Journal of Organometallic Chemistry, 47 (1973) 375–382

DIMERIC DICYCLOPENTADIENYLTITANIUM(III) HALIDES

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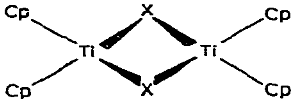
(Received June 19th, 1972)

SUMMARY

The synthesis and characterization of dicyclopentadienyltitanium(III) fluoride completes the series $(Cp_2Ti^{III}X)_2$ [where Cp = π-cyclopentadienyl; X = F, Cl, Br or I]. Two new methods of preparation are reported for the other members of the series.

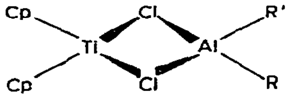
Structural investigation by means of molecular weight determinations, spectroscopic, and magnetic susceptibility measurements confirm the dimeric model shown below.



(X=F,Cl,Br and I)

INTRODUCTION

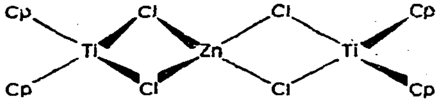
The reduction of dicyclopentadienyltitanium(IV) compounds with a range of reductants, including metals (Na, Zn, Mg, Al), Grignard reagents, lithium aluminium hydride, aluminiumalkyls, etc. has been used in the preparation of many lower-valent cyclopentadienyltitanium derivatives[1], including phosphides[2], allylic compounds[3], borohydride[4], as well as the extensive series of bimetallic compounds of general type[5–8] (I).



(R or R'= alkyl or halide)

(I)

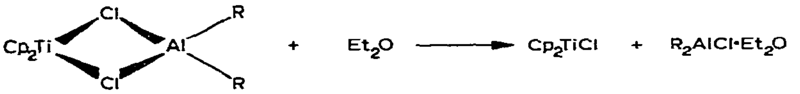
The original preparation of the chloride, $Cp_2Ti^{III}Cl$, was by reduction of Cp_2TiCl_2 with zinc dust in tetrahydrofuran (THF) as solvent[9]. The low yield in this preparation was later shown to be due to the formation of a bimetallic complex (II) which could not be easily decomposed[10].



(II)

The absence of evidence for Ti–Ti interaction in the ESR spectrum of zinc-reduced Cp_2TiCl_2 was originally attributed[11] to the presence of a solvated monomer of Cp_2TiCl. However, it has now been shown that the complex (II) is formed under these conditions[10]. Furthermore, there is no Ti–Ti interaction present and the magnetic susceptibility obeys a Curie law[10].

The bimetallic complexes of type (I) can be used to prepare Cp_2TiCl in good yield by complexing the aluminium with triethylamine or ether[5,12] according to eqn. (1).



(1)

The bromide and iodide derivatives of $Cp_2Ti^{III}X$ have not been isolated by reduction of $Cp_2Ti^{IV}X_2$ (X = Br or I). Reduction of Cp_2TiCl_2 with allylmagnesium bromide in ether has been claimed[3] to give solutions of $Cp_2Ti^{III}Br$ although the only evidence offered was a characteristic band in the visible spectrum and the appearance of an uncharacterized green precipitate. We find the compound to be red-brown in colour in agreement with the original synthesis report[13].

The polarographic reductions of $Cp_2Ti^{IV}X_2$ (X = F, Cl, Br and I) in both protic and aprotic solvents have been studied[14]. However, the titanium–halide bonds did not reduce cleanly; the reactions were complicated by hydrolysis, complexation or specific solvation, and no compound was isolated.

The chloride, bromide, and iodide members of the Cp_2Ti^{III} halide series have been prepared from the borohydride, Cp_2TiBH_4, by ligand exchange reactions with hydrogen halides[13] (eqn. 2), and also with boron trihalides[13] (eqn. 3). However the use

$$Cp_2Ti^{III}BH_4 + HX\ (Cl, Br\ or\ I) \rightarrow Cp_2Ti^{III}X + H_2 + \tfrac{1}{2}(BH_3)_2 \qquad (2)$$

$$3\,Cp_2Ti^{III}BH_4 + BX_3\ (X = Cl\ or\ Br) \rightarrow 3\,Cp_2Ti^{III}X + 2\,(BH_3)_2 \qquad (3)$$

of boron trifluoride did not give the expected fluoride derivatives but instead the borofluoride (eqn. 4). Few physical properties have been reported for these compounds.

$$3\,Cp_2Ti^{III}BH_4 + 4\,BF_3 \rightarrow 3\,Cp_2Ti^{III}BF_4 + 2\,(BH_3)_2 \qquad (4)$$

It was our intention to synthesize the outstanding fluoride derivative and then examine the physical properties of the completed series, in particular the magnetic behaviour. The dimeric[6] chloride shows antiferromagnetic behaviour[15,16] due to intramolecular titanium–titanium interaction probably via the bridging chloride atoms[15].

