

*Anal.* Calcd. for  $[\text{Co}(\text{C}_2\text{H}_5\text{N}_2)_2(\text{C}_2\text{O}_4)]\text{Cl}\cdot\text{H}_2\text{O}$ : C, 22.48; H, 5.66; N, 17.48. Found: C, 22.70; H, 5.76; N, 17.69.

*d*-Oxalatobisethylenediamine-cobalt(III) Iodide.—The *dl*-chloride, above, (12.84 g.) in water (80 ml., 65°), was shaken with silver acetate (6.4 g.) for 10 min. The silver chloride was removed and washed with hot water. To the filtrate at 60° was added *L*-K[CoEDTA]·2H<sub>2</sub>O (8.44 g.) and dissolved by shaking. Almost immediately the diastereoisomer *d*-[Coen<sub>2</sub>C<sub>2</sub>O<sub>4</sub>]-*L*-[Co(EDTA)]·3H<sub>2</sub>O commenced to separate, and the mixture was allowed to cool slowly to room temperature. The pink-violet diastereoisomer was then collected, washed with ice-water and then ethanol and air-dried (yield, 10.7 g.,  $[\alpha]_D = +550^\circ$ ).

*Anal.* Calcd. for  $[\text{Co}(\text{C}_2\text{H}_5\text{N}_2)_2(\text{C}_2\text{O}_4)]\text{I}\cdot\text{H}_2\text{O}$ : C, 28.75; H, 5.13; N, 12.58. Found: C, 29.0; H, 4.91; N, 12.63.

The diastereoisomer was ground up with water (50 ml.) containing potassium iodide (10 g.) and the insoluble *d*-iodide collected. The resolving agent was recovered from the filtrate by adding alcohol (yield, 7.2 g., 85%). The *d*-iodide

(7.0 g.) was recrystallized from a large volume of hot water. By standard methods using the appropriate silver salts, the chloride, bromide and sulfate were prepared. The specific rotations  $[\alpha]_D$  were: [Coen<sub>2</sub>C<sub>2</sub>O<sub>4</sub>]I, +720°; [Coen<sub>2</sub>C<sub>2</sub>O<sub>4</sub>]Br·H<sub>2</sub>O, +820°; [Coen<sub>2</sub>C<sub>2</sub>O<sub>4</sub>]Cl·H<sub>2</sub>O, +930°; [Coen<sub>2</sub>C<sub>2</sub>O<sub>4</sub>]<sub>2</sub>·SO<sub>4</sub>·7H<sub>2</sub>O, +800°.

*Anal.* Calcd. for  $[\text{Co}(\text{C}_2\text{H}_5\text{N}_2)_2(\text{C}_2\text{O}_4)]\text{I}$ : C, 18.28; H, 4.09; N, 14.22. Found: C, 18.51; H, 4.16; N, 13.90.

*l*-Oxalatobis-(ethylenediamine)-cobalt(III) Bromide 1-Hydrate.—The filtrate from the separation of the diastereoisomer above was treated at 60° with 50% aqueous ammonium bromide (20 ml.) and the crystalline *l*-bromide collected after cooling. It was recrystallized once from hot water (yield, 6.1 g., 83%;  $[\alpha]_D = -820^\circ$ ).

*Anal.* Calcd. for  $[\text{Co}(\text{C}_2\text{H}_5\text{N}_2)_2(\text{C}_2\text{O}_4)]\text{Br}\cdot\text{H}_2\text{O}$ : C, 19.74; H, 4.97; N, 15.35. Found: C, 19.80; H, 4.90; N, 15.38.

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[CONTRIBUTION FROM THE RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL COMPANY, DAYTON, OHIO]

## A Metal Carbonyl Compound of Titanium<sup>1</sup>

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A metal carbonyl derivative of titanium, bis-(cyclopentadienyl)-titanium dicarbonyl, has been prepared and some of its properties and reactions are reported. Attempts to prepare a zirconium carbonyl by methods analogous to those used in the preparation of the titanium carbonyl were unsuccessful.

Well characterized metal carbonyls of the group VIB and group VIII transition metals have been known for many years.<sup>3</sup> More recently carbonyls of the group VIIB metals manganese and rhenium and of a group VB metal vanadium have been described and characterized.<sup>4</sup> The discovery of the cyclopentadienyl metal compounds having the "sandwich" structure has led to the discovery of a variety of hybrid metal derivatives containing both cyclopentadienyl and carbon monoxide groups for those metals known to form carbonyls.<sup>5</sup> Thus, carbonyls and mixed cyclopentadienyl metal carbonyls have been described for metals in Groups VB-VIII.

