[Contribution from Stamford Laboratories, Research Division, American Cyanamid Company]

Cyclopentadienyltitanium Trihalides and Bis-cyclopentadienyltitanium Dihalides

By Carol L. Sloan and William A. Barber

Received July 29, 1958

Cyclopentadienyltitanium trihalides, new compounds containing only one cyclopentadienyl ring per molecule, have been prepared by reacting magnesium cyclopentadienide with a titanium tetrahalide. In addition, a new method has been developed for the preparation of bis-cyclopentadienyltitanium dihalides. Evidence is presented in support of an "open-sandwich" structure for the single-ring compounds.

Bis-cyclopentadienyltitanium dihalides have been known for several years. They have been prepared by the reaction of titanium tetrachloride with sodium[1] or lithium[2,3] cyclopentadienide or the cyclopentadienyl Grignard[1] and subsequent displacement of chlorine by the desired halogen. Small yields of the dichloride have been obtained by the direct reaction of cyclopentadiene with titanium tetrachloride in the presence of base.[4] Similar compounds containing *one* π-bonded cyclopentadiene ring per molecule have been reported only in cases where the central metal atom is bonded also to nitrosyl[5-7] or carbonyl [6-8] groups, is part of a chelate ring[9] or is bonded to oxygen.[10]

This paper reports the synthesis of simple single-ring cyclopentadienyltitanium trihalides, as well as an alternate method for the preparation of the bis-cyclopentadienyltitanium dihalides.[11]

Experimental

Materials.—All preparations were carried out in an atmosphere of prepurified nitrogen. The titanium tetrachloride (Matheson Coleman & Bell) was 99% pure. Titanium tetrabromide, titanium tetraiodide and dichlorotitanium diiodide (minimum purity 90%) were supplied by Rocky Mountain Research, Inc., Denver, Colorado. Magnesium cyclopentadienide was prepared by the reaction of monomeric cyclopentadiene with magnesium turnings (Baker and Adamson) at 500–600°.[12] The cyclopentadiene monomer was prepared by cracking Enjay dicyclopentadiene. Aromatic hydrocarbons used as solvents were freshly distilled from sodium. To ensure dryness, bottles of petroleum ether, b.p. 30–60° (Baker & Adamson), and chloroform (J. T. Baker) were freshly opened for each application.

General Method of Preparation.—The cyclopentadienyltitanium trihalides and bis-cyclopentadienyltitanium dihalides are prepared in an inert atmosphere from solutions of magnesium cyclopentadienide and the appropriate titanium tetrahalide. Generally, a 1:2 mole ratio of $Mg(C_5H_5)_2$ to TiX_4 seems to favor the formation of the single-ring compounds while a 1:1 mole ratio favors the formation of the double-ring compounds, but since the rate and order of addition also affect the nature of the product, mixtures often result.

After the addition of reagents, the mixture is stirred rapidly for several hours at the appropriate temperature as noted below, filtered, concentrated and kept in the dark. Single-ring compounds, especially $TiC_5H_5I_3$, require long periods for crystallization (in extreme cases 3–5 weeks). After the mother liquor is poured off, the crystalline product is washed rapidly by decantation with petroleum ether, which tends to suspend the contaminants, and poured onto a Büchner funnel, where it is quickly covered with a rubber sheet, dried by suction and stored under nitrogen.

Attempts to prepare $TiC_5H_5Cl_3$ from $TiCl_4$ and sodium cyclopentadienide in both xylene and tetrahydrofuran have shown this method to be less satisfactory. Even when 100% excess of $TiCl_4$ is used, both the dichloride and trichloride form at room temperature, and on refluxing the trichloride seems to be destroyed.

Analyses.—Titanium was determined colorimetrically according to the method of A. Weller.[13] Chlorine was titrated directly by the Volhard method. Compounds containing bromine were refluxed with 1 *N* sodium hydroxide until clear and colorless and titrated electrometrically with 0.01 *N* silver nitrate. Iodine-containing compounds were destroyed by the Schöniger combustion technique and titrated with sodium thiosulfate.

Molecular Weights.—These were determined ebullioscopically in chloroform. Cryoscopic measurements of molecular weight in benzene yield values which are very much higher than the theoretical for both cyclopentadienyltitanium trichloride and bis-cyclopentadienyltitanium dichloride. This behavior might be due to association in this poorly solvating medium.