This series offers an unusual opportunity to study the effect of the availability of orbitals of the bridging halide atom on metal–metal interaction in dimeric systems such as these.

RESULTS AND DISCUSSION

Polarographic data for $Cp_2Ti^{IV}F_2$ ($-E_{\frac{1}{2}}$ 1.21 V) in DMF as compared to Cp_2TiCl_2, Cp_2TiBr_2 or Cp_2TiI_2 ($-E_{\frac{1}{2}} < 0.6$ V)[14], indicated the need for stronger chemical reductants than say zinc ($-E^0_{red}$ 0.76 V) if $Cp_2Ti^{III}F_2$ was to be chemically reduced. The use of Mg or Na ($-E^0_{red} > 1.75$ V) might be expected to cause further reduction to Ti^{II} compounds. Such was the case when Cp_2TiF_2 or Cp_2TiCl_2 was treated with magnesium metal activated with iodine, the black-brown products were extremely reactive with chemical behaviour indicative of a probable oxidation state of +2. No characterization was attempted.

It was found that aluminium ($-E^0_{red}$ 1.67 V) would effect the reduction of Cp_2TiF_2 only if much care was used in activating the surface of the metal (see Experimental).

In the cases when X=Cl, Br, or I, activation was not necessary to produce total reduction.

The reduction of Cp_2TiX_2, where X=Cl, Br or I with aluminium foil in THF resulted in a solution of $Cp_2Ti^{III}X$*. The solution could be filtered free of the excess reductant and then pumped to low bulk and the precipitate formed washed free of aluminium halide using diethyl ether.

In the case of Cp_2TiF_2 however the reduction of the yellow compound with activated aluminium foil in THF resulted in a deep blue solution and a light blue precipitate. When this mixture was pumped to dryness and then sublimed at ≈250° at 10^{-4} mmHg, a green crystalline sublimate was obtained in 40% yield which was identified as $Cp_2Ti^{III}F$. The original blue compound is believed to be a bimetallic complex and is still under investigation.

The reduction of Cp_2TiI_2 with aluminium was somewhat anomalous in that the product always contained strongly coordinated ether in approximately 1/1 ratio. It was found that an alternative ligand exchange reaction provided a better product. The chloride could be used to prepare bromide or iodide by treatment with boron trihalides (eqn. 5). Again difficulty was encountered with the iodide reaction. It was

$$3\,Cp_2Ti^{III}Cl + BX_3 \rightarrow 3\,Cp_2Ti^{III}X + BCl_3 \qquad (X = Br\ or\ I) \tag{5}$$

found in several preparations that $Cp_2Ti^{IV}I_2$ was forming probably by dissociation of BI_3 into I_2 which then oxidized some of the $Cp_2Ti^{III}I$ (eqn. 6)

$$2\,Cp_2Ti^{III}I + I_2 \rightarrow 2\,Cp_2Ti^{IV}I_2 \tag{6}$$

When aluminium foil was added to this ligand exchange reaction oxidation was eliminated and pure $Cp_2Ti^{III}I$ could be isolated in good yields (≈70%).

Properties

The fluoride is coloured green; chloride; green brown; bromide, red brown; and iodide, black. On exposure to air all are oxidized to yellow-orange solids although the fluoride tends to show a decreased sensitivity to oxygen. All but the iodide can be purified by sublimation without decomposition taking place. All are soluble in air-free water, in THF, and in benzene, although the dissolution of the fluoride in organic solvents is very slow. Ebulliometric molecular weight determinations in benzene confirm the predicted dimeric structure.

Infrared data

The spectra of the four Cp_2TiX derivatives are closely similar in the region 4000–600 cm^{-1} as the metal to halogen stretching frequencies fall below 600 cm^{-1}.

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* Preparation of Cp_2TiCl by this method had been developed in these laboratories by Dr. Weigold[25].

This similarity is consistent with the presence of the common Cp_2Ti^{III} moiety. Thus all the compounds showed bands associated with the π-C_5H_5 ring[17], at 3100, 1440 ± 3, 1130 ± 10, 1015 ± 10, and 800 ± 10 cm^{-1}, which are assigned to CH in-plane stretching, CC in-plane skeletal stretch, CH out-of-phase deformation, CH in-plane deformation, and CH out-of-phase deformation.

