
H(141)	366(3)	-1165(5)	4030(3)	60
H(161)	619(3)	3777(5)	2382(3)	57
H(162)	1428(3)	3662(5)	2728(3)	57
H(163)	1190(3)	2885(5)	1942(3)	57
H(171)	1500(3)	-2052(5)	3972(3)	60
H(172)	2114(3)	-896(5)	3974(3)	60
H(173)	1882(3)	-1705(5)	3196(3)	60
H(201)	4817(2)	236(5)	3449(2)	56
H(211)	5094(2)	2603(6)	3505(3)	58
H(221)	4319(2)	4203(5)	2895(3)	52
H(241)	4082(3)	-1542(5)	3084(3)	58
H(242)	3248(3)	-1163(5)	3009(3)	58
H(243)	3680(3)	-1387(5)	2252(3)	58
H(251)	3312(3)	4766(5)	2159(3)	56
H(252)	2650(3)	3747(5)	2268(3)	56
H(253)	3085(3)	3656(5)	1505(3)	56
H(311)	3848(2)	-2452(5)	495(3)	55
H(312)	3573(2)	-2413(5)	1348(3)	55
H(313)	3320(2)	-3636(5)	772(3)	55
H(321)	1450(3)	-2339(5)	1645(2)	53
H(322)	2250(3)	-2102(5)	1998(2)	53
H(323)	2049(3)	-3498(5)	1535(2)	53
H(331)	650(2)	-510(5)	17(3)	50
H(332)	686(2)	-1988(5)	438(3)	50
H(333)	802(2)	-593(5)	929(3)	50
H(341)	2155(3)	238(5)	-1311(2)	51
H(342)	1423(3)	-614(5)	-1270(2)	51
H(343)	1505(3)	875(5)	-866(2)	51
H(351)	3101(2)	-312(5)	-1145(3)	57
H(352)	3729(2)	-475(5)	-488(3)	57
H(353)	3416(2)	-1817(5)	-932(3)	57

APPENDIX K – X-RAY STRUCTURE ANALYSIS OF Ti(η-C_5Me_5) {N(2,6-$C_6H_3Me_2$)C(N-4-C_6H_4Me)O}{MeC(N^{i}Pr)$_2$} (42)

K.1 Crystal data, data collection and refinement

Empirical formula	$C_{34}\ H_{48}\ N_4\ O_1\ Ti_1$
Formula weight	575.68
Crystal description	red prism
Crystal size	0.38 x 0.30 x 0.20 mm
Temperature	150 K
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 9.5758(3) Å α = 82.229(1) deg.
	b = 9.9197(3) Å β = 78.344(1) deg.
	c = 17.2651(6) Å γ = 84.112(1) deg.
Reflections for cell refinement	5893
Range in theta	2.910 to 27.485 deg.
Volume, Z	1586.63(9) Å^3, 2
Density (calculated)	1.20 Mg/m^3
Absorption coefficient	0.30 mm^{-1}
F(000)	618.57
Diffractometer type	Nonius KappaCCD
Wavelength	0.71073 A
Scan type	CCD
Theta range for data collection	2.9 to 27.5 deg.
Index ranges	-12<=h<=12, -12<=k<=12, 0<=l<=22
Reflections collected	12115
Independent reflections	7104 [R(merge) = 0.03]
Observed reflections	3842 [I>3sigma(I)]
Absorption correction	Multi-scan (Tmin = 0.914, Tmax = 0.942)
Structure solution	by direct methods and Fourier difference maps
Hydrogen atom location	geometric
Hydrogen atom treatment	riding model
Refinement method	Full-matrix least-squares on F
Weighting scheme	Chebychev
Data / restraints / parameters	3842 / 0 / 361

Goodness-of-fit on F	1.0488
Final R indices [I>3sigma(I)]	R1 = 0.0890, Rw = 0.0919
Extinction coefficient	none required
Final maximum delta/sigma	0.002150
Largest diff. peak and hole	0.52 and -0.80 e. $Å^{-3}$

K.2 Bond lengths (Å) and angles (°)

Ti(1)-N(1)	2.024(5)	Ti(1)-N(2)	2.150(5)
Ti(1)-N(3)	1.994(4)	Ti(1)-O(1)	1.973(4)
Ti(1)-C(25)	2.394(6)	Ti(1)-C(26)	2.411(6)
Ti(1)-C(27)	2.424(6)	Ti(1)-C(28)	2.445(6)
Ti(1)-C(29)	2.446(6)	$Ti(1)-Cp_{(cent)}$	2.106
N(1)-C(1)	1.470(7)	N(1)-C(4)	1.331(7)
N(2)-C(4)	1.327(8)	N(2)-C(6)	1.481(7)
N(3)-C(9)	1.387(6)	N(3)-C(17)	1.420(6)
N(4)-C(9)	1.283(7)	N(4)-C(10)	1.420(6)
O(1)-C(9)	1.347(6)	C(1)-C(2)	1.520(11)
C(1)-C(3)	1.54(1)	C(4)-C(5)	1.516(9)
C(6)-C(7)	1.51(1)	C(6)-C(8)	1.50(1)
C(10)-C(11)	1.395(7)	C(10)-C(15)	1.396(8)
C(11)-C(12)	1.400(8)	C(12)-C(13)	1.368(8)
C(13)-C(14)	1.366(8)	C(13)-C(16)	1.526(7)
C(14)-C(15)	1.394(8)	C(17)-C(18)	1.409(8)
C(17)-C(22)	1.384(8)	C(18)-C(19)	1.387(8)
C(18)-C(23)	1.507(8)	C(19)-C(20)	1.36(1)
C(20)-C(21)	1.36(1)	C(21)-C(22)	1.413(8)
C(22)-C(24)	1.514(9)	C(25)-C(26)	1.420(9)
C(25)-C(29)	1.384(9)	C(25)-C(30)	1.502(9)
C(26)-C(27)	1.411(9)	C(26)-C(31)	1.506(9)
C(27)-C(28)	1.411(9)	C(27)-C(32)	1.499(9)
C(28)-C(29)	1.46(1)	C(28)-C(33)	1.50(1)
C(29)-C(34)	1.509(9)		

N(1)-Ti(1)-N(2)	63.8(2)	N(1)-Ti(1)-N(3)	109.0(2)
N(2)-Ti(1)-N(3)	90.1(2)	N(1)-Ti(1)-O(1)	95.2(2)

