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# SYNTHETIC STUDIES OF ORGANODI-$\pi$-CYCLOPENTADIENYLTITANIUM(III) DERIVATIVES

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## Summary

Two synthetic routes to compounds of the type $\pi$-$Cp_2Ti^{III}R$ (R = $CH_3$, $CH_2Si(CH_3)_3$, $C_6F_5$) have been investigated: (a) chemical reduction of $\pi$-$Cp_2Ti^{IV}(R)Cl$ by zinc or aluminum metal in tetrahydrofuran, and (b) conventional organometallic syntheses using organo-lithium or -magnesium reagents and $[\pi\text{-}Cp_2Ti^{III}Cl]_2$. The preferred route is via an organolithium reagent, since chemical reduction gives a mixture of products. Green, monomeric complexes (R = $CH_2Si(CH_3)_3$, $C_6F_5$) were isolated and characterised. From the reaction of $\pi$-$Cp_2Ti^{IV}Cl_2$ and trimethylsilylmethyllithium in a 1/1 ratio, $\pi$-$CpTi^{IV}[CH_2Si(CH_3)_3]_3$ was obtained. Unlike $\pi$-$Cp_2Ti^{III}C_6F_5$, $\pi$-$Cp_2Ti^{III}CH_2Si(CH_3)_3$ does not form a blue complex with molecular nitrogen.

## Introduction

We recently reported that the electrochemical reduction of $\pi$-$Cp_2Ti^{IV}(R)Cl$* derivatives (R = $CH_3$, $C_6F_5$) proceeds via a one-electron step to give green solutions of $\pi$-$Cp_2Ti^{III}R$, which in ether solvents in the presence of n-$Bu_4NClO_4$ supporting electrolyte turn blue either under a dinitrogen or under an argon atmosphere [1]. Electrochemically generated $\pi$-$Cp_2Ti^{II}$ also forms deep blue solutions in ether solvents under an argon or helium atmosphere, suggesting a reaction between the reduced titanium complex and the ether solvent (or the electrolyte) [1,2]. We have now explored two routes to the chemical synthesis of $\pi$-$Cp_2Ti^{III}R$ complexes: (a) chemical reduction of $\pi$-$Cp_2Ti^{IV}(R)Cl$ by zinc or aluminum in tetrahydrofuran, and (b) conventional organometallic syntheses using organolithium reagents and $[\pi\text{-}Cp_2Ti^{III}Cl]_2$ in diethyl ether at low temperatures.

During the course of this work Teuben and De Liefde Meijer [3] have described the synthesis of a number of $\pi$-$Cp_2Ti^{III}R$ complexes (where R = aryl) by

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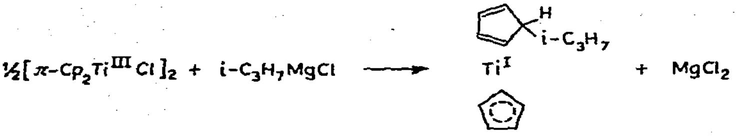
* $\pi$-Cp represents the *pentahapto*-cyclopentadienyl group ($h^5$-$C_5H_5$).

the Grignard route, and they isolated a blue, binuclear dinitrogen complex of empirical formula $[\pi\text{-Cp}_2\text{Ti}^{\text{III}}\text{C}_6\text{H}_5]_2\text{N}_2$, unstable above 0° [4]. They were, however, unable to isolate complexes in which R = alkyl, due to thermal decomposition, although $\pi\text{-Cp}_2\text{Ti}^{\text{III}}\text{CH}_3$ had been presumed to be stable at room temperature from the persistence of its ESR spectrum [5]. A number of other blue complexes of molecular nitrogen with lower valent di-π-cyclopentadienyltitanium derivatives have been isolated and characterised. These complexes are $[\pi\text{-Cp}_2\text{Ti}^{\text{II}}]_2\text{N}_2$ [2], $\pi\text{-Cp}_2\text{Ti}^{\text{III}}\text{—N=N—Ti}^{\text{III}}\text{-}\pi\text{-Cp}_2$ [6], and a compound of composition $[\pi\text{-Cp}_2\text{Ti-i-C}_3\text{H}_7]_2\text{N}_2$ for which it has been suggested that the dinitrogen ligand is coordinated to a *titanium(I)* centre formed as indicated in eqn. 1 [7].