In recent times, interest has been shown in the far infrared spectra of some dicyclopentadienyltitanium(IV) derivatives, in particular $Cp_2Ti^{IV}X_2$ (where X = halide). However the spectra are extremely difficult to interpret.

Fritz[17] assigned a weak peak at 595 cm^{-1} in the spectrum of Cp_2TiCl_2 to a metal–ring tilting vibration, whereas Maslowsky and Nakamoto[18] assign it to a cyclopentadienyl ring vibration due to its constant position as metal or halogen atom is changed. In going from F to I we observed no appreciable change in this frequency and so favour the latter assignment to a ring vibrational mode. The only other bands observed between 600–300 cm^{-1} in the spectra of all four members of the series was a strong band at 395 ± 3 cm^{-1} for X = Cl, Br or I; which moved to 380 cm^{-1} for the fluoride derivative, and a medium to weak band at 355 cm^{-1} which appeared as a weak shoulder at 360 cm^{-1} in the fluoride. In the series $Cp_2Ti^{IV}X_2$ bands at 416 ± 5 cm^{-1} and 370 ± 20 cm^{-1} were assigned to the asymmetric and symmetric metal–ring stretching vibrations respectively; again the higher energy band was strong relative to the lower energy band[18].

Since the pseudo-tetrahedral symmetry of Cp_2TiX_2 derivatives exists also around the titanium atom of the compounds under investigation, the metal–cyclopentadienyl stretching frequencies would be expected to occur in the same area. The decrease in frequency of some 20 cm^{-1} observed may be attributed to the lower oxidation state of the metal.

The metal–halogen stretching frequencies for bridging halides are expected below 250 cm^{-1} for chloride, bromide and iodide and were not observed in the range studied. The only other absorption present was a strong band at 470 cm^{-1} in the spectrum of the fluoride derivative, which must be assigned to a bridging titanium–fluoride stretching frequency.

Electronic spectral data

The spectra of the compound were measured, both as solid reflectance and in benzene solution, over the range 25000–5000 cm^{-1} (Table 1). The data is in close agreement for both solid and solution state so we can assume that the dimeric structure persists in benzene (as established by molecular weight determinations).

Magnetic data

The measurements of the variation of paramagnetic susceptibility with temperature were recorded between 80 and 380 K. In the case of the fluoride derivative no maximum in susceptibility was observed over the temperature range studied. However, a plot of effective magnetic moment per titanium atom *vs.* temperature immediately revealed a well-defined temperature dependency, suggesting that some exchange interaction may well be present (Table 2).

With the remainder of the halide series (X = Cl, Br or I) the susceptibility was observed to pass through a maximum value and then fall rapidly at lower temperatures.

TABLE 1

ELECTRONIC SPECTRAL DATA

Compound	*Medium*	*Assignments*				
		Charge transfer			*d–d transition* [ε_{max}]	
Cp_2TiF	Solid	22200			12500	8700
	Benzene				12900 (br)	8900 (br, sh)
Cp_2TiCl	Solid	21000		14500	12100 (sh)	8700
	Benzene			14500[40]	12100[32] (sh)	8700[7.5]
Cp_2TiBr	Solid	20300		14300	12100	8160
	Benzene			14300[42]	12100[27]	8160[8.6]
Cp_2TiI	Solid	20000	16700	15400 (sh)	12100 (sh)	7700
	Benzene		16700[550]	14900 (sh)		8160[7.5]

TABLE 2

MAGNETIC DATA

Compound	μ_{eff}				*Observed J*
	360 *K*	260 *K*	160 *K*	100 *K*	(cm^{-1})
Cp_2TiF	1.65	1.63	1.56	1.45	
Cp_2TiCl	1.54	1.47	1.18	0.85	140–170[a]
Cp_2TiBr	1.39	1.23	0.87	0.45	250
Cp_2TiI	1.51	1.41	1.20	0.80	150–160[a]

[a] Some reproduceable scattering is evident near the maxima suggesting phase changes may be taking place at the Néel temperature.

Extrapolation to temperatures >400 K should produce effective magnetic moments close to the "spin only" value (1.73 BM) for a single unpaired electron. Reduction of temperature to 80 K causes the magnetic moment to decrease monotonically, indicating that the dimers will become diamagnetic at lower temperatures (Table 2). These observations support the previous proposals of a thermal equilibrium between singlet and triplet states. As the temperature is lowered, the singlet state becomes progressively populated at the expense of the triplet level, so that the susceptibility and magnetic moment both decrease steadily, eventually to zero.

