

[CONTRIBUTION FROM THE JOHN CURTIN SCHOOL OF MEDICAL RESEARCH, AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA, AUSTRALIA]

## Oxalato- and Malonato-ethylenediaminecobalt(III) Complexes

BY FRANCIS P. DWYER, IAN K. REID AND FRANCIS L. GARVAN

RECEIVED OCTOBER 20, 1960

The bis-(oxalato) and bis-(malonato)-ethylenediamine cobaltate(III) anions have been prepared by the oxidation of mixtures of cobalt(II) acetate and potassium oxalate or potassium malonate and ethylenediamine-dihydrochloride or malonate with lead(IV) oxide. The monovalent anions which were similar in color to the ethylenediaminetetraacetato-cobaltate(III) ion were separated into the optical isomers through the optically active *cis*-dinitrobisethylenediamine-cobalt(III) cation. Photo-reduction of the former anion occurred in solution and in the solid state. The direct synthesis of oxalatobisethylenediamine-cobalt(III) chloride, and the complete resolution through the ethylenediaminetetraacetato cobaltate(III) ion, are described.

The complex anion bis-(oxalato)-ethylenediamine cobaltate(III),  $[\text{Coen}(\text{C}_2\text{O}_4)_2]^-$ , never has been isolated. Bushra and Johnson<sup>1</sup> who prepared the chromium analog attempted, without success, the oxidation of a suspension of cobalt(II) oxalate in an aqueous mixture of potassium oxalate and ethylenediamine, with air and also hydrogen peroxide. The reaction between ethylenediamine and potassium trisoxalato-cobaltate(III) yielded the trisethylenediamine-cobalt(III) cation in association with either oxalate or trisoxalato cobaltate anion. Synthesis has been effected by oxidation of a hot solution, containing cobalt(II) acetate (1 mole), potassium oxalate (6 moles) and ethylenediamine dihydrochloride (1.1 mole) with lead(IV) oxide. The sparingly soluble purplish red calcium salt was isolated in the presence of hydrochloric acid. The lead salt was also sparingly soluble, but the barium and alkali metal salts were readily soluble, yielding deep purple solutions, not unexpectedly, very similar to those containing the ethylenediaminetetraacetato-cobaltate anion. Photoreduction in the solid state and in solution, as with the  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  ion, changed the color to pink due to the formation of cobalt(II) oxalate and bisoxalato-cobaltate(II) ion.

Resolution was effected most expeditiously through the optical isomers of the *cis*-dinitrobisethylenediamine-cobalt(III) cation. Poor separation occurred when brucine and strychnine were used for resolution, and none when cinchonine was employed. The diastereoisomer *d*- $[\text{Coen}_2(\text{C}_2\text{O}_4)]$ -*l*- $[\text{Coen}(\text{C}_2\text{O}_4)_2]$  was so insoluble that the levo anion could not be recovered. The optical isomers were stable indefinitely in the dark in the solid state. Slow racemization accompanied by some decomposition occurred in boiling aqueous solution in the dark ( $t/2 = 7.5$  hr. approximately) and in cold solution containing 0.1 *N* sodium hydroxide. Photo-racemization occurred in solution and in the solid state. The bis-(oxalato)-ethylenediamine cobaltate(III) ion is thus more stable optically than the trisoxalato-cobaltate(III) ion<sup>1</sup> but less stable than the oxalatobisethylenediamine-cobalt(III) cation which apparently does not racemize.<sup>1</sup>

Potassium bis-(malonato)-ethylenediamine cobaltate(III) was prepared in a similar manner by the oxidation of a mixture of cobalt(II) acetate, potassium malonate and ethylenediamine malonate with lead(IV) oxide. The purplish red potassium salt was resolved with *d-cis*-dinitrobisethylenediamine-cobalt(III) cation. The optical isomers were stable in the light, but slow racemization (and decomposition) occurred in boiling aqueous solution and in the presence of cold alkali or acid.

Oxalatobisethylenediamine-cobalt(III) salts have been usually prepared by heating *cis*-dichlorobisethylenediamine-chloride with potassium or ammonium oxalate. Direct synthesis in good yield has been carried out by the oxidation of an aqueous solution of cobalt(II) acetate (1 mole), oxalic acid (1.5 moles) and ethylenediamine (3 moles), with lead(IV) oxide. Werner was unable to resolve the substance completely<sup>2,3</sup> but obtained the active bromides with  $[\alpha]_D = +736^\circ$  and  $-728^\circ$  from the optical isomers of *cis*- $[\text{Coen}_2\text{Cl}_2]\text{Cl}$ . Resolution has been effected by using the optical isomers of the ethylenediaminetetraacetato-cobaltate(III) ion<sup>4-6</sup> and the bromides  $[\alpha]_D = \pm 820^\circ$  obtained in 80% yield. The optical isomers of  $[\text{Coen}_2(\text{C}_2\text{O}_4)]^+$  ion could be used equally effectively to resolve the *dl*- $[\text{Co}(\text{EDTA})]^-$  ion, so that a small amount of one optical isomer of either substance could be used to prepare ultimately large amounts of all the isomers.