A cyclopentadienyl metal carbonyl of titanium, a group IVB metal, now has been prepared. This compound was prepared most readily by the reaction of titanium tetrachloride with more than four equivalents of cyclopentadienylsodium and subsequent treatment with carbon monoxide under pressure; the product was bis-(cyclopentadienyl)-titanium dicarbonyl (I). Carbonyl (I) was also prepared by reaction of bis-(cyclopentadienyl)-titanium dichloride (II) with more than two equiva-

lents of either cyclopentadienylsodium or butyllithium and then reaction with carbon monoxide.

There are several possible intermediates in the reaction to form I. Presumably, reaction of II with the metal alkyl initially yields a dialkyl bis-(cyclopentadienyl)-titanium. Examples of such compounds are known although they appear to be thermally unstable.<sup>6</sup> Decomposition of the dialkyl bis-(cyclopentadienyl)-titanium might form bis-(cyclopentadienyl)-titanium<sup>7</sup> as the active intermediate. In the case of reaction of titanium tetrachloride or II with cyclopentadienylsodium, a possible intermediate is tris-(cyclopentadienyl)-titanium. This compound has been isolated by Fischer and Lochner<sup>8</sup> since the original report of the preparation of I. Fischer and Lochner prepared tris-(cyclopentadienyl)-titanium in low yield by the reaction of II with excess cyclopentadienylsodium and converted it to I by heating with carbon monoxide. The low yield in the preparation of tris-(cyclopentadienyl)-titanium may have been due to difficulties in its isolation rather than an inherently low yield in the preparation.

The carbonyl was not formed by reaction of II with carbon monoxide or by reaction of diphenyl bis-(cyclopentadienyl)-titanium<sup>9</sup> with carbon monoxide.

The red-brown needles of I melt above 90° with decomposition. The carbonyl reacts extremely readily with oxygen and is immediately pyrophoric in air but is stable for a period of at

(1) For a preliminary communication see *J. Am. Chem. Soc.*, **81**, 752 (1959).

(2) General Electric Research Laboratory, P. O. Box 1088, Schenectady, New York.

(3) J. S. Anderson, *Quart. Rev. (London)*, **1**, 331 (1947). J. W. Cable and R. K. Sheline, *Chem. Revs.*, **56**, 1 (1956).

(4) (a) W. Hieber and H. Fuchs, *Z. Anorg. Chem.*, **248**, 256 (1941). (b) E. O. Brimm, M. A. Lynch, Jr., and W. J. Sesny, *J. Am. Chem. Soc.*, **76**, 3831 (1954). (c) L. F. Dahl, E. Ishishi and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957). (d) F. Calderazzo, R. Cini, P. Corradini, R. Ercoli and G. Natta, *Chem. and Ind. (London)*, 500 (1960).

(5) For example, see G. Wilkinson and F. A. Cotton in "Progress in Inorganic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1959, p. 1.

(6) K. Clauss, *et al.*, German Pat. App. No. F20038 (to Farbwerke Hoechst, April 13, 1956). T. S. Piper and G. Wilkinson, *J. Inorg. and Nuclear Chem.*, **3**, 104 (1956).

(7) A. K. Fischer and G. Wilkinson, *ibid.*, **2**, 149 (1956).

(8) E. O. Fischer and A. Lochner, *Z. Naturforsch.*, **15b**, 266 (1960).

(9) L. Summers, R. H. Uloth and A. Holmes, *J. Am. Chem. Soc.*, **77** 3604 (1955).

least several months in sealed vials under nitrogen. It can be sublimed at 90° and 1 mm. with appreciable decomposition. It is readily soluble in the common organic solvents (with a limited solubility even in hexane) but is decomposed by chlorinated solvents. Solutions of the carbonyl deposit an insoluble yellow solid on exposure to air. The solid carbonyl evolved over 90% of the theoretical amount of carbon monoxide (assuming both carbon monoxide groups were liberated) on being treated with iodine solution.<sup>10</sup> This reaction served as a convenient method for analysis of crude solutions of the carbonyl.