Melting Points.—Values below 300° were measured with a Fisher–Johns apparatus. For melting points above 300°, the compound was sealed in a capillary inserted in a heated aluminum block. All melting points are uncorrected. In all cases decomposition occurred on melting.

Cyclopentadienyltitanium Trichloride.—To 21.3 g. of magnesium cyclopentadienide (0.138 mole) in 600 ml. of xylene was added 30 ml. of xylene containing 52.0 g. of titanium tetrachloride (0.274 mole). The mixture was maintained at reflux for 3.5 hr. On cooling, orange crystals formed. These were isolated by decantation of the supernatant xylene slurry which was then filtered by suction to yield a black filter cake and a clear orange solution. Concentration of this solution under nitrogen yielded more orange crystals. Additional product was obtained by Soxhlet extraction of the filter cake with xylene in an inert atmosphere. A total of 47.3 g. of cyclopentadienyltitanium trichloride, orange crystals melting at 145.5–147° dec., was obtained in this experiment (78% of the theoretical based on the magnesium cyclopentadienide). This material can be recrystallized from xylene if care is taken to exclude air, light and moisture.

Anal. Calcd. for $TiC_5H_5Cl_3$: C, 27.37; H, 2.30; Cl, 48.48; Ti, 21.83; mol. wt., 219.3. Found: C, 27.72; H, 2.65; Cl, 48.42; Ti, 21.8; mol. wt., 224.

Bis-cyclopentadienyltitanium Dichloride.—To 42.8 g. of magnesium cyclopentadienide (0.277 mole) dissolved in 700 ml. of xylene was added a solution of 52.7 g. of titanium

---

[1] G. Wilkinson and J. M. Birmingham, This Journal, **76**, 4281 (1954).

[2] L. Summers and R. H. Uloth, Project NR 356 281, Interim Tech. Report, "Organometallic Chemistry of Transition Metals," Navy Contract Nonr-582(00), Univ. of N. Dakota, March 15, 1955.

[3] L. Summers, R. H. Uloth and A. Holmes, This Journal, **77**, 3604 (1955).

[4] J. M. Birmingham, D. Seyferth and G. Wilkinson, *ibid.*, **76**, 4179 (1954).

[5] T. S. Piper and G. Wilkinson, *J. Inorg. & Nuclear Chem.*, **3**, 104 (1956).

[6] T. S. Piper, F. A. Cotton and G. Wilkinson, *ibid.*, **1**, 165 (1955).

[7] T. S. Piper and G. Wilkinson, *ibid.*, **2**, 38 (1956).

[8] E. O. Fischer and W. Hafner, *Z. Naturforsch.*, **10b**, 140 (1955).

[9] J. C. Thomas, *Chemistry & Industry*, 1388 (1956).

[10] D. F. Herman, Paper No. 68, Division of Industrial and Engineering Chemistry, 131st National A.C.S. Meeting, Miami, Fla., April 7 to 12, 1957.

[11] After this paper was submitted for publication, a Communication to the Editor appeared [R. D. Gorsich, This Journal, **80**, 4744 (1958)] describing a preparation of "cyclopentadienyltitanium trichloride." The author reports it to be a yellow crystalline solid, melting with decomposition at about 185° in sharp disagreement with the experimental data obtained in these laboratories. In spite of the discrepancy in properties and in view of the additional information reported herein, no change has been made as a result of Gorsich's paper.

[12] W. A. Barber, *J. Inorg. & Nuclear Chem.*, **4**, 373 (1957).

[13] F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 159.

tetrachloride (0.278 mole) in 25 ml. of xylene. The mixture was refluxed with constant stirring for 3.5 hr. and on cooling yielded a crop of bright red crystals which were separated from the reaction mixture by decantation. The reaction mixture was then filtered to yield a black filter cake and a clear red xylene solution from which more of the red product was obtained. Additional solid was crystallized from the chloroform solutions obtained by Soxhlet extraction of the filter cake. The product, obtained in 24% yield and recrystallized preferably from chloroform or xylene, melts at 287–287.5° dec.

Anal. Calcd. for $Ti(C_5H_5)_2Cl_2$: C, 48.23; H, 4.05; Cl, 28.48; Ti, 19.24; mol. wt., 249.0. Found: C, 48.31; H, 4.10; Cl, 28.50; Ti, 19.2; mol. wt., 251.

