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

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$(\eta\text{-MeC}_5\text{H}_4)_2\text{TiX}_2$ (X = Br, I) have been prepared by the reaction of appropriate boron trihalides on $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiCl}_2$. Improvements have been suggested over the known methods for preparing $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiCl}_2$ and $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiF}_2$. $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiX}_2$ (X = Cl, Br, I) have also been prepared by an exchange reaction of haloacids on $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiF}_2$. The complexes have been characterized by elemental analysis, conductivity measurements, i.r. and ^{1}H n.m.r. spectroscopy.

Introduction

$(\eta\text{-C}_5\text{H}_5)_2\text{MX}_2$ 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 $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiCl}_2$ [5]. In this communication $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiX}_2$ (X = Br, I) have been prepared by the reaction of appropriate boron trihalide on $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiCl}_2$ in CH_2Cl_2. It is also suggested that the known methods for preparing $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiCl}_2$ [5] and $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiF}_2$ [6] can be modified to give better yield and ease of preparation. $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiX}_2$ (X = Cl, Br, I) have been prepared in quantitative yield by an exchange reaction of haloacids on $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiF}_2$. 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, CH_2Cl_2, $\text{C}_6\text{H}_5\text{NO}_2$ etc. were used throughout the studies. All other chemicals used were of A.R. quality. $(\eta\text{-MeC}_5\text{H}_4)\text{Tl(I)}$ was prepared as cited in the literature [5].

I.r. spectra were recorded on a Perkin-Elmer Model 621 grating spectrometer. ^{1}H 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 $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiCl}_2$ (Improved method)

(1.9 g, 0.01 mol) TiCl_4 and (5.66 g, 0.02 mol) $(\eta\text{-MeC}_5\text{H}_4)\text{Tl(I)}$ in 100 cm^3 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 CHCl_3 gave dark red $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiCl}_2$. (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 $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiX}_2$ (X = Br, I) from $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiCl}_2$

The solution of BBr_3 (1.3778 g, 0.0055 mol) or BI_3 (2.155 g, 0.0055 mol) in 5 cm^3 CH_2Cl_2 was added to the solution of (1.385 g, 0.005 mol) $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiCl}_2$ in 30 cm^3 CH_2Cl_2 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 CHCl_3 gave reddish brown $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiBr}_2$ (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 $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiI}_2$ (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 $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiF}_2$ from $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiCl}_2$

5 cm^3 of 10% aqueous solution of NH_4F was added to an aqueous solution of $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiCl}_2$ prepared by refluxing 1 g of $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiCl}_2$ in 100 cm^3 water (pH 1.2–2.0 w.r.t. HCl) for 30 min. The yellow precipitate formed was extracted with 5 × 10 cm^3 of CH_2Cl_2. The combined extract was dried over anhydrous MgSO_4, 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 (η-MeC$_5$H$_4$)$_2$TiX$_2$ (X = Cl, Br, I) from (η-MeC$_5$H$_4$)$_2$TiF$_2$

0.5 g, (η-MeC$_5$H$_4$)$_2$TiF$_2$ was stirred with 5 cm^3 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$_2$Cl$_2$ and reprecipitated by adding petroleum ether (60–80 °C). On drying the precipitate *in vacuo* dark red (η-MeC$_5$H$_4$)$_2$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 (η-MeC$_5$H$_4$)$_2$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 (η-MeC$_5$H$_4$)$_2$-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

(η-MeC$_5$H$_4$)$_2$TiCl$_2$ in high purity has been prepared in almost quantitative yield by the following reaction

$$2(\eta\text{-CH}_3\text{C}_5\text{H}_4)\text{Tl} + \text{TiCl}_4 \longrightarrow (\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2 + 2\text{TlCl}$$

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 Na(CH$_3$C$_5$H$_4$) and gives very poor yield <65%.

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

$$3(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2 + 2\text{BX}_3 \xrightarrow{\text{CH}_2\text{Cl}_2} 3(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiX}_2 + 2\text{BCl}_3$$

$$X = \text{Br, I}$$

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 (η-MeC$_5$H$_4$)$_2$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$_2$Cl$_2$ to give >90% yield.

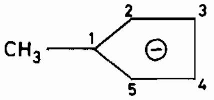
The fluoride of (η-MeC$_5$H$_4$)$_2$TiF$_2$ is not completely exchanged in aqueous solution on treatment with NaX (X = Cl, Br, I). We have, however, obtained (η-MeC$_5$H$_4$)$_2$TiX$_2$ in quantitative yield by an exchange reaction of HX on (η-MeC$_5$H$_4$)$_2$TiF$_2$. In case of HI, F is completely 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}. (η-MeC$_5$H$_4$)TiX$_2$ have wedge shaped sandwich structure. Solids are discrete, monomeric, substantially tetrahedral units in which MeC$_5$H$_4$ rings are slightly tilted in the plane [7]. Solution and solid i.r. spectra are identical.

^{1}H 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 ^{1}H n.m.r. spectrum in these complexes is interpretable using 1st order splitting approximations.



CH$_3$ shields protons at C$_{2,5}$ more than at 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 F > Cl > Br > I and is interpretable as indicative of p$_\pi$–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 $(\eta\text{-}MeC_5H_4)_2TiX_2$.

Complex	τ Values for Ring Protons, p.p.m.	τ Values for CH_3 Protons, p.p.m.	Molar Conductivity $ohm^{-1}\ cm^2\ mol^{-1}$	Concentration, *M*
$(\eta\text{-}MeC_5H_4)_2TiF_2$	3.66, 4.01	7.86	0.652	5×10^{-4}
$(\eta\text{-}MeC_5H_4)_2TiCl_2$	3.68	7.68	0.548	6×10^{-4}
$(\eta\text{-}MeC_5H_4)_2TiBr_2$	3.55	7.6	0.492	7×10^{-4}
$(\eta\text{-}MeC_5H_4)_2TiI_2$	3.15, 3.56	7.56	0.451	5×10^{-4}

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