The experimental results from $\chi_M(T)$ and $\mu_{eff}(T)$ curves can be compared with the theoretical curves derived from eqn. (1), which is appropriate to the singlet–triplet model[19], where J is the separation between singlet and triplet states.

$$\chi_M = \frac{N \cdot \beta^2}{3k \cdot T} \cdot g^2 \cdot \left[1 + \tfrac{1}{3} \exp\left(\frac{-J}{k \cdot T}\right)\right]^{-1} \qquad (1)$$

The experimental data is being extended to helium temperatures and the interpretation will be discussed elsewhere.

EXPERIMENTAL

General

Manipulations of air-sensitive materials were carried out in a nitrogen-filled glove-box or in vacuum, and all reactions were effected in a stream of purified argon. Infrared spectra were run in KBr disks protected by pure KBr pressed in either side of the sample, on a Perkin–Elmer 521 spectrophotometer. Visible spectra were measured in benzene solution on a Beckman DK2 spectrophotometer, or in the solid state by using a reflectance attachment on a Beckman DK2A spectrophotometer. Magnetic susceptibilities were determined by the Gouy method. Molecular weight values were obtained in a Gallenkamp ebulliometer modified to take a 3.5 ml cell under argon atmosphere.

Analysis

Titanium was estimated by ashing a hydrolysed, sulphated pellet of the sample. Carbon, hydrogen and halide were determined by the Australian Microanalytical Service, Melbourne, by treating weighed pellets sealed in aluminium capsules.

Materials

Cp_2TiF_2[24], Cp_2TiCl[23], Cp_2TiBr_2[24] and Cp_2TiI_2[24] were prepared by published methods, while Cp_2TiCl_2 was available commercially. The solvents THF and diethyl ether were purified by distillation from $LiAlH_4$ under argon.

Activation of aluminium foil

The activation of the metal surface is critical and not all attempted reductions of Cp_2TiF_2 would go to completion. The following method proved the most successful.

A large excess of aluminium foil was cut up into pieces ≈ 1 cm^2 and placed under argon. A hot saturated solution of mercurous nitrate in degassed water was then added. After ca. 30 sec the mixture reacted vigorously and the foil formed a shining surface due to amalgamation; the liquid was removed under argon by means of a hypodermic syringe. Immediately the foil was swamped with dry deoxygenated THF and shaken vigorously. The liquid was removed and the washing repeated 4–5 times. After removing the last washing the foil was used immediately or dried and kept under dry argon.

$(Cp_2TiF)_2$

Yellow Cp_2TiF_2 (10 g) was stirred in THF (50 ml) with activated aluminium. At room temperature a green colouration was evident after 1 h. After 24 h, a light blue solid and an intense blue solution were present. The reaction mixture was pumped to dryness and the residue was heated in a sublimation apparatus at ca. 250°C (10^{-4} mmHg) giving dicyclopentadienyltitanium(III) fluoride (4.1 g, 41% yield) as a green crystalline sublimate. (Found: C, 60.9; H, 5.2; Ti, 23.9; mol.wt. ebulliometric in benzene, 404. $C_{10}H_{10}FTi$ calcd.: C, 61.0; H, 5.1; Ti, 24.3%; mol.wt. dimer, 394.)

$(Cp_2TiCl)_2$ and $(Cp_2TiBr)_2$

General method. The dihalide Cp_2TiX_2 (X=Cl or Br) was stirred in THF with excess activated aluminium foil until reduction was complete (generally 1 to 2 h). The excess aluminium was removed by filtration and the filtrate was pumped to dryness, then extracted several times with diethyl ether to remove aluminium halide as the etherate. $(Cp_2TiCl)_2$, yield 85%. (Found: Cl, 16.7; Ti, 21.8; mol.wt. ebulliometric in benzene, 410. $C_{10}H_{10}ClTi$ calcd.: Cl, 16.7; Ti, 22.4%; mol.wt. dimer, 426.) $(Cp_2TiBr)_2$, yield 79%. (Found: C, 46.3; H, 4.6; Br, 30.6; Ti, 18.5; mol.wt. ebulliometric in benzene, 447. $C_{10}H_{10}BrTi$ calcd.: C, 46.5; H, 3.9; Br, 31.0; Ti, 18.5%; mol.wt. dimer, 516.)