In other preparations using an intermediate mole ratio of reactants, mixtures of the dichloride and trichloride were obtained. It has also been found that $Ti(C_5H_5)_2Cl_2$ will react with $TiCl_4$ to produce some $TiC_5H_5Cl_3$.

Cyclopentadienyltitanium Tribromide.—To a solution of 8.6 g. of titanium tetrabromide (0.023 mole) in 25 ml. of toluene was added dropwise and with constant stirring about 50 ml. of toluene solution containing 1.8 g. of magnesium cyclopentadienide (0.012 mole). The reaction mixture was stirred at room temperature for 1.5 hr. and filtered. Concentration of the filtrate under a heavy stream of nitrogen for a total of about 40 hr. yielded a crop of bright orange crystals (25% of the theoretical yield based on $TiBr_4$), m.p. 174.5–175.5° dec.

Anal. Calcd. for $TiC_5H_5Br_3$: C, 17.02; H, 1.43; Br, 67.97; Ti, 13.58. Found: C, 17.7; H, 1.8; Br, 68.1; Ti, 13.7.

Bis-cyclopentadienyltitanium Dibromide.—In this experiment, 8.6 g. of titanium tetrabromide (0.023 mole) in 25 ml. of toluene was added rapidly to 1.8 g. of magnesium cyclopentadienide (0.012 mole) in about 50 ml. of toluene, and the mixture was stirred at room temperature for 4 hr. Filtration and subsequent evaporation of the filtrate yielded only a small amount of dark red crystals of bis-cyclopentadienyltitanium dibromide, m.p. 309–310° dec.

Anal. Calcd. for $Ti(C_5H_5)_2Br_2$: C, 35.54; H, 2.98; Br, 47.30; Ti, 14.17. Found: C, 35.1; H, 3.0; Br, 48.1; Ti, 14.1.

Cyclopentadienyltitanium Triiodide.—To 18 g. of titanium tetraiodide (0.032 mole), only partially dissolved in 400 ml. of toluene, was added very slowly and with constant stirring about 75 ml. of a toluene solution containing 2.5 g. of magnesium cyclopentadienide (0.016 mole). After the mixture was stirred at room temperature for about 10 hr., filtration yielded some of the diiodide. Concentration of the filtrate by distillation under nitrogen yielded a small portion of deep red crystals of impure cyclopentadienyltitanium triiodide, m.p. 184–186° dec.

Anal. Calcd. for $TiC_5H_5I_3$: C, 12.16; H, 1.02. Found: C, 13.0; H, 1.3.

Bis-cyclopentadienyltitanium Diiodide.—Twenty-five grams of titanium tetraiodide (0.045 mole) was suspended in 200 ml. of xylene. To this mixture was added about 100 ml. of xylene solution containing 7.0 g. of magnesium cyclopentadienide (0.045 mole). The mixture was stirred rapidly for 2 hr. at room temperature and 3.5 hr. at reflux. On cooling, decantation and filtration yielded a black filter cake, a large crop of purple-black crystals remaining in the reaction flask and a dark purple filtrate which yielded more of the product, m.p. 317–318° dec., for a total of 18.9 g. [97% of the theoretical yield of $Ti(C_5H_5)_2I_2$ based on $Mg(C_5H_5)_2$].

Anal. Calcd. for $Ti(C_5H_5)_2I_2$: C, 27.81; H, 2.33; I, 58.77; Ti, 11.09. Found: C, 28.8; H, 2.6; I, 58.1; Ti, 10.9.

In another preparation, 30 ml. of a toluene solution containing 1.95 g. of magnesium cyclopentadienide (0.013 mole) was added to 4.7 g. of dichlorotitanium diiodide (0.013 mole) dissolved in 50 ml. of toluene. The reaction mass was stirred for about 12 hr. at room temperature and filtered through paper directly into a flask flushed continually with nitrogen. Successive crystallizations from the purple-black filtrate yielded bis-cyclopentadienyltitanium diiodide as the sole product.