N(2)-Ti(1)-O(1)	142.4(2)	N(3)-Ti(1)-O(1)	66.6(2)
N(1)-Ti(1)-C(4)	32.1(2)	N(2)-Ti(1)-C(4)	32.1(2)
N(3)-Ti(1)-C(4)	104.5(2)	O(1)-Ti(1)-C(4)	123.6(2)
N(1)-Ti(1)-C(9)	101.8(2)	N(2)-Ti(1)-C(9)	117.4(2)
N(3)-Ti(1)-C(9)	34.0(2)	O(1)-Ti(1)-C(9)	32.8(2)
C(4)-Ti(1)-C(9)	116.6(2)	N(1)-Ti(1)-C(25)	138.6(2)
N(2)-Ti(1)-C(25)	133.6(2)	N(3)-Ti(1)-C(25)	108.1(2)
O(1)-Ti(1)-C(25)	83.2(2)	C(4)-Ti(1)-C(25)	144.3(2)
N(1)-Ti(1)-C(26)	135.6(2)	N(2)-Ti(1)-C(26)	99.3(2)
N(3)-Ti(1)-C(26)	111.9(2)	O(1)-Ti(1)-C(26)	116.3(2)
C(4)-Ti(1)-C(26)	118.2(2)	N(1)-Ti(1)-C(27)	101.7(2)
N(2)-Ti(1)-C(27)	81.9(2)	N(3)-Ti(1)-C(27)	140.8(2)
O(1)-Ti(1)-C(27)	134.8(2)	C(4)-Ti(1)-C(27)	88.6(2)
N(1)-Ti(1)-C(28)	85.3(2)	N(2)-Ti(1)-C(28)	100.8(2)
N(3)-Ti(1)-C(28)	165.0(2)	O(1)-Ti(1)-C(28)	108.5(2)
C(4)-Ti(1)-C(28)	90.1(2)	N(1)-Ti(1)-C(29)	105.7(2)
N(2)-Ti(1)-C(29)	135.0(2)	N(3)-Ti(1)-C(29)	132.4(2)
O(1)-Ti(1)-C(29)	78.8(2)	C(4)-Ti(1)-C(29)	122.0(2)
C(9)-Ti(1)-C(25)	98.6(2)	C(9)-Ti(1)-C(26)	121.8(2)
C(25)-Ti(1)-C(26)	34.4(2)	C(9)-Ti(1)-C(27)	154.6(2)
C(25)-Ti(1)-C(27)	56.8(2)	C(26)-Ti(1)-C(27)	33.9(2)
C(9)-Ti(1)-C(28)	140.5(2)	C(25)-Ti(1)-C(28)	56.8(2)
C(26)-Ti(1)-C(28)	56.3(2)	C(27)-Ti(1)-C(28)	33.7(2)
C(9)-Ti(1)-C(29)	107.5(2)	C(25)-Ti(1)-C(29)	33.2(2)
C(26)-Ti(1)-C(29)	55.9(2)	C(27)-Ti(1)-C(29)	56.4(2)
C(28)-Ti(1)-C(29)	34.7(2)	$Cp_{(cent)}$-Ti(1)-N(1)	115.2
$Cp_{(cent)}$-Ti(1)-N(2)	111.7	$Cp_{(cent)}$-Ti(1)-N(3)	135.7
$Cp_{(cent)}$-Ti(1)-O(1)	105.4	Ti(1)-N(1)-C(1)	142.3(4)
Ti(1)-N(1)-C(4)	93.9(3)	C(1)-N(1)-C(4)	123.6(5)
Ti(1)-N(2)-C(4)	88.5(3)	Ti(1)-N(2)-C(6)	147.6(4)
C(4)-N(2)-C(6)	123.7(5)	Ti(1)-N(3)-C(9)	92.5(3)
Ti(1)-N(3)-C(17)	145.5(3)	C(9)-N(3)-C(17)	120.2(4)
C(9)-N(4)-C(10)	121.5(4)	Ti(1)-O(1)-C(9)	94.7(3)
N(1)-C(1)-C(2)	112.4(6)	N(1)-C(1)-C(3)	109.7(5)
C(2)-C(1)-C(3)	109.3(6)	N(1)-C(4)-N(2)	112.5(5)
Ti(1)-C(4)-C(5)	168.4(4)	N(1)-C(4)-C(5)	123.2(6)
N(2)-C(4)-C(5)	124.2(5)	N(2)-C(6)-C(7)	110.7(5)
N(2)-C(6)-C(8)	108.7(5)	C(7)-C(6)-C(8)	110.1(6)
N(3)-C(9)-N(4)	124.4(5)	Ti(1)-C(9)-O(1)	52.5(2)
N(3)-C(9)-O(1)	105.7(4)	N(4)-C(9)-O(1)	129.9(5)

N(4)-C(10)-C(11)	124.9(5)	N(4)-C(10)-C(15)	117.9(4)
C(11)-C(10)-C(15)	117.1(5)	C(10)-C(11)-C(12)	119.9(5)
C(11)-C(12)-C(13)	122.4(5)	C(12)-C(13)-C(14)	117.8(5)
C(12)-C(13)-C(16)	120.8(5)	C(14)-C(13)-C(16)	121.4(5)
C(13)-C(14)-C(15)	121.4(5)	C(10)-C(15)-C(14)	121.2(5)
N(3)-C(17)-C(18)	119.2(5)	N(3)-C(17)-C(22)	120.7(5)
C(18)-C(17)-C(22)	120.0(5)	C(17)-C(18)-C(19)	119.3(6)
C(17)-C(18)-C(23)	119.6(5)	C(19)-C(18)-C(23)	121.0(6)
C(18)-C(19)-C(20)	120.1(6)	C(19)-C(20)-C(21)	121.8(6)
C(20)-C(21)-C(22)	119.6(6)	C(17)-C(22)-C(21)	119.1(6)
C(17)-C(22)-C(24)	121.7(5)	C(21)-C(22)-C(24)	119.2(6)
Ti(1)-C(25)-C(26)	73.4(4)	Ti(1)-C(25)-C(29)	75.5(4)
C(26)-C(25)-C(29)	108.6(6)	Ti(1)-C(25)-C(30)	120.4(4)
C(26)-C(25)-C(30)	126.8(6)	C(29)-C(25)-C(30)	124.4(6)
Ti(1)-C(26)-C(25)	72.2(3)	Ti(1)-C(26)-C(27)	73.6(4)
C(25)-C(26)-C(27)	108.0(6)	Ti(1)-C(26)-C(31)	129.0(4)
C(25)-C(26)-C(31)	125.2(6)	C(27)-C(26)-C(31)	125.8(6)
Ti(1)-C(27)-C(26)	72.5(3)	Ti(1)-C(27)-C(28)	74.0(3)
C(26)-C(27)-C(28)	108.7(6)	Ti(1)-C(27)-C(32)	126.8(4)
C(26)-C(27)-C(32)	127.2(6)	C(28)-C(27)-C(32)	123.5(6)
Ti(1)-C(28)-C(27)	72.3(3)	Ti(1)-C(28)-C(29)	72.7(3)
C(27)-C(28)-C(29)	106.5(5)	Ti(1)-C(28)-C(33)	124.8(5)
C(27)-C(28)-C(33)	124.8(6)	C(29)-C(28)-C(33)	128.5(6)
Ti(1)-C(29)-C(25)	71.3(3)	Ti(1)-C(29)-C(28)	72.6(3)
C(25)-C(29)-C(28)	108.1(6)	Ti(1)-C(29)-C(34)	122.4(4)
C(25)-C(29)-C(34)	125.2(7)	C(28)-C(29)-C(34)	126.7(6)

