

Isolation and Characterization of Bis(η -methylcyclopentadienyl)dihalotitanium(IV)

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(η -MeC₅H₄)₂TiX₂ (X = Br, I) have been prepared by the reaction of appropriate boron trihalides on (η -MeC₅H₄)₂TiCl₂. Improvements have been suggested over the known methods for preparing (η -MeC₅H₄)₂-TiCl₂ and (η -MeC₅H₄)₂TiF₂. (η -MeC₅H₄)₂TiX₂ (X = Cl, Br, I) have also been prepared by an exchange reaction of haloacids on (η -MeC₅H₄)₂TiF₂. The complexes have been characterized by elemental analysis, conductivity measurements, i.r. and ¹H n.m.r. spectroscopy.

Introduction

(η -C₅H₅)₂MX₂ type complexes (X = F, Cl, Br, I and M = Ti, Zr, Hf) have been investigated by several workers [1–4]. The first alkyl substituted cyclopentadienyl complex reported was (η -MeC₅H₄)₂TiCl₂ [5]. In this communication (η -MeC₅H₄)₂TiX₂ (X = Br, I) have been prepared by the reaction of appropriate boron trihalide on (η -MeC₅H₄)₂TiCl₂ in CH₂-Cl₂. It is also suggested that the known methods for preparing (η -MeC₅H₄)₂TiCl₂ [5] and (η -MeC₅H₄)₂-TiF₂ [6] can be modified to give better yield and ease of preparation. (η -MeC₅H₄)₂TiX₂ (X = Cl, Br, I) have been prepared in quantitative yield by an exchange reaction of haloacids on (η -MeC₅H₄)₂TiF₂. The complexes have been characterised by physical techniques and possible structures have been suggested.

Experimental

Reagents and Techniques

Well dried and purified solvents such as THF, CH₂Cl₂, C₆H₅NO₂ etc. were used throughout the studies. All other chemicals used were of A.R. quality. (η -MeC₅H₄)Ti(I) was prepared as cited in the literature [5].

I.r. spectra were recorded on a Perkin-Elmer Model 621 grating spectrometer. ¹H n.m.r. spectra were

recorded on a Varian A-60 spectrometer at a sweep width of 500 Hz, using TMS as an internal standard. The conductance measurements were made in nitrobenzene solution with a Beckman RC-18A conductivity bridge.

Preparation of (η -MeC₅H₄)₂TiCl₂ (Improved method)

(1.9 g, 0.01 mol) TiCl₄ and (5.66 g, 0.02 mol) (η -MeC₅H₄)Ti(I) in 100 cm³ of THF were stirred in a flask fitted with mercury seal for 30 min. The resulting red coloured solution was filtered and the THF was evaporated off *in vacuo*. The residue on recrystallization from CHCl₃ gave dark red (η -MeC₅H₄)₂TiCl₂. (95% yield) m.p. 216 °C. *Anal.* Found: C, 52.12; H, 5.19; Cl, 25.68; Ti, 17.40; M. W. 282.8. *Calcd.*: C, 51.98; H, 5.05; Cl, 25.63; Ti, 17.33%; M.W. 277.

Preparation of (η -MeC₅H₄)₂TiX₂ (X = Br, I) from (η -MeC₅H₄)₂TiCl₂

The solution of BBr₃ (1.3778 g, 0.0055 mol) or BI₃ (2.155 g, 0.0055 mol) in 5 cm³ CH₂Cl₂ was added to the solution of (1.385 g, 0.005 mol) (η -MeC₅H₄)₂TiCl₂ in 30 cm³ CH₂Cl₂ dropwise with constant stirring. The reaction mixture was further stirred for 30 min. The volatile compounds were removed *in vacuo* and the residue on recrystallization from CHCl₃ gave reddish brown (η -MeC₅H₄)₂TiBr₂ (90% yield) m.p. 224 °C (*Anal.* Found: C, 40.23; H, 3.79; Br, 43.98; Ti, 13.20%; M.W. 374.4. *Calcd.*: C, 39.34; H, 3.82; Br, 43.71; Ti, 13.12%; M.W. 366) or black (η -MeC₅H₄)₂TiI₂ (90% yield) m.p. 235 °C (d) (*Anal.* Found: C, 30.88; H, 3.16; I, 55.44; Ti, 10.50%; M.W. 468.3. *Calcd.*: C, 31.30; H, 3.04; I, 55.22; Ti, 10.43%; M.W. 460).

