Electronic Supporting Information for Chemical Communications article by Perera and Gillan, "High-temperature stabilized anatase TiO_2 from an aluminum-doped $TiCl_3$ precursor".

Detailed Experimental Procedures

The synthesis of β-$TiCl_3$ was performed similar to literature procedures (F. Auriemma, V. Busico, P. Corradini and M. Trifuoggi, *Eur. Polym. J.*, 1992, **28**, 513). All solutions were degassed with nitrogen and manipulations were performed using standard air-free Schlenk techniques. A dropping funnel was loaded with 42 ml heptane and 32 ml (64 mmol) of 2 M Me_3Al (Aldrich in heptane) and this solution was added slowly over a 30 min period to a 50 °C solution consisting of 80 ml distilled heptane and 7.4 ml (67.4 mmol) of $TiCl_4$ (Aldrich, 99.9%). The mixture was stirred at 50 °C for 2 days, producing a brown precipitate that was then separated from the solution by filtration. The brown product was washed with hot heptane (2x) and then hexane. It was then dried under vacuum at 50 °C for 2 hr then 200 °C for 20 min and transferred to an inert atmosphere glovebox. Selected titanium chlorides were further purified by vacuum sublimation in evacuated sealed glass ampoules placed in a furnace temperature gradient (350 - ~50 °C). In high Al content materials, a white transported material was observed.

Air hydrolysis and oxidation was carried out using glass vials that were covered with Parafilm that had holes poked in it. In each experiment, approximately 100 mg of the $TiCl_3$ precursor was loaded into a glass vial in an inert atmosphere glovebox and then placed in the air overnight (~15 hr) to allow room-temperature hydrolysis and oxidation to slowly occur. The $TiCl_3$ precursors were well-behaved upon air exposure and gained weight and lost most of their color. Room temperature and relative humidity were not regulated, but are typically around 27 °C and 60% RH in the laboratory. Samples were weighed before and after air hydrolysis and portions of the hydrolyzed sample were placed in a ceramic boat. The high-temperature calcination step was performed by placing the loaded boat in a horizontal tube furnace open to the air and quickly heating the sample to 1000 °C in a 30 min period.

X-ray diffraction was performed on ground samples using a Siemens D5000 diffractometer and ICP-AE quantitative analysis of Ti and Al was obtained using a Perkin Elmer Plasma 400 Emission Spectrometer. ICP samples were either dissolved in 1.6 M HCl (metal halide precursors) or in concentrated phosphoric/sulfuric acid mixtures (metal oxide products) followed by dilution in 1.6 M HCl. SEM was performed using a Hitachi S-4000 field emission system that includes an IXRF X-ray microanalysis system.

For methylene blue (MB) photocatalysis studies, 10 mg TiO_2 was stirred with 10 ml of a 0.03 mM aqueous MB solution in closed glass vials in the dark for 20 min and a centrifuged solution was analyzed to obtain a t = 0 MB concentration, then the solution and solids were recombined. The MB solution concentration was determined by its absorption in the 650 - 670 nm range using an HP 8453 diode array spectrometer. UV irradiation was performed in successive 5 min periods using open glass vial that were irradiated from above with a broad spectrum mercury lamp (ACE-Hanovia 450 W high pressure mercury lamp, Pyrex water jacket). After each irradiation period, the solution was centrifuged and spectroscopically analyzed as described above.

Table S1. Hydrolysis and ICP analytical data

sample[1]	**Precursor Ti : Al wt%[2]**	**Weight (mg) before (after) hydrolysis**	**Weight (mg) before (after) calcination**	**Product TiO_2 Ti:Al wt%[2]**
β-$TiCl_3$(om)	28.8 : 0.532	99 (117)	102 (44)	49.4 : 0.419
α-$TiCl_3$(om, sub)	28.5 : 0.452	99 (122)	117 (50)	46.7 : 0.328
α-$TiCl_3$(com)	28.7 : <0.05[3]	100 (132)	109 (44)	54.9 : 0.00[3]
α-$TiCl_3$(com-25% Al)[4]	22.5 : 4.37	101 (115)	78 (35)	40.7 : 6.37
α-$TiCl_3$(com-25% Al, sub)	29.8 : 0.453	100 (130)	112 (45)	53.7 : 0.431

1) $TiCl_3$ phase (α or β) determined by XRD; om=organometallic synthesis, com=commercial, sub=sublimed. 2) from ICP-AE. 3) Al at baseline detection limits. 4) no crystalline $AlCl_3$ was observed.

Figure S1. SEM images of 1000 °C calcined rutile TiO_2 from (a) $TiCl_3$(com-25% Al) and (b) $TiCl_3$(com-25% Al, sub).