(1)

## Experimental

### *General procedures*

The preparations of di-π-cyclopentadienyltitanium(III) derivatives were carried out under a pure argon atmosphere in Schlenk-type reaction vessels. After removal of solvents, all further manipulations of air-sensitive materials were performed in a Vacuum Atmospheres Dry Box using a dinitrogen atmosphere (prepurified 99.997% min.) passed through a 30 cm column of freshly activated Ridox reagent (Fisher Scientific Co.). Microanalyses were performed by Alfred Bernhardt, W. Germany.

### *Instruments*

The following instruments were used for spectroscopic measurements: Infrared spectra (Perkin—Elmer 337 and Beckman IR20). Spectra were obtained as mulls (nujol and perfluorokerosene) using KBr optics. Ultraviolet/visible spectra (Beckman DB G), mass spectra (Varian CH5). Magnetic susceptibility measurements were carried out with single temperature Gouy and Faraday equipment. The susceptibilities were corrected for induced magnetism.

### *Materials*

Tetrahydrofuran (THF), anhydrous diethyl ether, 1,4-dioxane, 1,2-dimethoxyethane, benzene, toluene, n-pentane and n-hexane were obtained as reagent grade solvents. They were dried over sodium wire, then freshly distilled from $\text{LiAlH}_4$ and degassed (Argon, 3h) before use. Ether solvents were tested for the absence of peroxides.

The following chemicals were obtained commercially and used without further purification: zinc powder, lithium, $\text{LiAlH}_4$, $\pi\text{-Cp}_2\text{TiCl}_2$, pentafluorobenzene, chloromethyl(trimethyl)silane, n-butyllithium (2 *M* in hexane) and methyllithium (1.5 *M* in diethyl ether). $\pi\text{-Cp}_2\text{Ti}^{\text{IV}}(\text{C}_6\text{F}_5)\text{Cl}$ [1,8] and $\pi\text{-Cp}_2\text{Ti}^{\text{IV}}(\text{CH}_3)\text{Cl}$ [1,9] were prepared according to literature methods. $[\pi\text{-Cp}_2\text{Ti}^{\text{III}}\text{Cl}]_2$ was obtained in 89% yield by the reduction of $\pi\text{-Cp}_2\text{Ti}^{\text{IV}}\text{Cl}_2$ with activated aluminum in THF [10] [Found: C, 56.1; H, 4.9; Cl, 16.9. $C_{10}H_{10}ClTi$ calcd.: C, 56.4; H, 4.7; Cl, 16.7%. M.p. 278—280° (lit. m.p. 282—283°) [11]].

### *Preparation of $\pi$-$Cp_2Ti^{III}C_6F_5$*

*(a) from [$\pi$-$Cp_2Ti^{III}Cl]_2$ and pentafluorophenyllithium.* A freshly prepared solution of pentafluorophenyllithium [12] (17 mmoles in diethyl ether) was added by syringe to a suspension of $[\pi\text{-}Cp_2Ti^{III}Cl]_2$ (3.64 g, 8.5 mmoles) in diethyl ether (50 ml) at —78°. The reaction mixture was stirred (4 h) and allowed to reach room temperature. Insoluble solids were filtered off, and solvents were removed from the filtrate at $10^{-2}$ mm to give an air-sensitive solid which was recrystallised from toluene to give green crystals of $\pi$-$Cp_2Ti^{III}C_6F_5$ (4.40 g, 12.7 mmoles, 75%) m.p. 111—113° (dec.) [lit. [3]: brown-purple crystals, m.p. 106° (dec.)]. [Found: C, 55.4; H, 3.1; F, 27.3; Ti, 13.7. $C_{16}H_{10}F_5Ti$ calcd.: C, 55.7; H, 2.9; F, 27.5; Ti, 13.9%.] $\mu_{eff}$ 1.73 BM. The infrared spectrum (Nujol) showed bands at 1640 w, 1540 w, 1510 s, 1450 s, 1430 s, 1380 m, 1345 w, 1260 w, 1100 w, 1055 s, 1045 s, 1020 m, 955 vs, 845 m, 820 vs, 810 vs, 690 s, 600 m $cm^{-1}$. The mass spectrum (70 eV) showed high abundance peaks at *m/e* 345, 215, 178, 168 and 167 corresponding to the ions $C_{10}H_{10}{}^{48}TiC_6F_5^+$, $C_6F_5$-${}^{48}Ti^+$, $C_{10}H_{10}{}^{48}Ti^+$, $C_6F_5H^+$ and $C_6F_5^+$, respectively.