Preparation of (η -MeC₅H₄)₂TiF₂ from (η -MeC₅H₄)₂-TiCl₂

5 cm³ of 10% aqueous solution of NH₄F was added to an aqueous solution of (η -MeC₅H₄)₂TiCl₂ prepared by refluxing 1 g of (η -MeC₅H₄)₂TiCl₂ in 100 cm³ water (pH 1.2–2.0 w.r.t. HCl) for 30 min. The yellow precipitate formed was extracted with 5 × 10 cm³ of CH₂Cl₂. The combined extract was dried over anhydrous MgSO₄, filtered and evaporated

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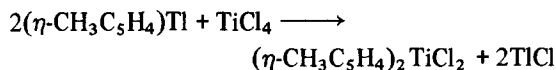
to 1/5th of its volume *in vacuo*. On adding petroleum ether (60–80 °C), yellow precipitate was obtained which on drying *in vacuo* gave more than 95% yield, m.p. 183 °C. *Anal.* Found: C, 60.12; H, 5.79; F, 15.49; Ti, 19.48%; M.W. 248.4. *Calcd.*: C, 59.02; H, 5.74; F, 15.57; Ti, 19.67%, M.W. 244).

Preparation of $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiX}_2$ ($X = \text{Cl, Br, I}$) from $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiF}_2$

0.5 g, $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiF}_2$ was stirred with 5 cm³ of 35% HCl or 47% HBr or 55% HI (refluxed under nitrogen) for 15 min. The resulting suspension was filtered and dried below 100 °C. The residue was dissolved in the minimum amount of CH_2Cl_2 and reprecipitated by adding petroleum ether (60–80 °C). On drying the precipitate *in vacuo* dark red $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiCl}_2$ was obtained in quantitative yield, m.p. 216 °C (*Anal.* Found: C, 52.02; H, 5.15; Cl, 25.55; Ti, 17.42%; M.W. 285. *Calcd.*: C, 51.98; H, 5.05; Cl, 25.63; Ti, 17.33%; M.W. 277) or reddish brown $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiBr}_2$ in quantitative yield, m.p. 224 °C (*Anal.* Found: C, 40.22; H, 3.75; Br, 43.95; Ti, 13.22%; M.W. 375. *Calcd.*: C, 39.34; H, 3.82; Br, 43.71; Ti, 13.12%; M.W. 366) or black $(\eta\text{-MeC}_5\text{H}_4)_2\text{-TiI}_2$ was obtained in quantitative yield, m.p. 235 °C (d) (*Anal.* Found: C, 30.80; H, 3.12; I, 55.38; Ti, 10.48%; M.W. 470. *Calcd.*: C, 31.30; H, 3.04; I, 55.22; Ti, 10.43%; M.W. 460).

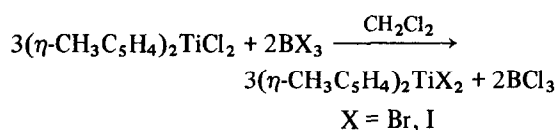
Results and Discussion

$(\eta\text{-MeC}_5\text{H}_4)_2\text{TiCl}_2$ in high purity has been prepared in almost quantitative yield by the following reaction



The reaction was completed within 30 min. It is an improvement over the known method [5] which takes 12 to 14 hr involving the use of $\text{Na}(\text{CH}_3\text{C}_5\text{H}_4)$ and gives very poor yield <65%.