i) $Cp_{(cent)}$ refers to the computed C_5Me_5 ring carbon centroid

K.3 Atomic coordinates ($\times 10^4$) and isotropic or equivalent isotropic displacement parameters ($Å^2 \times 10^3$). $U_{(eq)}$ is defined as one third of the trace of the orthogonalised U_{ij} tensor

	x	y	z	$U_{(eq)}$
Ti(1)	950(1)	2250(1)	7705(1)	32
N(1)	-533(5)	3726(4)	7404(3)	36
N(2)	135(5)	2044(5)	6658(3)	37
N(3)	2850(5)	2636(5)	7030(3)	34
N(4)	4147(5)	4306(5)	7362(3)	32
O(1)	2007(4)	3464(4)	8153(2)	35
C(1)	-1288(7)	5021(6)	7634(4)	50
C(2)	-1003(8)	5353(7)	8419(5)	60
C(3)	-840(1)	6193(7)	6975(5)	74
C(4)	-805(6)	3094(6)	6824(4)	39
C(5)	-2091(7)	3496(7)	6432(4)	52
C(6)	161(7)	1241(7)	5991(3)	45
C(7)	552(8)	2104(9)	5201(4)	61
C(8)	1231(7)	35(8)	6050(5)	60
C(9)	3096(5)	3545(5)	7523(3)	30
C(10)	4344(5)	5206(5)	7897(3)	28
C(11)	3899(7)	5002(6)	8722(3)	43
C(12)	4295(7)	5874(7)	9200(3)	44
C(13)	5116(6)	6941(6)	8889(3)	35
C(14)	5496(6)	7183(6)	8079(4)	39
C(15)	5114(6)	6342(6)	7583(3)	35
C(16)	5625(7)	7799(7)	9432(4)	49
C(17)	3744(5)	2557(5)	6271(3)	27
C(18)	3560(6)	3578(6)	5640(3)	38
C(19)	4390(7)	3472(7)	4891(4)	46
C(20)	5347(7)	2376(7)	4764(4)	50
C(21)	5571(6)	1387(6)	5367(4)	45
C(22)	4757(6)	1471(6)	6141(3)	38
C(23)	2491(7)	4782(6)	5794(4)	44
C(24)	5051(7)	398(7)	6813(4)	57
C(25)	1344(7)	702(7)	8844(4)	46
C(26)	915(6)	-83(6)	8315(4)	44

C(27)	-509(6)	363(6)	8254(4)	42
C(28)	-991(7)	1400(6)	8751(4)	45
C(29)	195(7)	1579(7)	9133(3)	47
C(30)	2765(8)	566(8)	9101(4)	57
C(31)	1735(8)	-1343(6)	8009(5)	53
C(32)	-1467(7)	-271(7)	7842(4)	53
C(33)	-2485(7)	2053(9)	8900(5)	64
C(34)	185(9)	2531(8)	9746(4)	59

K.4 Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic 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)	27(1)	42(1)	29(1)	-13(1)	1(1)	-7(1)
N(1)	29(2)	28(2)	49(3)	-11(2)	-7(2)	5(2)
N(2)	38(3)	39(3)	36(2)	-13(2)	-6(2)	-7(2)
N(3)	31(2)	43(3)	29(2)	-17(2)	1(2)	-10(2)
N(4)	28(2)	41(3)	30(2)	-15(2)	-6(2)	-6(2)
O(1)	30(2)	45(2)	30(2)	-12(2)	0(1)	-6(2)
C(1)	40(3)	30(3)	75(4)	-16(3)	3(3)	2(2)
C(2)	52(4)	45(4)	84(5)	-24(4)	-7(4)	7(3)
C(3)	92(6)	35(4)	82(6)	-12(4)	8(5)	5(4)
C(4)	37(3)	38(3)	44(3)	-2(2)	-10(2)	-10(2)
C(5)	48(4)	50(4)	63(4)	-1(3)	-25(3)	-4(3)
C(6)	50(4)	59(4)	35(3)	-16(3)	-10(3)	-22(3)
C(7)	63(4)	77(5)	46(4)	-18(3)	-5(3)	-25(4)
C(8)	51(4)	68(5)	66(4)	-41(4)	3(3)	-10(3)
C(9)	33(3)	31(3)	27(2)	-11(2)	-4(2)	-4(2)
C(10)	28(2)	31(3)	27(2)	-12(2)	-9(2)	1(2)
C(11)	52(3)	47(3)	31(3)	-10(2)	-2(2)	-22(3)
C(12)	51(4)	53(4)	32(3)	-15(3)	-4(2)	-17(3)
C(13)	31(3)	38(3)	42(3)	-23(2)	-10(2)	4(2)
C(14)	39(3)	34(3)	47(3)	-3(2)	-15(3)	-8(2)