Infrared Spectra.—The infrared absorption spectra of the cyclopentadienyltitanium trihalides and bis-cyclopentadienyltitanium dihalides in mineral oil (Nujol) were obtained using a Perkin-Elmer Model 21 double beam infrared spectrophotometer with rock-salt optics. The C–H regions were studied using hexachlorobutadiene mulls.

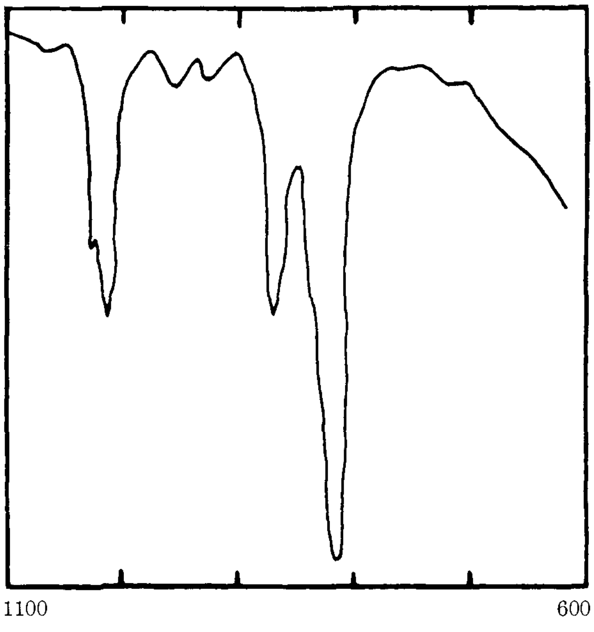

Fig. 1.—Infrared absorption spectrum of $Ti(C_5H_5)_2Cl_2$.

Although the spectra of $Ti(C_5H_5)_2Cl_2$ and $TiC_5H_5Cl_3$ from 1100 to 4000 cm.$^{-1}$ are very similar, the spectra are easily distinguishable in the region 600–1100 cm.$^{-1}$. The intense broad band near 770 cm.$^{-1}$ seen in Fig. 2 is characteristic of each of the single-ring compounds studied, whereas absorption at this wave length does not occur in pure $Ti(C_5H_5)_2Cl_2$ (as shown in Fig. 1) nor in any of the dihalides studied.

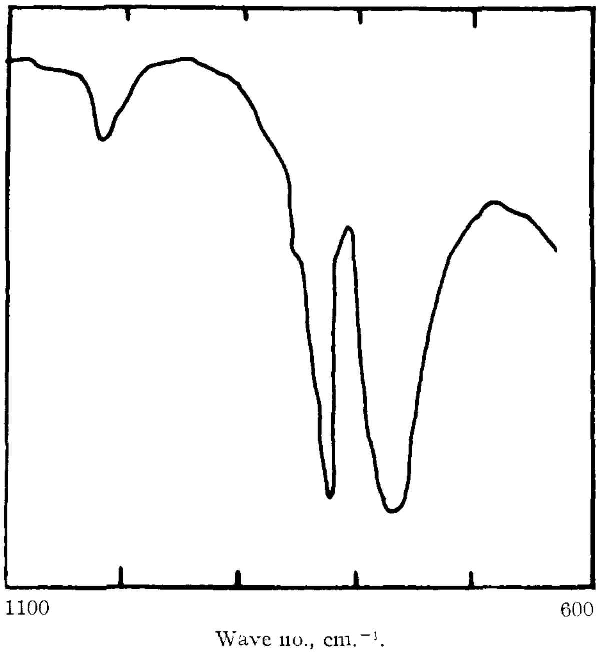

Fig. 2.—Infrared absorption spectrum of $TiC_5H_5Cl_3$.

Nuclear Magnetic Resonance Spectra.—N.m.r. proton spectra were obtained using a Varian V3000B Super High Resolution Spectrometer operating at 40 megacycles and equipped with a field stabilizer. High sensitivity and resolution were obtained by spinning saturated tetrahydrofuran solutions sealed in 5 mm. Pyrex glass tubes. The lower of the two major solvent peaks, which occurs 124 c.p.s. to the high field side of benzene, was used for reference (position established by inserting a benzene capillary in a tube containing pure tetrahydrofuran). The shift of the characteristic cyclopentadienyl peak to the low field side of the reference point was measured at 25° as follows: $Ti(C_5H_5)_2Cl_2$, 117 c.p.s.; $Ti(C_5H_5)_2I_2$, 129 c.p.s.; $Zr(C_5H_5)_2Cl_2$, 112 c.p.s.; $TiC_5H_5Cl_3$, 141 c.p.s.