The halogens are not completely exchanged even on long refluxing of KI or KBr with $(\eta\text{-MeC}_5\text{H}_4)_2\text{-TiCl}_2$ in water, contradictory to the observation of Wilkinson and Birmingham [1]. Alternatively we have successfully prepared $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiX}_2$ in quantitative yield by the following reaction



It is a good method and gives pure product owing to the ease of separation of the desired product from BCl_3 which is volatile at 12 °C and 760 mm pressure.

The known aqueous method for $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiF}_2$ [6] gives poor yield (<60%) due to its high solubility

in water. We have improved the method by extracting almost all the fluorocomplex from aqueous solution in CH_2Cl_2 to give >90% yield.

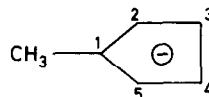
The fluoride of $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiF}_2$ is not completely exchanged in aqueous solution on treatment with NaX ($X = \text{Cl, Br, I}$). We have, however, obtained $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiX}_2$ in quantitative yield by an exchange reaction of HX on $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiF}_2$. In case of HI, F is completely exchanged only on refluxing.

I.r. Spectra

I.r. spectra of these complexes cannot be used for characterization as these are identical and show characteristic bands around 3100, 1495, 1370, 1130, 1025, 820–850 and 590 cm^{-1} . $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiX}_2$ have wedge shaped sandwich structure. Solids are discrete, monomeric, substantially tetrahedral units in which MeC_5H_4 rings are slightly tilted in the plane [7]. Solution and solid i.r. spectra are identical.

¹H n.m.r. Spectra

In these complexes a sharp signal due to CH_3 protons and a multiplet for ring protons are obtained. The integrals of these signals are in 6:8 ratio. The ring proton part of the ¹H n.m.r. spectrum in these complexes is interpretable using 1st order splitting approximations.



CH_3 shields protons at $\text{C}_{2,5}$ more than at $\text{C}_{3,4}$. Adjacent and cross coupling constants ($J_{2,3}$; $J_{2,4}$) are nearly equal and smaller than the chemical shifts differences between the two pairs of protons so that these should appear as an unsymmetrical triplet. In fluoro complex as F is n.m.r. active, each signal due to ring protons splits into a triplet and due to overlap, two broad multiplets are obtained [8], whereas in case of bromo and chloro complexes one broad multiplet is obtained. In iodocomplex iodine due to large size affects the ring protons and as a combined effect of I atom and CH_3 group two unsymmetrical triplets are obtained.

The τ values for ring protons are sufficiently separated (4.01–3.15 p.p.m.). Thus the n.m.r. spectrum is of much importance in characterization of these complexes. A trend in τ values for ring and CH_3 protons in these complexes is $\text{F} > \text{Cl} > \text{Br} > \text{I}$ and is interpretable as indicative of $p_\pi\text{-d}_\pi$ bonding from halogen to titanium [9] (Table I).

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TABLE I. Proton Chemical Shifts (τ values in p.p.m.) in CDCl_3 and Conductivity Data for $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiX}_2$.

Complex	τ Values for Ring Protons, p.p.m.	τ Values for CH_3 Protons, p.p.m.	Molar Conductivity $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$	Concentration, M
$(\eta\text{-MeC}_5\text{H}_4)_2\text{TiF}_2$	3.66, 4.01	7.86	0.652	5×10^{-4}
$(\eta\text{-MeC}_5\text{H}_4)_2\text{TiCl}_2$	3.68	7.68	0.548	6×10^{-4}
$(\eta\text{-MeC}_5\text{H}_4)_2\text{TiBr}_2$	3.55	7.6	0.492	7×10^{-4}
$(\eta\text{-MeC}_5\text{H}_4)_2\text{TiI}_2$	3.15, 3.56	7.56	0.451	5×10^{-4}

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