Attempts to obtain the molecular weight of I were unsuccessful. The monomeric structure for the carbonyl was proposed for several reasons. The infrared spectra of I in benzene or tetrahydrofuran solution showed two strong bands in the metal carbonyl region at 5.09 and 5.31 microns. These bands are at somewhat longer wave lengths than is common for terminal carbon monoxide groups,<sup>11</sup> but they are not in the carbonyl bridging region and are not out of line with the trend of absorption spectra for the monomeric cyclopentadienyl metal carbonyls from cobalt through manganese and vanadium.<sup>12</sup> Treating the carbonyl with concentrated aqueous hydrochloric acid gave what was probably impure II. Also, the monomeric structure having  $\pi$  bonded cyclopentadienyl groups and two carbon monoxide groups would have the krypton configuration and should therefore be stable.

Several attempts to prepare a cyclopentadienyl zirconium carbonyl by methods analogous to those used in the preparation of the titanium compound were unsuccessful.

**Acknowledgment.**—The author wishes to thank the Instrumental Analysis Group under the direction of Donald R. Beasecker for the infrared spectra and gas phase chromatography data.

### Experimental<sup>13</sup>

**Bis-(cyclopentadienyl)-titanium Dicarboxyl (I).** (a) **Preparation from Bis-(cyclopentadienyl)-titanium Dichloride (II) and Cyclopentadienyl Sodium.**—Cyclopentadienyl sodium was prepared in liquid ammonia from 7.6 g. of sodium (as sodium amide<sup>14</sup>) and 27.3 g. of freshly distilled cyclopentadiene. The resulting mixture was warmed to remove most of the ammonia and 300 ml. of benzene (or tetrahydrofuran) then added. This mixture was refluxed for 10 minutes to remove excess ammonia and then cooled to room temperature under dry nitrogen (General Electric Company Lamp Grade). To this solution was added 37.4 g. (0.15 mole) of bis-(cyclopentadienyl)-titanium dichloride (II) and the resulting mixture stirred 0.5 hr. at room temperature under nitrogen and then heated to reflux for an hour. The mixture was added to a 1-l. rocking autoclave under nitrogen and the autoclave purged and pressurized with carbon monoxide to a pressure of 110 atm. The autoclave was heated to 100° for 8 hr. After cooling, the contents were removed under

nitrogen and the autoclave washed out with air-free benzene.

In this manner there was obtained 400 g. of dark red-brown solution of the carbonyl in benzene (or tetrahydrofuran). Measurement of the gas evolved on treatment of an aliquot of this solution with iodine in toluene<sup>10</sup> indicated that the conversion to carbonyl based on II was 50%.

To isolate the pure carbonyl a solution of the crude carbonyl in benzene, which by the iodine analysis contained 2.22 g. of the carbonyl, was placed in a double "Schlenk" tube (all operations under General Electric Company Lamp Grade nitrogen and using deaerated solvents) and the benzene removed by distillation at reduced pressure. The residue was treated with 100 ml. of hot hexane, the solution filtered and the residue again extracted with an additional 30 ml. of hot hexane. The filtrate was cooled overnight over Dry Ice. The red-brown needles which formed were removed by filtration, washed thoroughly with cold hexane and dried at room temperature *in vacuo*. There was isolated 0.8 g. (18% over-all yield) of red-brown needles which decomposed above 90° under nitrogen.

*Anal.* Calcd. for  $C_{15}H_{10}TiO_2$ : C, 61.56; H, 4.31; Ti, 20.46. Found: C, 61.56; H, 4.55; Ti, 20.38.

(b) **Preparation from Titanium Tetrachloride and Cyclopentadienyl Sodium.**—Cyclopentadienyl sodium was prepared in liquid ammonia as above from 18.4 g. (0.8 mole) of sodium and 52.8 g. (0.8 mole) of cyclopentadiene; most of the ammonia was removed and replaced with dry benzene. After refluxing for 10 minutes to remove excess ammonia the mixture was cooled to room temperature under nitrogen and a solution of 28.4 g. (0.15 mole) of titanium tetrachloride added and the resulting mixture stirred 1.5 hr. at room temperature. This solution was charged to the bomb and heated under carbon monoxide as above. The product was removed from the bomb, filtered and the solution analyzed for carbonyl by titration with iodine.<sup>10</sup> Analysis indicated that the over-all conversion to carbonyl was 45%. Infrared analysis showed the strong metal carbonyl bands at 5.09 and 5.31 microns.

(c) **Preparation from Bis-(cyclopentadienyl)-titanium Dichloride (II) and Butyl Lithium.**—Butyl lithium was prepared by the method of Gilman<sup>15</sup> from 2.6 g. (0.375 mole) of lithium and 20.8 g. (0.15 mole) of *n*-butyl bromide in 80 ml. of ether. To this solution at -10° was added 16.9 g. (0.07 mole) of bis-(cyclopentadienyl)-titanium dichloride (II). The mixture was stirred 1 hr. under nitrogen allowing it to warm to room temperature. It was then charged to a 300 ml. rocking bomb, pressured to 240 atm. with carbon monoxide and heated to 150° for 8 hr. The product had the characteristic metal carbonyl bands in the infrared and evolved carbon monoxide on treatment with iodine solution.