C(15)	37(3)	43(3)	27(3)	-5(2)	-11(2)	-3(2)
C(16)	46(3)	57(4)	51(4)	-32(3)	-7(3)	-11(3)
C(17)	26(2)	33(3)	24(2)	-15(2)	4(2)	-9(2)
C(18)	36(3)	45(3)	36(3)	-8(3)	-6(2)	-14(2)
C(19)	50(4)	57(4)	32(3)	-11(3)	0(2)	-13(3)
C(20)	51(4)	57(4)	42(3)	-22(3)	5(3)	-12(3)
C(21)	41(3)	46(3)	45(3)	-22(3)	13(3)	-13(3)
C(22)	37(3)	34(3)	42(3)	-7(2)	-3(2)	-8(2)
C(23)	46(3)	39(3)	42(3)	1(3)	-6(3)	-1(3)
C(24)	49(4)	55(4)	56(4)	0(3)	4(3)	12(3)
C(25)	44(3)	48(4)	41(3)	7(3)	-4(3)	-4(3)
C(26)	41(3)	43(3)	44(3)	-3(3)	1(3)	-7(3)
C(27)	36(3)	40(3)	46(3)	-2(3)	3(2)	-7(2)
C(28)	42(3)	47(3)	43(3)	-2(3)	6(3)	-11(3)
C(29)	55(4)	51(4)	28(3)	-4(3)	11(3)	-16(3)
C(30)	62(4)	62(4)	50(4)	7(3)	-30(3)	-2(3)
C(31)	53(4)	33(3)	70(5)	1(3)	-7(3)	-4(3)
C(32)	42(3)	52(4)	65(4)	-3(3)	-7(3)	-15(3)
C(33)	41(4)	80(5)	68(5)	-26(4)	17(3)	-17(3)
C(34)	72(5)	72(5)	33(3)	-18(3)	-1(3)	-11(4)

K.5 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$)

	x	y	z	$U_{(eq)}$
H(11)	-2338(7)	4931(6)	7701(4)	59
H(21)	-1544(8)	6231(7)	8562(5)	75
H(22)	-1318(8)	4597(7)	8844(5)	75
H(23)	44(8)	5434(7)	8370(5)	75
H(31)	-1360(1)	7071(7)	7130(5)	84
H(32)	220(1)	6262(7)	6909(5)	84
H(33)	-1070(1)	6004(7)	6462(5)	84
H(51)	-2090(7)	2886(7)	6016(4)	70
H(52)	-2984(7)	3408(7)	6845(4)	70
H(53)	-2051(7)	4464(7)	6179(4)	70

H(61)	-793(7)	899(7)	6008(3)	60
H(71)	582(8)	1557(9)	4751(4)	74
H(72)	1510(8)	2454(9)	5160(4)	74
H(73)	-185(8)	2891(9)	5174(4)	74
H(81)	1273(7)	-527(8)	5605(5)	69
H(82)	930(7)	-531(8)	6571(5)	69
H(83)	2197(7)	357(8)	6026(5)	69
H(111)	3307(7)	4225(6)	8969(3)	52
H(121)	3966(7)	5710(7)	9790(3)	54
H(141)	6041(6)	7993(6)	7837(4)	48
H(151)	5402(6)	6544(6)	6992(3)	41
H(161)	6204(7)	8523(7)	9096(4)	65
H(162)	6226(7)	7211(7)	9777(4)	65
H(163)	4777(7)	8235(7)	9775(4)	65
H(191)	4273(7)	4205(7)	4445(4)	57
H(201)	5911(7)	2296(7)	4216(4)	59
H(211)	6293(6)	599(6)	5261(4)	57
H(231)	2493(7)	5398(6)	5285(4)	55
H(232)	2759(7)	5292(6)	6197(4)	55
H(233)	1514(7)	4459(6)	5999(4)	55
H(241)	4499(7)	455(7)	7366(4)	65
H(242)	5792(7)	-373(7)	6701(4)	65
H(301)	2764(8)	1255(8)	9473(4)	75
H(302)	2929(8)	-372(8)	9378(4)	75
H(303)	3544(8)	726(8)	8624(4)	75
H(311)	1202(8)	-1705(6)	7650(5)	62
H(312)	1852(8)	-2055(6)	8465(5)	62
H(313)	2698(8)	-1101(6)	7704(5)	62
H(321)	-2418(7)	265(7)	7898(4)	66
H(322)	-1596(7)	-1233(7)	8087(4)	66
H(323)	-1029(7)	-263(7)	7264(4)	66
H(331)	-2564(7)	2752(9)	9276(5)	72
H(332)	-3184(7)	1353(9)	9129(5)	72
H(333)	-2698(7)	2506(9)	8378(5)	72
H(341)	-773(9)	3047(8)	9858(4)	72
H(342)	392(9)	1996(8)	10250(4)	72
H(343)	937(9)	3187(8)	9534(4)	72

APPENDIX L – X-RAY STRUCTURE ANALYSIS OF [Ti(η-C_5Me_5)(μ-S){PhC($NSiMe_3$)$_2$}]$_2$ (58)

L.1 Crystal data, data collection and refinement

Empirical formula	C_{46} H_{76} N_4 S_2 Si_4 Ti_2
Formula weight	957.4
Crystal description	dark red block
Crystal size	0.50 x 0.40 x 0.40 mm
Temperature	150 K
Crystal system	Monoclinic
Space group	C 2/m
Unit cell dimensions	a = 20.5239(8) Å α = 90 deg.
	b = 14.2637(7) Å β = 104.031(3) deg.
	c = 10.5071(4) Å γ = 90 deg.
Reflections for cell refinement	3427
Range in theta	2.910 to 28.700 deg.
Volume, Z	2984.2 Å^3, 2
Density (calculated)	1.07 Mg/m^3
Absorption coefficient	0.44 mm^{-1}
F(000)	1024
Diffractometer type	Nonius KappaCCD
Wavelength	0.71073 A
Scan type	2 \q/ \w
Theta range for data collection	3.19 to 28.69 deg.
Index ranges	-27<=h<=27, -19<=k<=15, -13<=l<=14
Reflections collected	5706
Independent reflections	3971 [R(merge) = 0.04]
Observed reflections	2459 [I>3sigma(I)]
Absorption correction	Multi-scan
Tmin, Tmax	0.670, 0.670
Structure solution	by direct methods and
	Fourier difference maps
Hydrogen atom location	geometric
Hydrogen atom treatment	riding model
Refinement method	Full-matrix least-squares on F
Weighting scheme	Chebychev

Data / restraints / parameters	2459 / 0 / 154
Goodness-of-fit on	F 0.9111
Final R indices [I>3sigma(I)]	R1 = 0.0744, Rw = 0.0900
Extinction coefficient	none required
Final maximum delta/sigma	0.0058
Largest diff. peak and hole	0.72 and -0.59 e. $Å^{-3}$

Comments:

The choice of spacegroup as C 2/m over the possible non-centrosymmetric alternatives is favoured by examination of the normalised structure factors with the expected values, and by the satisfactory refinement in C 2/m

L.2 Bond lengths (Å) and angles (°)

