

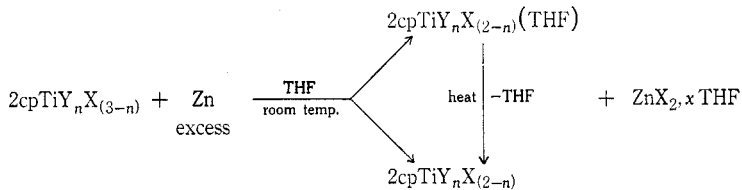
MONOCYCLOPENTADIENYLTITANIUM(III) COMPOUNDS

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[Manuscript received December 15, 1970]

Although organotitanium(III) chemistry has expanded rapidly over the last decade, more than 85% of all compounds reported have contained the bis(cyclopentadienyl)titanium(III) moiety.¹ At present the literature contains only six references to mono(cyclopentadienyl)titanium(III) derivatives.¹⁻⁶ Our objective in this area of organotitanium chemistry has been to synthesize a variety of new compounds of this type and to establish the preferred coordination number, and hence bonding modes.

We report here a versatile general method of synthesis which leads to the isolation of several classes of mono(cyclopentadienyl)titanium(III) derivatives. Unlike previous synthetic methods^{3,5,6} extremely mild reaction conditions are employed, namely the reduction of a suitable organotitanium(IV) compound by means of zinc dust in tetrahydrofuran at room temperature under anaerobic conditions. In some instances the reduction, which is usually complete within 1 hr, leads to the formation of stable, intermediate solvates, as shown in Scheme 1.



Scheme 1.—Products of zinc reduction. For $n = 0$, $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{OMe}, \text{OEt}$, but not OPr^i . For $n = 1$, $\text{X} = \text{Cl}$ or Br , $\text{Y} = \text{OR}$ or SR .

In the case where $n = 0$ and $\text{X} = \text{Cl}, \text{Br}$, or I , blue or green crystalline complexes were isolated which analysed for $\text{cpTiX}_2(\text{THF})$. The chloride complex was thermally unstable and tended to lose the THF ligand in working up the product. As a result, it was necessary to remove excess solvent by pumping under high vacuum at temperatures below 0° . The composition of the sky-blue crystals so obtained varied from

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¹ Coutts, R. S. P., and Wailes, P. C., *Adv. organomet. Chem.*, 1970, **9**, 135.

² Canty, A. J., Coutts, R. S. P., and Wailes, P. C., *Aust. J. Chem.*, 1968, **21**, 807.

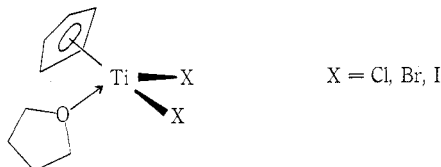
³ Bartlett, P. D., and Seidel, B., *J. Am. chem. Soc.*, 1961, **83**, 581.

⁴ Alyea, E. C., Bradley, D. C., Lappert, M. F., and Sanger, A. R., *Chem. Commun.*, 1969, 1064.

⁵ Van Oven, H. O., and De Liefde Meijer, H. J., *J. organomet. Chem.*, 1969, **19**, 373.

⁶ Ungureanu, C., and Cecal, A., *J. inorg. nucl. Chem.*, 1969, **31**, 1735.

preparation to preparation with respect to the amount of residual solvent. The sample used for characterization analysed for $[\text{cpTiCl}_2(\text{THF})]_2 \cdot \frac{1}{2} \text{THF}$. The magnetic data showed the compounds to be magnetically dilute following the Curie-Weiss law. Ebulliometric molecular weight measurements in THF indicated that the complexes were monomeric. Infrared results confirmed that the cyclopentadienyl ligand was π -bonded and that the ether molecule was complexed to the metal, since the ν_{COC} (asym) band which occurs in THF at 1070 cm^{-1} was shifted to $1040 \pm 5 \text{ cm}^{-1}$ by coordination. The complexes can best be represented by a pseudotetrahedral stereochemistry.



Pyrolysis of these complexes at $120\text{--}150^\circ$ under high vacuum provided the highly coloured compounds cpTiX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). These are insoluble in non-polar solvents but dissolve in coordinating solvents. Complexes are readily formed with ethers, alcohols, amines, and alkyl cyanides as well as the normal chelating agents such as dipyridyl, *o*-phenylenediamine, etc. Some of these complexes will be described in a future publication. The halides showed interesting magnetic behaviour indicated by θ values of *c.* $+20^\circ\text{K}$ using the expression

$$\mu_e = 2.83\sqrt{\chi_A(T + \theta)}$$

Further investigation is in progress and will be reported at a later date. Some degree of association must be expected in these compounds to satisfy both a coordination number greater than three, and the observed physical properties.

When $n = 0$ and $\text{X} = \text{OMe}$ or OEt (but not OPr^1) red-brown products were obtained which analysed for $\text{cpTi}(\text{OR})_2$. These compounds were extremely sensitive to oxygen and moisture and were sufficiently soluble for molecular weight determinations. The dimethoxide was found to be tetrameric in boiling tetrahydrofuran.

When $n = 1$ and $\text{X} = \text{Cl}$ a range of Y groups was examined including $\text{Y} = \text{OMe}$, OEt , and SPh . Polymeric, sparingly soluble products were obtained corresponding to $[\text{cpTiCl}(\text{Y})]_n$. When $\text{X} = \text{Br}$ the reduction proceeded as evidenced by the usual colour changes, but the products isolated could not be identified from elementary analyses as the expected $[\text{cpTiBr}(\text{Y})]_n$.