*(b) from $\pi$-$Cp_2Ti^{IV}(C_6F_5)Cl$ and aluminium.* $\pi$-$Cp_2Ti^{IV}(C_6F_5)Cl$ (0.5 g, 1.3 mmoles) and activated aluminum (0.16 g, 6 mmoles) in THF (50 ml) were stirred for 1 h. The initial orange colour of the solution became dark green. After 24 h excess of aluminum was filtered off and the solution was concentrated to ca. 20 ml. Cooling to —78° deposited green crystals of impure $\pi$-$Cp_2Ti^{III}C_6F_5$ (0.3 g) m.p. 108—110° (dec.). (Found: C, 47.7; H, 3.6; F, 21.5; Ti, 13.5%.) Attempted further purification of this sample by recrystallisation was unsuccessful.

### *Preparation of $\pi$-$Cp_2Ti^{III}CH_2Si(CH_3)_3$*

Freshly prepared trimethylsilylmethyllithium [13] (37 ml of a 0.34 *M* solution in n-pentane, 12.5 mmoles) was added by syringe to a slurry of $[\pi\text{-}Cp_2Ti^{III}Cl]_2$ (2.68 g, 6.25 mmoles) in THF (50 ml) at —78°. The reaction mixture was stirred for 5 h and allowed to reach room temperature. Lithium chloride was filtered off and partial removal of the solvents at $10^{-2}$ mm caused the precipitation of green crystals which were filtered from the mother liquor and identified as di-$\pi$-cyclopentadienyltrimethylsilylmethyltitanium(III) (1.8 g, 6.8 mmoles, 54%) m.p. 145° (dec.). (Found: C, 62.8; H, 7.9; Si, 10.2; Ti, 18.6. $C_{14}H_{21}SiTi$ calcd.: C, 63.4; H, 8.0; Si, 10.6; Ti, 18.1%). The infrared spectrum (nujol and perfluorokerosene) showed bands at 2950 w, 2920 w, 2850 w, 1450 w, 1250 m, 1240 s, 1122 w, 1062 w, 1014 s, 900 (sh), 890 m, 840 s, 808 vs, 740 s, 710 s, 675 m, 600 w, 447 m $cm^{-1}$. The major bands in the mass spectrum (70 eV) were at *m/e* 265 (9), 178 (23), 73 (100), 66 (48), corresponding to the ions $C_{10}H_{10}TiCH_2Si(CH_3)_3^+$, $C_{10}H_{10}{}^{48}Ti^+$, $(CH_3)_3{}^{28}Si^+$ and $C_5H_6^+$, respectively. Relative abundances in parentheses.

### *Reaction of $\pi$-$Cp_2Ti^{IV}Cl_2$ with $(CH_3)_3SiCH_2Li$ in a 1/1 ratio*

Freshly prepared trimethylsilylmethyllithium (37 ml of a 0.52 *M* solution in n-pentane, 19.2 mmoles) was added to a suspension of $\pi$-$Cp_2Ti^{IV}Cl_2$ (5.0 g, 20.0 mmoles) in diethyl ether (60 ml) at 0°. The reaction mixture was stirred for 4 h and then filtered to remove lithium chloride and unreacted $\pi$-$Cp_2Ti^{IV}Cl_2$. Removal of solvent from the filtrate gave a brownish yellow solid which was sublimed (55°/$10^{-2}$ mm) to give yellow crystals of $\pi$-$CpTi^{IV}[CH_2Si(CH_3)_3]_3$ m.p. 60—62°. (Found: C, 54.3; H, 10.0; Si, 22.2; Ti, 12.6. $C_{17}H_{38}Si_3Ti$ calcd.: C, 54.5; H, 10.2; Si, 22.5; Ti, 12.8%.) Yield: 1.0 g, 13%. The $^1H$ NMR spectrum ($CDCl_3$) showed signals at $\tau$ 3.69 ($C_5H_5$), 8.12 ($CH_2$), and 10.01 $[Si(CH_3)_3]_2$ with relative areas 5/5.5/27, respectively. The infrared spectrum (nujol) showed bands at 1305 w, 1255 s, 1242 vs, 1020 m, 915 s(sh), 884 vs, 842 vs, 808 vs, 743 s, 731 s, 698 s, 682 s, 613 w, 527 m, 495 w, 420 m $cm^{-1}$.