### Experimental

All rotations were measured at 20° in a 1 dm. tube unless specified otherwise.

**Calcium Bis-(oxalato)-ethylenediamine cobaltate(III), 4-Hydrate.**—A solution of cobalt(II) acetate (10 g.), in water (50 ml.), was added to a hot solution of potassium oxalate (25 g.) in hot water (50 ml., 80°) and ethylenediamine dihydrochloride (5.76 g.) then dissolved in the deep red solution. The mixture was stirred mechanically while being heated to boiling, lead(IV) oxide (25 g.) added gradually and boiled for a further 0.5 hr. The hot solution, which had become alkaline, was filtered, diluted to 200 ml. with water and oxalic acid (9 g.) added gradually. After boiling for a further 15 min. the solution was cooled to room temperature, and sufficient hydrochloric acid (10 *N*) added to make it approximately 2 *N*. Calcium chloride 6-hydrate (25 g.) in a little cold water was added, the sides of the vessel scratched with a glass rod and crystallization allowed to proceed for five minutes. Longer crystallization times caused much calcium oxalate to separate. The dark purplish-red crystalline powder was washed with normal hydrochloric

(2) A. Werner, *Ber.*, **47**, 2171 (1912).

(3) A. Werner and J. Bosshart, *ibid.*, **47**, 2171 (1914).

(4) F. P. Dwyer, E. C. Gyarfás and D. P. Mellor, *J. Phys. Chem.*, **59**, 296 (1955).

(5) S. Kirchner, Y. K. Wei and J. C. Bailar, *THIS JOURNAL*, **79**, 5877 (1957).

(6) F. P. Dwyer and F. L. Garvan, "Inorganic Syntheses," E. Rochow, Ed. Vol. VI, in publication.

(1) E. Bushra and C. H. Johnson, *J. Chem. Soc.*, 1936 (1937).

acid and alcohol and further freed from calcium oxalate by suspending in normal hydrochloric acid (25 ml. at 40°) and filtering while warm. After washing with warm normal hydrochloric acid, water, alcohol and finally acetone, the solid was air dried (yield, 8.6 g., 60%). It was very sparingly soluble in boiling water to a purple solution but decomposed gradually in contact with concentrated acids.

*Anal.* Calcd. for  $\text{Ca}[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)(\text{C}_2\text{O}_4)_2] \cdot 4\text{H}_2\text{O}$ : C, 20.52; H, 3.44; N, 7.98. Found: C, 20.65; H, 3.52; N, 8.05.

*dl*-Sodium Bis-(oxalato)-ethylenediamine-cobaltate(III) 1-Hydrate.—A suspension of the calcium salt above (25 g.) in hot water (500 ml., 65°) containing sodium oxalate (6.2 g.) was heated to boiling while being rapidly stirred mechanically. The boiling and stirring were continued until decomposition of the calcium salt was complete (15–20 min.) and the mixture cooled and filtered. The filtrate was evaporated on the steam-bath in a current of air and, after cooling and filtering, ethanol was added gradually until crystallization was complete. The dark red crystalline material (25 g.) was recrystallized from water by adding ethanol. The potassium salt was prepared in a similar manner.

*Anal.* Calcd. for  $\text{Na}[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)(\text{C}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$ : C, 21.44; H, 3.00; N, 8.34; for  $\text{K}[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)(\text{C}_2\text{O}_4)_2] \cdot 1.5\text{H}_2\text{O}$ : C, 19.95; H, 3.07; N, 7.76. Found: C, 21.44; H, 3.02; N, 8.30; C, 20.12; H, 3.06; N, 7.79.