Properties.—The cyclopentadienyltitanium trihalides are more unstable to hydrolysis, heat and light than the corresponding dihalides. Within both groups chemical instability increases with the size of the halogen atom. Although dry crystals of the trichloride have on occasion remained unchanged for several hours in moist air, refluxing of the trichloride in water for about an hour first causes the formation of a bright yellow compound containing both the cyclopentadienyl ring and OH, but continued refluxing soon ruptures the ring-to-metal bond.

Cyclopentadienyltitanium trihalides are fairly soluble in aromatic hydrocarbons, chloroform and quite soluble in polar solvents such as tetrahydrofuran. In general, the trihalide is somewhat more soluble than the corresponding dihalide in a given solvent. Compounds of both groups seem to react with lower alcohols.

Discussion

Structure.—Several structures might be proposed for a compound of the empirical formula $[TiC_5H_5Cl_3]_x$

(1) if $x = 1$, the simple compound $TiC_5H_5Cl_3$
(2) if $x = 2$, an ionic compound of the form $Ti(C_5H_5)_2{}^{++}$-$TiCl_6{}^{=}$, or
(3) a dimer containing bridged chlorine atoms with a structure similar to that proposed for the complex $Ti(C_5H_5)_2Cl_2Al(C_2H_5)_2$.[14]

Molecular weight data obtained for solutions of this compound in chloroform preclude the third possibility. The ionic compound, $Ti(C_5H_5)_2{}^{++}$ $TiCl_6{}^{=}$, if it were wholly ionized in chloroform, could not be distinguished from the simple compound, $TiC_5H_5Cl_3$, by molecular weight data, but conductivity measurements made on these solutions show that there is no appreciable ionization in chloroform. This is, therefore, a monomeric compound having one cyclopentadienyl ring per molecule.

Ring-to-Metal Bond.—Moffitt[15] characterizes the cyclopentadienyl radical in bis-cyclopentadienyltitanium dibromide (as well as in ferrocene, nickelocene, etc.) as a five-membered aromatic ring bonded to the central metal atom through the π orbitals. The evidence suggests that such a structure exists also in $TiC_5H_5Cl_3$.

The infrared spectra of $TiC_5H_5Cl_3$ and $Ti(C_5H_5)_2Cl_2$ are strikingly similar. The presence of a single band in the C–H stretch (3110 cm.$^{-1}$) and C–H bend regions (1445 cm.$^{-1}$) and the absence of peaks in the C═C stretch region (1575–1700 cm.$^{-1}$) suggest for the ring a resonance structure in which there are no formal double bonds.

As further evidence for π-bonding, $TiC_5H_5Cl_3$ absorbs ultraviolet radiation in the region 320–375 mμ. Compounds possessing conjugated double bonds such as bis-cyclopentadienylmercury[16] and homologs of cyclopentadiene absorb at 240–250 mμ and rarely above 300 mμ.

Proton magnetic resonance spectra obtained for solutions of $TiC_5H_5Cl_3$, $Ti(C_5H_5)_2Cl_2$, $Ti(C_5H_5)_2I_2$ and $Zr(C_5H_5)_2Cl_2$ in tetrahydrofuran show that all these compounds display one very sharp single peak 110–150 c.p.s. below the lower of the two strong peaks in tetrahydrofuran. These data are consistent with a structure in which all the protons are equivalent.

Since titanium appears capable of forming "open-sandwich" compounds, other metals such as Zr, V, Fe, Co and Cr might also form such derivatives.

Acknowledgments.—We wish to thank Mrs. E. C. Grim and her associates and E. H. Burroughs for the analytical data, N. Colthup for the infrared data and Dr. J. Lancaster for his kind assistance with n.m.r. and structural considerations.

STAMFORD, CONNECTICUT

---

(14) G. Natta, P. Corradini and I. W. Bassi, THIS JOURNAL, **80**, 755 (1958).

(15) W. Moffitt, *ibid.*, **76**, 3386 (1954).

(16) G. Wilkinson and T. S. Piper, *J. Inorg. Nuclear Chem.*, **2**, 32 (1956).