### *Attempted preparation of $\pi$-$Cp_2Ti^{III}CH_3$ from $[\pi$-$Cp_2Ti^{III}Cl]_2$ and methyllithium*

To a suspension of $[\pi$-$Cp_2Ti^{III}Cl]_2$ in diethyl ether or toluene at —78° was added by syringe the stoichiometric amount of methyllithium. At —78° a green solution was observed with the precipitation of lithium chloride. After filtration, the solution was warmed to room temperature to give a brown-black precipitate whose infrared spectrum showed bands characteristic of the $\pi$-$C_5H_5$ group [14], but no band at ca. 450 $cm^{-1}$ for a Ti—C $\sigma$-bond [9,15]. The mass spectrum showed strong peaks at *m/e* 259, 257, 194, 192 corresponding to the ions $C_{10}H_{10}{}^{48}Ti^{81}Br^+$, $C_{10}H_{10}{}^{48}Ti^{79}Br^+$, $C_5H_5{}^{48}Ti^{81}Br^+$ and $C_5H_5{}^{48}Ti^{79}Br^+$, respectively, indicating the presence of $[\pi$-$Cp_2Ti^{III}Br]_2$.

## Results and discussion

Although the polarographic data [1] for $\pi$-$Cp_2Ti^{IV}(C_6F_5)Cl$ ($-E_{1/2}$ = 0.84 V) and $\pi$-$Cp_2Ti^{IV}(CH_3)Cl$ ($-E_{1/2}$ = 1.26 V) suggested the need for a stronger reducing agent than zinc ($-E^{\circ}_{red}$ 0.76 V), orange solutions of these complexes in THF soon become green when stirred with zinc (ca. 1 h) indicating reduction to $\pi$-$Cp_2Ti^{III}R$. The green solids isolated, however, were mixtures and, in the case of the pentafluorophenyl complex, $[\pi$-$Cp_2Ti^{III}Cl]_2$ was precipitated on addition of hexane to the filtered solution, suggesting that cleavage of the Ti—$C_6F_5$ bond and cleavage of the Ti—Cl bond are competing processes in the chemical reduction. As in the synthesis of di-$\pi$-cyclopentadienyltitanium(III) halides [10], the use of aluminum as a reducing agent was more successful, although an analytically pure sample of $\pi$-$Cp_2Ti^{III}C_6F_5$ was not obtained. We found that the preferred route to this complex is the reaction of pentafluorophenyllithium with $[\pi$-$Cp_2Ti^{III}Cl]_2$ in diethyl ether at —78°. Good yields of $\pi$-$Cp_2Ti^{III}C_6F_5$ were obtained, which showed a parent ion in its mass spectrum, and bands characteristic of the $C_6F_5$ group [16] and the $\pi$-$C_5H_5$ group [14] in the IR spectrum. The observed magnetic moment, $\mu_{eff}$ 1.73 BM, corresponds to the spin-only value for one unpaired electron per titanium atom, and suggests that, like other $\pi$-$Cp_2Ti^{III}$aryl complexes [3], the compound is monomeric. In all our preparations of $\pi$-$Cp_2Ti^{III}C_6F_5$, the solid was green, although Teuben and De Liefde Meijer reported it to be purple [3].