Ti(1)...Ti(1C)	3.262(2)	$Cp_{(cent)}$-Ti(1)	2.101
Ti(1)-S(1)	2.259(1)	Ti(1)-S(1B)	2.259(1)
Ti(1)-N(1)	2.193(3)	Ti(1)-N(1B)	2.193(3)
Ti(1)-C(11)	2.392(4)	Ti(1)-C(12)	2.424(3)
Ti(1)-C(12B)	2.424(3)	Ti(1)-C(13)	2.435(4)
Ti(1)-C(13B)	2.435(4)	N(1)-Si(1)	1.757(3)
N(1)-C(1)	1.325(4)	Si(1)-C(8)	1.861(4)
Si(1)-C(9)	1.872(4)	Si(1)-C(10)	1.870(4)
C(1)-C(2)	1.505(6)	C(2)-C(3)	1.393(7)
C(2)-C(7)	1.390(8)	C(3)-C(4)	1.393(7)
C(4)-C(5)	1.38(1)	C(5)-C(6)	1.368(9)
C(6)-C(7)	1.385(8)	C(11)-C(12)	1.420(5)
C(11)-C(12B)	1.420(5)	C(11)-C(14)	1.495(7)
C(12)-C(13)	1.422(5)	C(12)-C(15)	1.492(5)
C(13)-C(13B)	1.422(7)	C(13)-C(16)	1.496(5)
.$Cp_{(cent)}$-Ti(1)-S(1)	113.6	$Cp_{(cent)}$-Ti(1)-S(1B)	113.6
.$Cp_{(cent)}$-Ti(1)-N(1)	111.2	$Cp_{(cent)}$-Ti(1)-N(1B)	111.2
Ti(1C)...Ti(1)-S(1)	43.78(3)	Ti(1C)...Ti(1)-S(1B)	43.78(3)
S(1)-Ti(1)-S(1B)	87.56(7)	Ti(1C)...Ti(1)-N(1)	116.59(9)
S(1)-Ti(1)-N(1)	132.67(9)	S(1B)-Ti(1)-N(1)	88.21(8)
Ti(1C)...Ti(1)-N(1B)	116.59(9)	S(1)-Ti(1)-N(1B)	88.21(8)

S(1B)-Ti(1)-N(1B)	132.67(9)	N(1)-Ti(1)-N(1B)	61.6(2)
Ti(1C)...Ti(1)-C(11)	93.3(1)	S(1)-Ti(1)-C(11)	92.40(9)
S(1B)-Ti(1)-C(11)	92.40(9)	N(1)-Ti(1)-C(11)	134.9(1)
N(1B)-Ti(1)-C(11)	134.9(1)	Ti(1C)...Ti(1)-C(12)	110.48(9)
S(1)-Ti(1)-C(12)	85.63(9)	S(1B)-Ti(1)-C(12)	125.55(9)
N(1)-Ti(1)-C(12)	132.7(1)	N(1B)-Ti(1)-C(12)	101.0(1)
Ti(1C)...Ti(1)-C(12B)	110.48(9)	S(1)-Ti(1)-C(12B)	125.55(9)
S(1B)-Ti(1)-C(12B)	85.63(9)	N(1)-Ti(1)-C(12B)	101.0(1)
N(1B)-Ti(1)-C(12B)	132.7(1)	Ti(1C) -Ti(1)-C(13)	144.51(9)
S(1)-Ti(1)-C(13)	112.70(9)	S(1B) -Ti(1)-C(13)	142.18(9)
N(1)-Ti(1)-C(13)	98.8(1)	N(1B) -Ti(1)-C(13)	81.6(1)
Ti(1C) ...Ti(1)-C(13B)	144.51(9)	S(1)-Ti(1)-C(13B)	142.18(9)
S(1B) -Ti(1)-C(13B)	112.70(9)	N(1)-Ti(1)-C(13B)	81.6(1)
N(1B) -Ti(1)-C(13B)	98.8(1)	C(11)-Ti(1)-C(12)	34.3(1)
C(11)-Ti(1)-C(12B)	34.3(1)	C(12)-Ti(1)-C(12B)	56.7(2)
C(11)-Ti(1)-C(13)	56.8(1)	C(12)-Ti(1)-C(13)	34.0(1)
C(12B) -Ti(1)-C(13)	56.6(1)	C(11)-Ti(1)-C(13B)	56.8(1)
C(12)-Ti(1)-C(13B)	56.6(1)	C(12B)-Ti(1)-C(13B)	34.0(1)
C(13)-Ti(1)-C(13B)	33.9(2)	Ti(1)-S(1)-Ti(1C)	92.44(7)
Ti(1)-N(1)-Si(1)	141.1(2)	Ti(1)-N(1)-C(1)	91.1(2)
Si(1)-N(1)-C(1)	127.1(2)	N(1)-Si(1)-C(8)	109.9(2)
N(1)-Si(1)-C(9)	112.7(2)	C(8)-Si(1)-C(9)	106.7(2)
N(1)-Si(1)-C(10)	113.2(2)	C(8)-Si(1)-C(10)	106.3(2)
C(9)-Si(1)-C(10)	107.7(2)	N(1)-C(1)-N(1B)	116.1(4)
N(1)-C(1)-C(2)	122.0(2)	N(1B) -C(1)-C(2)	122.0(2)
C(1)-C(2)-C(3)	121.4(4)	C(1)-C(2)-C(7)	120.0(4)
C(3)-C(2)-C(7)	118.7(4)	C(2)-C(3)-C(4)	120.4(5)
C(3)-C(4)-C(5)	120.0(5)	C(4)-C(5)-C(6)	119.8(5)
C(5)-C(6)-C(7)	121.0(5)	C(2)-C(7)-C(6)	120.1(5)
Ti(1)-C(11)-C(12)	74.1(2)	Ti(1)-C(11)-C(12B)	74.1(2)
C(12)-C(11)-C(12B)	108.5(4)	Ti(1)-C(11)-C(14)	122.7(3)
C(12)-C(11)-C(14)	125.6(2)	C(12B) -C(11)-C(14)	125.6(2)
Ti(1)-C(12)-C(11)	71.6(2)	Ti(1)-C(12)-C(13)	73.4(2)
C(11)-C(12)-C(13)	107.7(3)	Ti(1)-C(12)-C(15)	126.4(3)
C(11)-C(12)-C(15)	124.3(3)	C(13)-C(12)-C(15)	127.6(4)
Ti(1)-C(13)-C(12)	72.6(2)	Ti(1)-C(13)-C(13B)	73.03(9)
C(12)-C(13)-C(13B)	108.1(2)	Ti(1)-C(13)-C(16)	127.4(2)
C(12)-C(13)-C(16)	127.3(3)	C(13B) -C(13)-C(16)	124.0(2)

i) Symmetry transformations used to generate equivalent atoms carrying the suffix 'B': #2 x,-y,z; carrying the suffix 'C': #1 -x+1,-y,-z.

