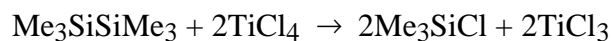


## Chapter Six

# TITANIUM(III) CHLORIDE\*

### 50. AN ACTIVE FORM OF TITANIUM(III) CHLORIDE



Submitted by ANN R. HERMES<sup>†</sup> and GREGORY S. GIROLAMI<sup>†</sup>

Checked by RICHARD A. ANDERSEN<sup>‡</sup>

The reduction of  $\text{TiCl}_4$  with hexamethyldisilane does not afford titanium(II) chloride as reported by Narula and Sharma.<sup>1</sup> Instead, the method affords an active form of titanium(III) chloride that is useful for the preparation of other titanium(III) species.

#### *Procedure*

A 50-mL, three-necked, round bottomed flask is equipped with a dropping funnel, reflux condenser, and a magnetic stir bar. The glassware should be oven dried, assembled, and purged with dry nitrogen gas. The flask is charged with 1.6 mL (2.8 g, 15 mmol) of titanium tetrachloride and the dropping funnel is charged with 3.0 mL (2.15 g, 15 mmol) of hexamethyldisilane. The flask is cooled in an ice bath and the hexamethyldisilane is added dropwise over 5 min. The stirred solution turns orange. The ice bath is removed and the reaction mixture is heated to 115°C for 4 h. The dark brown solid is

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<sup>†</sup> School of Chemical Sciences, The University of Illinois at Urbana-Champaign, Urbana, IL 61801.

<sup>‡</sup> Department of Chemistry, The University of California at Berkeley, Berkeley, CA 94720.

collected by filtration, washed twice with 10 mL of dichloromethane, and dried under vacuum. Yield: 2.0 g (86 %).<sup>§</sup>

*Anal.* Calcd. for  $\text{TiCl}_3$ : Ti, 31.0; Cl, 68.9. Found: Ti, 28.3; Cl, 62.5; C, 2.1.

### *Properties*

The microanalytical data suggest that the product consists of  $\text{TiCl}_3$  contaminated with about 9 wt % of organic impurities (probably containing  $\text{Me}_3\text{Si}$ - or  $\text{Me}_3\text{SiO}$ - groups). The  $\beta$ -form of  $\text{TiCl}_3$  is brown,<sup>2,3</sup> and it is likely that this is the material formed in the synthesis. The product is air sensitive and insoluble in hydrocarbons and chlorocarbons. The identification of the product as titanium(III) chloride rather than titanium(II) chloride is supported by the 1:2.98 Ti:Cl ratio and by its reactivity. The product dissolves readily in hot tetrahydrofuran to generate blue solutions from which  $\text{TiCl}_3(\text{thf})_3$  can be crystallized. By comparison, the purple form of  $\text{TiCl}_3$  dissolves slowly (22 h) in refluxing tetrahydrofuran.<sup>4</sup> In addition, the checker finds that the brown form dissolves in hot acetonitrile to generate blue solutions which after concentration and cooling afford  $\text{TiCl}_3(\text{MeCN})_3$ .<sup>5</sup> [It is notable that  $\text{TiCl}_2(\text{MeCN})_2$  is a black insoluble solid.<sup>6</sup>] The checker also finds that addition of 3 equivalents of  $\text{LiN}(\text{SiMe}_3)_2$  to the brown form of  $\text{TiCl}_3$  gives a blue solution; taking the solution to dryness and crystallizing the resulting solid from pentane affords  $\text{Ti}[\text{N}(\text{SiMe}_3)_2]_3$ .<sup>7</sup> In contrast, this amide complex cannot be made from the purple form of  $\text{TiCl}_3$ .

The reactivity studies show that the reduction of  $\text{TiCl}_4$  with  $\text{Me}_3\text{SiSiMe}_3$  gives a form of  $\text{TiCl}_3$  that is more reactive than the purple form of  $\text{TiCl}_3$  available commercially.

### *References*

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<sup>§</sup> Communication to the editor: Narula subsequently confirmed the above results and has isolated pure (~99%)  $\text{TiCl}_3$  by performing the experiment at reduced pressure followed by repeated (10-15) washings of the product with 5-7 mL portions of warm (33°C)  $\text{CCl}_4/\text{CH}_2\text{Cl}_2$  under anhydrous conditions. *Anal.* Calcd.  $\text{TiCl}_3$ , Ti, 31.06; Cl, 68.93; Found: Ti, 30.67, Cl, 68.63%. A dark brown resinous mass (~0.1 g) was recovered from the filtrate after evaporation of solvent. <sup>1</sup>H NMR spectra identify ( $\text{Me}_3\text{Si}/\text{Me}_3\text{SiO}$ ) groups in the impurity.