There has been considerable interest recently in elimination-stabilized alkyls of transition metals [17—19] e.g. alkyl = $CH_2Si(CH_3)_3$. Such derivatives are usually more thermally stable than simple alkyls, so we have investigated the reaction of $[\pi\text{-Cp}_2\text{Ti}^{III}\text{Cl}]_2$ with trimethylsilylmethyllithium. A green solid was obtained, stable at room temperature, and characterised as $\pi\text{-Cp}_2\text{Ti}^{III}\text{CH}_2\text{Si(CH}_3)_3$, the first alkyl derivative of this class. The mass spectrum at 70 eV showed a weak parent ion at *m/e* 265, and strong peaks at *m/e* 178 and 73 corresponding to $C_{10}H_{10}Ti^+$ and $(CH_3)_3Si^+$, respectively. The infrared spectrum showed bands characteristic of π-bonded cyclopentadienyl and of the $(CH_3)_3SiCH_2$ group [18], and a medium intensity band at 447 $cm^{-1}$ characteristic of a Ti—C stretching vibration [9,15]. Attempts to prepare $\pi\text{-Cp}_2\text{Ti}^{III}\text{CH}_3$ from methyllithium and $[\pi\text{-Cp}_2\text{Ti}^{III}\text{Cl}]_2$ were unsuccessful due to thermal decomposition. However, $[\pi\text{-Cp}_2\text{Ti}^{III}\text{Br}]_2$ was identified among the products and arises via halogen exchange between $[\pi\text{-Cp}_2\text{Ti}^{III}\text{Cl}]_2$ and lithium bromide (present in commercial samples of methyllithium in diethyl ether). Halogen exchange has recently been applied to the synthesis of di-π-cyclopentadienyltitanium(III) halides from boron trihalides and $[\pi\text{-Cp}_2\text{Ti}^{III}\text{Cl}]$ [10] and was also reported in the reaction of $\pi\text{-Cp}_2\text{Ti}^{IV}\text{Cl}_2$ and methylmagnesium bromide or iodide [20].

An interesting result was found in the attempted synthesis of $\pi\text{-Cp}_2\text{Ti}^{IV}[\text{CH}_2\text{Si(CH}_3)_3]\text{Cl}$. From the reaction of trimethylsilylmethyllithium with $\pi\text{-Cp}_2\text{Ti}^{IV}\text{Cl}_2$ in a 1/1 ratio we consistently obtained (by sublimation) thermally stable yellow crystals identified as $\pi\text{-CpTi}^{IV}[\text{CH}_2\text{Si(CH}_3)_3]_3$. This observation parallels the findings of Bradley and co-workers who report that $\pi\text{-CpTi(NMe}_2)_3$ is formed preferentially from $\pi\text{-Cp}_2\text{TiCl}_2$ and dimethylaminolithium [21]. $\pi\text{-CpTi}^{IV}[\text{CH}_2\text{Si(CH}_3)_3]_3$ is much more stable thermally than $\pi\text{-CpTi}^{IV}(\text{CH}_3)_3$ which decomposes rapidly at 40° [22].

We have studied the interaction of $\pi\text{-Cp}_2\text{Ti}^{III}\text{R}$ complexes [R = $C_6F_5$, $CH_2Si(CH_3)_3$] with molecular nitrogen. The green solution of the pentafluorophenyl complex in toluene (but not the $CH_2Si(CH_3)_3$ derivative) becomes deep blue on cooling to —80° in a nitrogen atmosphere (the solution remains green under argon or vacuum)*. When the solution is warmed it reverts to green at about —50° as molecular nitrogen is released. Repeated attempts to isolate the blue complex were unsuccessful. Although the stoichiometry of the complex is unknown it seems likely that it will be similar to the previously reported $[\pi\text{-Cp}_2\text{TiC}_6\text{H}_5]_2\text{N}_2$, which is stable up to 0° [4]. The order of thermal stability of these dinitrogen complexes of titanium(III) as a function of R group is thus: $C_6H_5 > C_6F_5 \gg CH_2Si(CH_3)_3$. The stability is therefore not a simple function of the electron-releasing or -acceptor properties of the R group, since, although $CH_2Si(CH_3)_3$ is strongly electron-releasing [23], the $C_6F_5$ group is considerably more electronegative than the $C_6H_5$ group [24]. Conceivably, steric factors could also be of importance in bridged complexes of this type.

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* In dilute solutions ($10^{-3}$ *M*) in ether solvents, the $\pi\text{-Cp}_2\text{Ti}^{III}\text{R}$ derivatives or $[\pi\text{-Cp}_2\text{Ti}^{III}\text{Cl}]_2$ rapidly form blue-violet solutions ($\lambda_{max}$ 567 nm) either under dinitrogen, argon or vacuum. On the basis of complete analytical data and IR spectra, the thermally stable, air-sensitive, dark violet solids isolated after removal of solvent from ether solutions of $[\pi\text{-Cp}_2\text{Ti}^{III}\text{Cl}]_2$ appear to result from loss of a cyclopentadienyl group and incorporation of a solvent-derived alkoxy group in the final structure [25].

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