Chapter Six

TITANIUM(III) CHLORIDE*

50. AN ACTIVE FORM OF TITANIUM(III) CHLORIDE

\[
\text{Me}_3\text{SiSiMe}_3 + 2\text{TiCl}_4 \rightarrow 2\text{Me}_3\text{SiCl} + 2\text{TiCl}_3
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The reduction of TiCl₄ with hexamethyldisilane does not afford titanium(II) chloride as reported by Narula and Sharma. 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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collected by filtration, washed twice with 10 mL of dichloromethane, and
dried under vacuum. Yield: 2.0 g (86 %).§

Anal. Calcd. for TiCl₃: 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 TiCl₃ con-
taminated with about 9 wt % of organic impurities (probably containing
Me₃Si- or Me₃SiO- groups). The β-form of TiCl₃ is brown²,³ 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 sup-
ported 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
TiCl₃(thf)₃ can be crystallized. By comparison, the purple form of TiCl₃
dissolves slowly (22 h) in refluxing tetrahydrofuran.⁴ In addition, the checker
finds that the brown form dissolves in hot acetonitrile to generate blue
solutions which after concentration and cooling afford TiCl₃(MeCN)₃.⁵ [It is
notable that TiCl₂(MeCN)₂ is a black insoluble solid.⁶] The checker also
finds that addition of 3 equivalents of LiN(SiMe₃)₂ to the brown form of
TiCl₃ gives a blue solution; taking the solution to dryness and crystallizing
the resulting solid from pentane affords Ti[N(SiMe₃)₂]₃.⁷ In contrast, this
amide complex cannot be made from the purple form of TiCl₃.

The reactivity studies show that the reduction of TiCl₄ with Me₃SiSiMe₃
gives a form of TiCl₃ that is more reactive than the purple form of TiCl₃
available commercially.

References


§ Communication to the editor: Narula subsequently confirmed the above results and has
isolated pure (~99%) TiCl₃ 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) CCl₄/CH₃Cl
under anhydrous conditions. Anal. Calcd. TiCl₃, 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. ¹H NMR spectra identify (Me₃Si/Me₃SiO) groups in the impurity.