ii) $Cp_{(cent)}$ refers to the computed C_5Me_5 ring carbon centroid

L.3 Atomic coordinates ($\times 10^4$) and isotropic or equivalent isotropic displacement parameters ($Å^2 \times 10^3$). $U_{(eq)}$ is defined as one third of the trace of the orthogonalised U_{ij} tensor

	x	y	z	$U_{(eq)}$
Ti(1)	5815(1)	0	229(1)	28
S(1)	5000	-1096(1)	0	44
N(1)	6387(2)	788(2)	1928(3)	33
Si(1)	6505(1)	1935(1)	2550(1)	37
C(1)	6596(2)	0	2563(4)	30
C(2)	7044(3)	0	3929(4)	30
C(3)	6779(3)	0(1)	5030(4)	35
C(4)	7203(3)	0(1)	6285(5)	45
C(5)	7889(3)	0(1)	6444(5)	45
C(6)	8152(3)	0(1)	5366(6)	46
C(7)	7738(3)	0(1)	4110(5)	41
C(8)	6153(3)	2792(3)	1227(4)	56
C(9)	6070(2)	2150(3)	3896(4)	48
C(10)	7410(2)	2252(3)	3188(4)	49
C(11)	5763(3)	0	-2070(4)	34
C(12)	6139(2)	-808(3)	-1552(3)	34
C(13)	6744(2)	-498(3)	-679(3)	34
C(14)	5114(3)	0(1)	-3093(5)	43
C(15)	5954(2)	-1785(3)	-2005(4)	45
C(16)	7334(2)	-1084(3)	-24(4)	44

L.4 Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic 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)	42(1)	25(1)	14(1)	0	2(1)	0
S(1)	40(1)	48(1)	41(1)	0	8(1)	0
N(1)	44(2)	31(1)	19(1)	-1(1)	-3(1)	2(1)
Si(1)	49(1)	29(1)	29(1)	-5(1)	0(1)	-3(1)
C(1)	32(2)	37(3)	20(2)	0	4(2)	0
C(2)	40(2)	29(2)	19(2)	0	3(2)	0
C(3)	48(3)	32(2)	23(2)	0	4(2)	0
C(4)	72(4)	40(3)	19(2)	0	6(2)	0
C(5)	56(3)	39(3)	29(2)	0	-12(2)	0
C(6)	39(3)	46(3)	44(3)	0	-7(2)	0
C(7)	39(3)	48(3)	34(2)	0	5(2)	0
C(8)	83(3)	29(2)	46(2)	0(2)	-5(2)	0(2)
C(9)	53(2)	42(2)	45(2)	-15(2)	3(2)	1(2)
C(10)	53(2)	41(2)	48(2)	-10(2)	5(2)	-7(2)
C(11)	40(3)	44(3)	17(2)	0	5(2)	0
C(12)	44(2)	38(2)	21(1)	-5(1)	7(1)	0(2)
C(13)	40(2)	38(2)	23(1)	-1(1)	5(1)	4(2)
C(14)	45(3)	61(4)	20(2)	0	4(2)	0
C(15)	62(2)	36(2)	35(2)	-14(2)	7(2)	0(2)
C(16)	40(2)	50(2)	42(2)	-1(2)	7(2)	9(2)

L.5 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$)

	x	y	z	$U_{(eq)}$
H(31)	6301(3)	0(1)	4916(4)	42
H(41)	7017(3)	0(1)	7040(5)	52
H(51)	8177(3)	0(1)	7312(5)	53
H(61)	8631(3)	0(1)	5483(6)	59
H(71)	7924(3)	0(1)	3356(5)	52
H(81)	6218(3)	3419(3)	1568(4)	61
H(82)	6372(3)	2725(3)	522(4)	61
H(83)	5682(3)	2672(3)	907(4)	61
H(91)	6149(2)	2784(3)	4201(4)	64
H(92)	6241(2)	1726(3)	4607(4)	64
H(93)	5596(2)	2050(3)	3569(4)	64
H(101)	7447(2)	2883(3)	3515(4)	63
H(102)	7637(2)	2200(3)	2493(4)	63
H(103)	7611(2)	1830(3)	3884(4)	63
H(141)	4963(3)	-634(1)	-3277(5)	49
H(142)	5177(3)	-288(1)	-3881(5)	49
H(143)	4785(3)	-346(1)	-2776(5)	49
H(151)	5515(2)	-1791(3)	-2591(4)	58
H(152)	6276(2)	-2026(3)	-2450(4)	58
H(153)	5953(2)	-2169(3)	-1255(4)	58
H(161)	7673(2)	-692(3)	509(4)	59
H(162)	7514(2)	-1391(3)	-677(4)	59
H(163)	7195(2)	-1547(3)	519(4)	59

APPENDIX M – X-RAY STRUCTURE ANALYSIS OF [Ti(η-C_5H_4Me)(μ-S){PhC($NSiMe_3$)$_2$}]$_2$ (60)

M.1 Crystal data, data collection and refinement

Empirical formula	C_{38} H_{60} N_4 S_2 Si_4 Ti_2
Formula weight	845.18
Crystal description	Orange block
Crystal size	0.40 x 0.35 x 0.30 mm
Temperature	175 K
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 9.416(1) Å α = 93.934(6) deg.
	b = 10.684(2) Å β = 94.552(8) deg.
	c = 12.409(2) Å γ = 115.495(8) deg.
Reflections for cell refinement	7160
Range in theta	0 to 27 deg.
Volume, Z	1115.9 Å^3, 1
Density (calculated)	1.26 Mg/m^3
Absorption coefficient	0.58 mm^{-1}
F(000)	448
Diffractometer type	Enraf-nonius DIP2000
Wavelength	0.71069 A
Scan type	\w
Theta range for data collection	2.76 to 26.29 deg.
Index ranges	0<=h<=11, -13<=k<=11, -15<=l<=15
Reflections collected	7160
Independent reflections	2555 [R(merge) = 0.035]
Observed reflections	2379 [I>3sigma(I)]
Absorption correction	Multi-scan
Tmin, Tmax	0.813, 0.838
Decay correction	Not measured
Structure solution	by direct methods
	and Fourier difference maps
Hydrogen atom location	Geometric
Hydrogen atom treatment	Riding model
Refinement method	Full-matrix least-squares on F

Weighting scheme	Chebychev polynomial
Data / restraints / parameters	2379 / 0 / 226
Goodness-of-fit on F	1.0971
Final R indices [I>3sigma(I)]	R1 = 0.0636, Rw = 0.0534
Extinction coefficient	None
Final maximum delta/sigma	0.0290
Largest diff. peak and hole	0.30 and -0.28 e. $Å^{-3}$