**Reaction of I with Iodine.**—To determine whether the iodine analysis method<sup>10</sup> could be applied to the carbonyl, a sample of the solid carbonyl (0.1278 g.) was added to a 5% solution of iodine in toluene. In a few minutes 22.8 ml. (corrected to S.T.P.) of carbon monoxide was evolved. This represents 92% of the theoretical amount of carbonyl assuming both molecules of carbon monoxide are evolved.

**Reaction of I with Hydrochloric Acid.**—A sample of the solid carbonyl was treated with concentrated aqueous hydrochloric acid under nitrogen overnight. During this time the solid turned bright red and gas was evolved. The resulting solid was then dissolved in ethylene dichloride, the solution filtered to remove a trace of insoluble material and the red solid precipitated by the addition of hexane. The red solid (m.p. dec. above about 260°) was probably an impure sample of II; m.p. reported for bis-(cyclopentadienyl)-titanium dichloride (II), 289–291°.

*Anal.* Calcd. for  $C_{10}H_{10}TiCl_2$ : C, 48.23; H, 4.05; Ti, 19.24; Cl, 28.68. Found: C, 48.75; H, 4.30; Ti, 17.93; Cl, 26.73.

On reaction of the carbonyl with 2.8 *N* HCl in ethanol, 90% of the theoretical amount of carbon monoxide was evolved, but the red color of bis-(cyclopentadienyl)-titanium dichloride (II) was not observed; the solution was light green and none of the dichloride II could be isolated.

**Bis-(cyclopentadienyl)-zirconium Dichloride.**—This compound was prepared by reaction of zirconium tetrachloride (186 g., 0.8 mole) with cyclopentadienyl sodium (from

(10) H. W. Sternberg, I. Wender and M. Orchin, *Anal. Chem.*, **24**, 174 (1952).

(11) F. A. Cotton in "Modern Coordination Chemistry," Edited by J. Lewis and R. G. Wilkins, Interscience Publishers, Inc., New York, N. Y., 1960, p. 344.

(12) F. A. Cotton, A. D. Liehr and G. Wilkinson, *J. Inorg. and Nuclear Chem.*, **1**, 175 (1955).

(13) The microanalyses were performed by the Schwartzkopf Microanalytical Laboratory, Woodside 77, New York.

(14) C. R. Hauser, F. W. Swamer and J. T. Adams, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 122.

(15) H. Gilman, *et al.*, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

36.8 g., 1.6 moles of sodium) in refluxing benzene. No apparent reaction occurred until the mixture had been refluxed for 30 minutes; an exothermic reaction then started and some of the benzene boiled out of the top of the condenser and the product in the flask set up to a solid mass. This product was recrystallized from benzene yielding 109 g. (47%) of bis-(cyclopentadienyl)-zirconium dichloride, m.p. 241–243°.

*Anal.* Calcd. for  $C_{10}H_{10}ZrCl_2$ : C, 41.09; H, 3.45; Cl, 24.26; Zr, 31.21. Found: C, 41.10; H, 3.81; Cl, 24.30; Zr, 31.15.

**Attempts to Prepare Carbonyls of Zirconium.**—Zirconium tetrachloride in tetrahydrofuran was treated with four equivalents of cyclopentadienyl sodium at room temperature and the resulting product heated with carbon monoxide or carbon monoxide–hydrogen to 150° at 280 atm. for 8 hr. The product showed no characteristic metal carbonyl infrared bands and did not evolve carbon monoxide on treatment with iodine. Also, reaction of bis-(cyclopentadienyl)-zirconium dichloride with butyl lithium followed by reaction with carbon monoxide–hydrogen at 150° and 280 atm. gave no product identifiable as a zirconium carbonyl.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CONNECTICUT, STORRS, CONNECTICUT]

## Replacement of Potassium Ions in Solid Potassium Hexatitanate by Sodium Ions from a Chloride Flux

BY ARTHUR L. PLUMLEY AND WILLIAM C. ORR

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Samples of fibrous potassium hexatitanate,  $K_2Ti_6O_{13}$ , were heated in a flux containing various mixtures of radiosodium chloride, sodium chloride and potassium chloride to study the replacement of potassium ions by sodium ions and to attempt the preparation of sodium hexatitanate having the same fibrous character as the potassium compound. An equilibrium constant of unity is indicated for the system  $Na_{melt} + K_{solid} \rightleftharpoons Na_{solid} + K_{melt}$ . The exchange studies using  $Na^{22}Cl$  in the melt and X-ray studies indicate preparation of sodium hexatitanate. Preliminary microscopic examination of the compound reveals that it too is fibrous in nature.

