

Synthesis, Structure and Catalytic Activity of an Air-stable Titanium Triflate Supported by an Amine Tris(phenolate) Ligand

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1 Synthesis and Spectroscopic Characterisation of 2a and 3

1.1 General Considerations

All reactions and manipulations were carried out under an atmosphere of dry argon or dinitrogen gas using standard Schlenk and glove-box techniques. Tris-(2-hydroxy-3,5-dimethylbenzyl)amine **1a** was prepared from commercially available starting materials according to literature procedures.¹ For the preparation and characterisation of titanium complexes, and in subsequent catalytic studies, all reactions and manipulations were performed under an inert atmosphere of argon or dinitrogen using standard Schlenk or glove-box techniques and all solvents were freshly distilled over suitable drying agents and degassed prior to use. ¹H and ¹³C NMR spectra were recorded on either a Varian 400 MHz spectrometer or a Bruker 300 MHz spectrometer.

1.2 Synthesis of titanium tris-(2-oxy-3,5-dimethylbenzyl)amine isopropoxide, **2a**.

Ti(OiPr)₄ (3.1ml, 10mmol) was added dropwise by syringe, to a stirred suspension of **1a** (4.2g, 10mmol) in toluene (50ml) at 0 °C. The reaction mixture was allowed to warm to

1) M. Kol, M. Shamis, I. Goldbreg, Z. Goldschmidt, S. Alfi and E. Hayut-Salant, *Inorg. Chem. Commun.*, 2001, **4**, 177.

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room temperature, with stirring, resulting in a yellow solution. Removal of solvent under reduced pressure resulted in the precipitation of a yellow residue, which was re-dissolved in a minimum of fresh hexane (20ml), with heating. The solution was filtered hot to remove insoluble residues. A yellow crystalline solid was obtained on standing for 3hrs at 0°C. The solid was collected by filtration, washed with cold hexane, and dried in vacuo. Yield: 4.6g, 88%. Anal. Calcd for C₃₀H₃₇N₁O₄Ti₁: C, 68.8; H, 7.1; N, 2.7; Found: C, 68.5; H, 7.1; N, 2.6; ¹H NMR (400 MHz, 23°C), CDCl₃ (ppm): δ 1.45 (d, *J*=6Hz, 6H, OCH(CH₃)₂), 2.14 (s, 9H, L(Me/Me)), 2.17 (s, 9H, L(Me/Me)), 2.75 (d, 3H, CH₂(AB system), *J*=10.6Hz), 3.9 (d, 3H, CH₂(BA system), *J*=10.6Hz), 5.13 (hept, *J*=6Hz, 1H, OCH(CH₃)₂), 6.62 (s, 3H, arom.), 6.78 (s, 3H, arom.); ¹³C{¹H} NMR (100 MHz) δ 16.4 (s, CH₃), 20.7 (s, CH₃), 25.7 (s, CH(CH₃)₂), 58.6 (s, CH₂), 79.8 (s, CH(CH₃)₂), 123.5 (C, Aromatic), 124.1 (C, Aromatic), 127.3 (CH, Aromatic), 129.1 (C, Aromatic), 130.5 (CH, Aromatic), 159.4 (ipso-phenyl O-C, aromatic); MS(FAB): (m/z) 523.5 (M⁺).

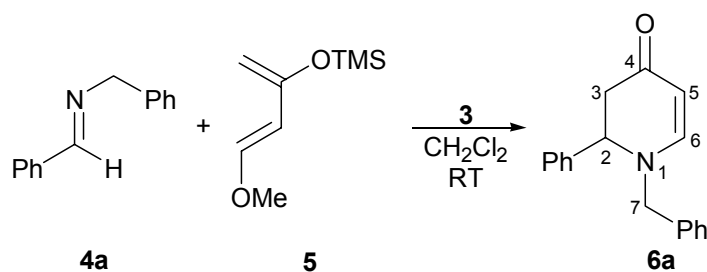
1.3 Synthesis of titanium tris-(2-oxy-3,5-dimethylbenzyl)amine triflate, **3**