Synthesis of $(Cp_2TiI)_2$

Method I. Attempted reduction of Cp_2TiI_2 with activated aluminium in THF resulted in a dark brown slurry. The solution was decanted after settling and the mother-liquor was treated with diethyl ether. A red brown solid resulted which was extremely air-sensitive. The IR spectrum suggested that ether was still present even after prolonged pumping at $\approx 50°$. At higher temperatures decomposition occurred. The compound is believed to be the etherate $Cp_2TiI \cdot Et_2O$. (Found: C, 41.2; H, 5.7; I, 32.3; Ti, 13.9%. $C_{12}H_{20}IOTi$ calcd.: C, 44.2; H, 5.3; I, 33.5; Ti, 12.7%.)

Method II. Cp_2TiCl (2.1 g) was stirred with BI_3 (1.4 g) in benzene (60 ml) in the presence of aluminium foil. The mixture was stirred overnight at room temperature and the resulting red-brown solution was filtered to remove Al and the filtrate was reduced to low bulk. The red brown precipitate of dicyclopentadienyltitanium(III) iodide (2.1 g, 69% yield) was collected by filtration under argon and was washed with diethyl ether then pumped dry. (Found: C, 39.7; H, 3.3; I, 38.4; Ti, 15.8; mol.wt. ebulliometric in benzene, 590. $C_{10}H_{10}ITi$ calcd.: C, 39.4; H, 3.3; I, 41.5; Ti, 15.7%; mol.wt., 610.)

ACKNOWLEDGEMENT

One of the authors (RSPC) is grateful to the Division of Applied Chemistry, CSIRO, for leave of absence which enabled this work to be carried out at the Department of Inorganic Chemistry, University of Melbourne.

REFERENCES

1 R. S. P. Coutts and P. C. Wailes, *Advan. Organometal. Chem.*, 9 (1970)
2 K. Issleib and H. Häckert, *Z. Naturforsch. B*, 21 (1966) 519.
3 H. A. Martin and F. Jellinek, *J. Organometal. Chem.*, 12 (1968) 149 (and refs. therein).
4 H. Nöth and R. Hartwimmer, *Chem. Ber.*, 93 (1960) 2238.
5 D. S. Breslow and N. R. Newburg, *J. Amer. Chem. Soc.*, 81 (1959) 81.
6 G. Natta, G. Dall'astra, G. Mazzanti, U. Giannini and S. Cesca, *Angew. Chem.*, 71 (1959) 205.
7 G. Natta and G. Mazzanti, *Tetrahedron*, 8 (1960) 86.
8 G. Natta, G. Mazzanti, U. Giannini and S. Cesca, *Angew. Chem.*, 72 (1960) 39.
9 J. M. Birmingham, A. F. Fischer and G. Wilkinson, *Naturwissenschaften*, 42 (1955) 96.
10 J. J. Salzmann, *Helv. Chim. Acta*, 51 (1968) 526.
11 H. Brintzinger, *J. Amer. Chem. Soc.*, 89 (1967) 6871.
12 K. Clauss and H. Bestian, *Justus Liebigs Ann. Chem.*, 654 (1962) 8.
13 H. Nöth and R. Hartwimmer, *Chem. Ber.*, 93 (1960) 2246.
14 S. P. Gubin and S. A. Smirnova, *J. Organometal. Chem.*, 20 (1969) 229.
15 R. L. Martin and G. Winter, *J. Chem. Soc.*, (1965) 4709.

16 A. J. Canty, R. S. P. Coutts and P. C. Wailes, *Aust. J. Chem.*, 21 (1968) 807.
17 H. P. Fritz, *Advan. Organometal. Chem.*, 1 (1964)
18 E. Maslowsky Jr. and K. Nakamoto, *Appl. Spectrosc.*, 25 (1971) 187.
19 B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, (1956) 3837.
20 Ref. 1, p. 169.
21 M. F. Lappert and A. R. Sanger, *J. Chem. Soc. A*, (1971) 1314.
22 M. F. Lappert and A. R. Sanger, *J. Chem. Soc. A*, (1971) 874.
23 A. F. Reid and P. C. Wailes, *Aust. J. Chem.*, 18 (1965) 9.
24 P. M. Druce, B. M. Kingston, M. F. Lappert, T. R. Spalding and R. C. Srivastava, *J. Chem. Soc. A*, (1969) 2106.
25 P. C. Wailes and H. Weigold, *J. Organometal. Chem.*, in preparation.