### Introduction

Potassium hexatitanate,  $K_2Ti_6O_{13}$ , recently has been prepared<sup>1</sup> in the form of slender, fibrous crystals. This physical form and its high melting point (1370°) suggested its use as a solid phase in studies of the distribution of ions between solids and molten salts. When a sample was heated in a low-melting  $NaCl$ – $NaNO_3$  flux containing sodium-22 as a tracer, the radioactivity acquired by the solid indicated an appreciable replacement of potassium by sodium. Carried out quantitatively, a series of such experiments could be expected to show whether or not the process was reversible, whether equilibrium was attained and whether complete exchange of one cation by the other was possible.

### Experimental

Replacement experiments were conducted by holding solid fibrous potassium hexatitanate at 900°, covered by a flux of sodium and potassium chloride, for a period of 8 hr. About 20 mg. of titanate and 2 g. of the chlorides, in various proportions, were used in each run. The temperature was selected to be above the melting point of the flux but considerably below that of the hexatitanate. Sodium chloride of known specific activity was used as the source of sodium-22 tracer in preparing the flux mixture.

The procedure consisted in weighing the required materials into a platinum crucible and heating them in a thermostatically controlled oven. (The use of porcelain crucibles was found to be unsatisfactory, as excessive amounts of the tracer were absorbed in the glaze.) After cooling, the halides were leached from the fused mass with water and the titanate, now containing labeled sodium, was collected on sintered glass, washed and dried for 1 hr. at 110°. Samples of the titanate were weighed and mounted for counting by collection on paper filters supported in perforated plastic planchets.<sup>2</sup> Samples of about 10 mg. were mounted, as this was a sufficient quantity of the rather fluffy titanate to cover the planchet uniformly and to give an adequate counting rate. Counting standards were prepared by evaporating aliquots

of a standard solution of the tracer sodium chloride on similar, unperforated planchets. After a scintillation counter of the well type became available, certain samples were transferred to glass vials, reweighed and counted again. Appropriate counting standards were prepared by evaporation of the standard solution in similar glass vials. The data that are used in the calculation of an equilibrium constant were obtained with this more efficient counting system.

In order to obtain samples for X-ray study, replacement reactions were repeated without the presence of tracer in the flux mixtures. Powder diffraction patterns of the products were made with a Debye–Scherrer camera using  $CuK\alpha$  radiation. For diffraction patterns of the hexatitanate samples before and after complete replacement of the potassium by sodium, a General Electric recording diffractometer, Model XRD-5, was used.

The fibrous potassium hexatitanate used in this work was supplied by E. I. du Pont de Nemours & Co., Wilmington, Delaware.<sup>3</sup>

The tracer sodium chloride was prepared by evaporating a sodium chloride solution to which had been added sodium-22, obtained in HCl solution from Nuclear Science and Engineering Corp., Pittsburgh. The solid was fused, then ground and stored in a screw-capped vial.

Reagent grade sodium and potassium chlorides were fused, ground in a mortar and stored under vacuum prior to use.

### Results and Discussion

Prior to conducting an equilibrium study, determination of the conditions for equilibrium necessitated some early experiments of an exploratory nature. The first of these experiments, using a low melting (300°) flux of  $NaNO_3$ – $NaCl$  in a 20:1 ratio, indicated that up to 70% replacement of potassium by sodium could be achieved after 1 hr. Use of a pure sodium chloride flux (m.p. 801°) resulted in approximately 85% replacement for the same period of time. Reaction time was increased until it was found that nearly complete replacement could be achieved within 4 to 5 hr. As a result of these observations, a heating period of 8 hr. was judged to be ample for attainment of complete replacement. The data for these experiments are shown in Table I.

(3) Courtesy of R. M. Joyce, Asst. Laboratory Director, Central Research Department.

(1) K. L. Berry, V. D. Aftandilian, W. W. Gilbert, E. P. H. Meibohm and H. S. Young, *J. Inorg. Nuclear Chem.*, **14**, 231 (1960).

(2) T. E. Burgess, J. Looby and W. C. Orr, *J. Chem. Educ.*, to be published.