TMSOTf (1.8ml, 2.22g, 10mmol) was added dropwise by syringe, to a stirred toluene solution (50ml) of **2a** (5.23g, 10mmol). The reaction mixture was stirred at room temperature for 3hrs stirring, resulting in a deep red solution. Removal of solvent under reduced pressure resulted in the precipitation of a red/brown residue, which was re-dissolved in a minimum of fresh toluene (20ml), with heating. The solution was filtered hot to remove insoluble residues. Deep red crystals of **3**, were obtained on standing at 5°C, overnight. The solid was collected by filtration, washed with cold hexane, and dried in vacuo. Yield: 6.05g, 98.6%. Anal. Calcd for C₂₈H₃₀F₃N₁O₆S₁Ti₁: C, 54.8; H, 4.9; N,

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2.3: Found: C, 54.8; H, 5.03; N, 2.26; ^1H NMR (400 MHz, 23°C), CD_2Cl_2 (ppm): δ 2.23 (s, 9H, L(Me/Me)), 2.27 (s, 9H, L(Me/Me)), 3.7 (br s, 6H, CH₂), 6.86 (s, 3H, arom.), 6.95 (s, 3H, arom.); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) δ 16.1 (s, CH₃), 21.1 (s, CH₃), 59.3 (s, CH₂), 123.4 (C, Aromatic), 124.6 (C, Aromatic), 128.9 (CH, Aromatic), 132.1 (CH, Aromatic), 133.1 (C, Aromatic), 160.9 (ipso-phenyl O-C, aromatic) ; ^{19}F NMR (376MHz) δ -78.15 (s, 3F, CF₃); MS(FAB): (m/z) 613.5 (M^+).

1.4 Representative aza-Diels-Alder reaction between *N*-benzyl-phenylimine **4a** and Danishefsky's Diene **5** catalysed by triflate **3**:



Experimental Procedure

Catalyst **3** (0.023 g, 0.013 mmol, 10 mol%) was added to a solution of *N*-benzyl-phenylimine, **4a**, (0.08 mL, 0.42 mmol) and Danishefsky's diene, **5**, (0.25 mL, 1.26 mmol) in CH_2Cl_2 (1 mL) at room temperature. The mixture was then stirred for 45 minutes before addition of silica (0.50 g) and removal of solvent *in vacuo*. The crude reaction mixture was purified *via* column chromatography (SiO_2 , 60:40 EtOAc:PE) to afford *N*-benzyl-2,3-dihydro-2-phenyl-1H-pyridin-4-one, **6a**, (0.0804 g, 73%) as a viscous yellow oil which whose spectroscopic data were identical to those reported previously²: ^1H NMR (300MHz, CDCl_3) 2.60 (1H, dd, $J=16.6\text{Hz}$, 7.9Hz , C(3)-Ha), 2.77

2) K. Hattori, H. Yamamoto, *Tetrahedron*, **1993**, *49*, 1749.

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(1H, dd, $J=16.6\text{Hz}$, 7.9Hz , C(3)-Hb), 3.95 (1H, AB system, $J=15.1\text{Hz}$, N-CHaHbPh), 4.17 (1H, BA system, $J=15.1\text{Hz}$, N-CHaHbPh), 4.42 (1H, t, $J=7.5\text{Hz}$, C(2)-H), 5.01 (1H, d, $J=7.5\text{Hz}$, C(5)-H), 7.06 (d, 1H, $J=7.5\text{Hz}$, C(6)-H), 7.15-7.31 (10H, m, Ar-H); ^{13}C NMR (75MHz, CDCl_3) 44.1 (C(2)-H), 57.7 (N-CH₂-Ph), 61.1 (C(3)-H₂), 99.1 (C(6)-H), 127.5 (ArC-H), 128.6 (ArC-H), 128.7 (ArC-H), 129.3 (ArC-H), 129.4 (ArC-H), 136.3 (ArC), 138.9 (ArC), 154.6 (C5-H), 190.8 (C4).

2 X-ray data for 2a & 3

Data for **2a** and **3** were collected on a Nonius Kappa CCD diffractometer. Anisotropic atomic displacement parameters were used throughout for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions and refined using a riding model.

The asymmetric unit of both **2a** and **3** consists of a two molecules of complex.

In the case of **3** it was evident that some solvent had crystallized in the lattice, lying close to the centre of inversion and as such was disordered over two sites. This toluene molecule was modelled by refining each unique carbon atom with occupancy of 50% in anisotropic displacement parameters. One unique orientation was located for the toluene methyl group and its hydrogen atoms, which was also modelled at 50% occupancy.

For both **2a** and **3** absorption corrections were not found to be necessary.