M.2 Bond lengths (Å) and angles (°)

Ti(1)-N(1)	2.135(3)	Ti(1)-N(2)	2.197(3)
Ti(1)-S(1)	2.304(1)	Ti(1)-S(1B)	2.363(1)
$Cp_{(cent)}$-Ti(1)	2.061	Ti(1)-C(15)	2.388(4)
Ti(1)-C(16)	2.377(4)	Ti(1)-C(17)	2.371(4)
Ti(1)-C(18)	2.383(4)	Ti(1)-C(19)	2.394(4)
Si(1)-N(1)	1.748(3)	Si(1)-C(8)	1.873(4)
Si(1)-C(9)	1.861(6)	Si(1)-C(10)	1.846(5)
Si(2)-N(2)	1.746(3)	Si(2)-C(11)	1.838(6)
Si(2)-C(12)	1.872(4)	Si(2)-C(13)	1.863(4)
N(1)-C(1)	1.327(4)	N(2)-C(1)	1.323(4)
C(1)-C(2)	1.506(4)	C(2)-C(3)	1.394(5)
C(2)-C(7)	1.367(6)	C(3)-C(4)	1.396(5)
C(4)-C(5)	1.354(7)	C(5)-C(6)	1.381(6)
C(6)-C(7)	1.406(5)	C(14)-C(15)	1.496(5)
C(15)-C(16)	1.399(6)	C(15)-C(19)	1.410(6)
C(16)-C(17)	1.410(5)	C(17)-C(18)	1.403(7)
C(18)-C(19)	1.400(5)		

$Cp_{(cent)}$-Ti(1)-S(1)	119.3	$Cp_{(cent)}$-Ti-(S1B)	110.1
$Cp_{(cent)}$-Ti(1)-N(1)	112.5	$Cp_{(cent)}$-Ti(1)-(N2)	108.2
N(1)-Ti(1)-N(2)	62.1(1)	N(1)-Ti(1)-S(1)	125.6(1)
N(2)-Ti(1)-S(1)	86.39(8)	N(1)-Ti(1)-S(1B)	88.89(8)
N(2)-Ti(1)-S(1B)	138.63(9)	S(1)-Ti(1)-S(1B)	88.27(4)
N(1)-Ti(1)-C(15)	134.5(1)	N(2)-Ti(1)-C(15)	133.1(1)
S(1)-Ti(1)-C(15)	99.7(1)	S(1B)-Ti(1)-C(15)	88.20(9)
N(1)-Ti(1)-C(16)	135.6(1)	N(2)-Ti(1)-C(16)	100.2(1)
S(1)-Ti(1)-C(16)	90.2(1)	S(1B) -Ti(1)-C(16)	120.9(1)

C(15)-Ti(1)-C(16)	34.2(1)	N(1)-Ti(1)-C(17)	101.3(1)
N(2)-Ti(1)-C(17)	78.3(1)	S(1)-Ti(1)-C(17)	115.0(1)
S(1B)-Ti(1)-C(17)	139.6(1)	C(15)-Ti(1)-C(17)	56.9(1)
N(1)-Ti(1)-C(18)	82.3(1)	N(2)-Ti(1)-C(18)	94.1(1)
S(1)-Ti(1)-C(18)	147.1(1)	S(1B)-Ti(1)-C(18)	111.5(1)
C(15)-Ti(1)-C(18)	57.1(1)	N(1)-Ti(1)-C(19)	100.4(1)
N(2)-Ti(1)-C(19)	128.2(1)	S(1)-Ti(1)-C(19)	133.1(1)
S(1B)-Ti(1)-C(19)	83.2(1)	C(15)-Ti(1)-C(19)	34.3(1)
C(16)-Ti(1)-C(17)	34.6(1)	C(16)-Ti(1)-C(18)	57.3(2)
C(17)-Ti(1)-C(18)	34.3(2)	C(16)-Ti(1)-C(19)	56.9(2)
C(17)-Ti(1)-C(19)	56.7(2)	C(18)-Ti(1)-C(19)	34.1(1)
N(1)-Si(1)-C(8)	113.1(2)	N(1)-Si(1)-C(9)	110.4(2)
C(8)-Si(1)-C(9)	108.9(3)	N(1)-Si(1)-C(10)	108.5(2)
C(8)-Si(1)-C(10)	106.5(3)	C(9)-Si(1)-C(10)	109.3(2)
N(2)-Si(2)-C(11)	110.9(2)	N(2)-Si(2)-C(12)	112.2(2)
C(11)-Si(2)-C(12)	109.9(3)	N(2)-Si(2)-C(13)	108.5(2)
C(11)-Si(2)-C(13)	109.6(2)	C(12)-Si(2)-C(13)	105.4(2)
Ti(1)-N(1)-Si(1)	136.1(1)	Ti(1)-N(1)-C(1)	92.6(2)
Si(1)-N(1)-C(1)	131.3(2)	Ti(1)-N(2)-Si(2)	138.2(1)
Ti(1)-N(2)-C(1)	90.0(2)	Si(2)-N(2)-C(1)	131.0(2)
Ti(1)-S(1)-Ti(1B)	91.73(4)	N(1)-C(1)-N(2)	115.0(3)
N(1)-C(1)-C(2)	121.9(3)	N(2)-C(1)-C(2)	123.1(3)
C(1)-C(2)-C(3)	119.5(4)	C(1)-C(2)-C(7)	121.2(3)
C(3)-C(2)-C(7)	119.2(3)	C(2)-C(3)-C(4)	120.0(4)
C(3)-C(4)-C(5)	120.2(4)	C(4)-C(5)-C(6)	120.8(4)
C(5)-C(6)-C(7)	119.1(4)	C(2)-C(7)-C(6)	120.7(4)
Ti(1)-C(15)-C(14)	122.5(3)	Ti(1)-C(15)-C(16)	72.5(2)
C(14)-C(15)-C(16)	126.2(4)	Ti(1)-C(15)-C(19)	73.1(2)
C(14)-C(15)-C(19)	125.8(4)	C(16)-C(15)-C(19)	108.0(3)
Ti(1)-C(16)-C(15)	73.3(2)	Ti(1)-C(16)-C(17)	72.5(2)
C(15)-C(16)-C(17)	107.7(4)	Ti(1)-C(17)-C(16)	73.0(2)
Ti(1)-C(17)-C(18)	73.3(2)	C(16)-C(17)-C(18)	108.4(3)
Ti(1)-C(18)-C(17)	72.4(3)	Ti(1)-C(18)-C(19)	73.4(2)
C(17)-C(18)-C(19)	107.6(3)	Ti(1)-C(19)-C(15)	72.6(2)
Ti(1)-C(19)-C(18)	72.5(2)	C(15)-C(19)-C(18)	108.3(4)

i) Symmetry transformation used to generate equivalent atoms bearing the suffix 'B': -x,-y+1,-z

ii) $Cp_{(cent)}$ refers to the computed C_5H_4Me ring carbon centroid

M.3 Atomic coordinates ($\times 10^4$) and isotropic or equivalent isotropic displacement parameters ($Å^2 \times 10^3$). $U_{(eq)}$ is defined as one third of the trace of the orthogonalised U_{ij} tensor

	x	y	z	$U_{(eq)}$
Ti(1)	-508(1)	4914(1)	1266(1)	32
Si(1)	-2188(1)	1255(1)	1616(1)	49
Si(2)	2994(1)	6252(1)	3331(1)	39
N(1)	-811(4)	3009(3)	1881(2)	36
N(2)	1212(4)	5016(3)	2613(2)	35
S(1)	1647(1)	6352(1)	466(1)	39
C(1)	510(4)	3639(3)	2569(2)	34
C(2)	1181(4)	2829(3)	3211(3)	36
C(3)	902(5)	2671(4)	4291(3)	45
C(4)	1442(6)	1859(4)	4877(3)	49
C(5)	2238(6)	1220(4)	4399(3)	53
C(6)	2522(6)	1355(4)	3328(4)	55
C(7)	1975(5)	2170(4)	2735(3)	45
C(8)	-2287(7)	250(6)	2810(5)	98
C(9)	-1719(7)	391(5)	435(5)	73
C(10)	-4179(5)	1171(5)	1300(4)	57
C(11)	4696(6)	6133(5)	2787(5)	73
C(12)	3094(6)	6085(5)	4824(3)	70
C(13)	3114(6)	8023(4)	3212(4)	58
C(14)	-2424(6)	6581(4)	-48(3)	55
C(15)	-2148(5)	6089(4)	1014(3)	43
C(16)	-952(6)	6863(4)	1865(3)	48
C(17)	-1165(6)	6032(5)	2729(3)	54
C(18)	-2486(6)	4746(5)	2409(3)	51
C(19)	-3099(5)	4784(5)	1352(3)	48

M.4 Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic 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)	39(1)	43(1)	24(1)	12(1)	7(1)	26(1)
Si(1)	45(1)	43(1)	49(1)	18(1)	-2(1)	10(1)
Si(2)	43(1)	38(1)	34(1)	9(1)	3(1)	17(1)
N(1)	38(2)	42(1)	32(1)	15(1)	5(1)	19(1)
N(2)	39(2)	40(1)	31(1)	12(1)	5(1)	21(1)
S(1)	44(1)	45(1)	27(1)	11(1)	8(1)	18(1)
C(1)	39(2)	40(2)	26(1)	14(1)	8(1)	19(1)
C(2)	37(2)	35(2)	35(1)	13(1)	1(1)	15(1)
C(3)	58(2)	53(2)	32(2)	16(1)	8(2)	29(2)
C(4)	65(3)	54(2)	36(2)	19(2)	6(2)	31(2)
C(5)	62(3)	50(2)	54(2)	23(2)	2(2)	29(2)
C(6)	67(3)	59(2)	62(2)	26(2)	19(2)	42(2)
C(7)	59(3)	51(2)	40(2)	21(1)	19(2)	33(2)
C(8)	74(4)	76(3)	105(4)	60(3)	-23(3)	-6(3)
C(9)	65(3)	46(2)	101(4)	-10(2)	-5(3)	22(2)
C(10)	45(2)	61(2)	52(2)	9(2)	4(2)	11(2)
C(11)	51(3)	63(3)	98(4)	-6(3)	6(3)	20(2)
C(12)	73(3)	74(3)	37(2)	12(2)	-8(2)	9(3)
C(13)	74(3)	44(2)	56(2)	2(2)	-1(2)	28(2)
C(14)	70(3)	58(2)	50(2)	14(2)	1(2)	39(2)
C(15)	49(2)	56(2)	42(2)	9(1)	10(2)	39(2)
C(16)	57(3)	61(2)	43(2)	5(2)	9(2)	43(2)
C(17)	69(3)	88(3)	30(2)	7(2)	12(2)	55(3)
C(18)	57(3)	72(3)	42(2)	23(2)	25(2)	38(2)
C(19)	42(2)	67(2)	47(2)	10(2)	11(2)	35(2)

M.5 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$)

	x	y	z	$U_{(eq)}$
H(31)	318(5)	3108(4)	4625(3)	57
H(41)	1278(6)	1782(4)	5628(3)	63
H(51)	2577(6)	646(4)	4808(3)	71
H(61)	3103(6)	917(4)	2993(4)	78
H(71)	2137(5)	2261(4)	1985(3)	63
H(81)	-3055(7)	-702(6)	2615(5)	114
H(82)	-2593(7)	655(6)	3410(5)	114
H(83)	-1267(7)	281(6)	3015(5)	114
H(91)	-2482(7)	-571(5)	300(5)	93
H(92)	-1753(7)	850(5)	-198(5)	93
H(93)	-678(7)	446(5)	596(5)	93
H(101)	-4954(5)	215(5)	1150(4)	70
H(102)	-4421(5)	1610(5)	1913(4)	70
H(103)	-4193(5)	1651(5)	676(4)	70
H(111)	5660(6)	6824(5)	3193(5)	88
H(112)	4689(6)	6289(5)	2034(5)	88
H(113)	4631(6)	5221(5)	2855(5)	88
H(121)	4087(6)	6783(5)	5189(3)	75
H(122)	2239(6)	6206(5)	5113(3)	75
H(123)	3004(6)	5174(5)	4934(3)	75
H(131)	4089(6)	8717(4)	3603(4)	71
H(132)	2236(6)	8090(4)	3510(4)	71
H(133)	3076(6)	8173(4)	2458(4)	71
H(141)	-3328(6)	5851(4)	-482(3)	75
H(142)	-2614(6)	7389(4)	79(3)	75
H(143)	-1506(6)	6815(4)	-425(3)	75
H(161)	-131(6)	7790(4)	1857(3)	76
H(171)	-523(6)	6285(5)	3421(3)	77
H(181)	-2910(6)	3979(5)	2834(3)	70
H(191)	-4005(5)	4043(5)	927(3)	71