*d*-Sodium Bis-(oxalato)-ethylenediamine-cobaltate(III) 1-hydrate.—The calcium salt (14.1 g.) was added to a mechanically stirred solution at 50–55° of *d*-*cis*-dinitrobis-ethylenediamine-cobalt(III) oxalate (14.1 g.) from *d*- $\text{Coen}_2(\text{NO}_2)_2\text{Br}$  (16.5 g.), and silver oxalate (6.8 g.), and the stirring continued for 0.5 hr. The calcium oxalate was removed and to the filtrate, containing *d*- $[\text{Coen}_2(\text{NO}_2)_2]d$ - $[\text{Coen}(\text{C}_2\text{O}_4)_2]$  (2 moles), was added sodium bis-(oxalato)-ethylenediaminecobaltate(III) (13.86 g., 2 moles). The mixture was then maintained at 50–55° whilst being stirred for 15–20 min. and then filtered hot. The purplish-brown precipitate of the diastereoisomer *d*- $[\text{Coen}_2(\text{NO}_2)_2]l$ - $[\text{Coen}(\text{C}_2\text{O}_4)_2]$  (7.2 g.) was reserved and subsequent fractions (5) caused to crystallize by gradual evaporation at 50° in a stream of air. All of these fractions were levorotatory and contained the diastereoisomer *d*- $[\text{Coen}_2(\text{NO}_2)_2]l$ - $[\text{Coen}(\text{C}_2\text{O}_4)_2]$ . When the volume had been reduced to about 100 ml., the solution was chilled, filtered and the remainder of the resolving agent recovered by the addition of sodium iodide (8.0 g.). The precipitate of *d*- $[\text{Coen}_2(\text{NO}_2)_2]l$  was removed and ethanol (300 ml.) added to the filtrate when *dl*- $\text{Na}[\text{Coen}(\text{C}_2\text{O}_4)_2]$  was recovered. The dextro diastereoisomer (fraction 1) was converted to the sodium salt by grinding in a mortar with warm 20% sodium iodide (30 ml.) and filtering off the insoluble iodide of the resolving agent. The active salt crystallized on the addition of ethanol and was recrystallized to constant rotation from aqueous ethanol. A 0.02% aqueous solution gave  $\alpha_D = +0.20^\circ$  (2 dm. tube),  $\alpha_{5461} = -0.28^\circ$ ,  $\alpha_{5780} = 0$  whence  $[\alpha]_D = +500^\circ$ ;  $[\alpha]_{5461} = -1400^\circ$ . Unlike the racemic form, the optically active calcium salt was quite soluble in cold water but the lead salt could be recrystallized from hot water.

The rate of racemization was determined at 99° in the dark using a 0.04% aqueous solution. The half-life was found to be 7.5 hr. The rotation of a 0.02% solution in 0.1 *N* sodium hydroxide decreased 20% in 20 hr. at 20°. No rotational change occurred under the latter conditions in 1 *N* hydrochloric acid.

*Anal.* Calcd. for  $\text{Na}[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)(\text{C}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$ : C, 21.44; H, 3.00; N, 8.34. Found: C, 21.44; H, 3.02; N, 8.30.

*l*-Sodium Bis-(oxalato)-ethylenediamine-cobaltate(III) 1-Hydrate.—The levorotatory diastereoisomeric fractions above were combined and recrystallized by dissolution in the minimum volume of water at 60° and then standing at room temperature for two days. Further fractions were obtained by concentration at 50° in a stream of air. The less soluble (most active) fractions were recrystallized as before to yield the pure diastereoisomer, from which the sodium salt was obtained in the same manner as the dextro isomer above. A 0.02% solution gave  $[\alpha]_D = -500^\circ$ .

*Anal.* Found: C, 21.7; H, 3.1; N, 8.3.

Potassium Bis-(malonato)-ethylenediamine-cobaltate(III) 1-Hydrate.—A solution of cobalt(II) acetate (20 g.) in water (50 ml.) was added to a solution of potassium malonate (50 g.) in water (50 ml.), at 50°, and ethylenediamine malonate (16 g.) in water (25 ml.) added. The mixture was stirred mechanically, heated to 75°, lead(IV) oxide (15 g.) gradually added and maintained at 75° for 0.5 hr. The hot mixture was filtered, the filtrate evaporated on the steam-bath in a current of air until crystallization commenced (80 ml.) and then allowed to stand at room temperature for 3 hr. The purplish red solid was washed with 80% aqueous methanol, methanol and finally acetone. The substance was recrystallized twice from water (30 ml.) by gradually adding ethanol (130 ml.). The mother liquors were evaporated to 30 ml. and cooled when a further amount of the substance crystallized. After washing with 80% aqueous methanol, until a red soluble impurity was removed, the residue was recrystallized from water as before (yield, 25 g., 83%). Salts of the bis-(malonato)-ethylenediamine-cobaltate(III) ion with the common metals were all very soluble in water.

*Anal.* Calcd. for  $\text{K}[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$ : C, 25.26; H, 3.71; N, 7.37. Found: C, 25.36; H, 3.84; N, 7.54.

*d*-Potassium Bis-(malonato)-ethylenediamine-cobaltate (III) 2-Hydrate.—*levo*- $[\text{Coen}_2(\text{NO}_2)_2]l_2$  (5.23 g.) was transformed to the acetate by shaking with silver acetate (2.2 g.) in water (50 ml.) at 40°. After removal of the silver iodide, solid  $\text{K}[\text{Coen}(\text{C}_3\text{H}_2\text{O}_4)_2]$  (10 g.) was dissolved in the filtrate, to which ethanol (200 ml.) was added gradually. The sides of the vessel were scratched with a glass rod and the mixture cooled. The brownish purple diastereoisomer, *l*- $[\text{Coen}_2(\text{NO}_2)_2]d$ - $[\text{Coen}(\text{C}_3\text{H}_2\text{O}_4)_2]$  (6.0 g.) that separated was collected and recrystallized from water by adding alcohol.

*Anal.* Calcd. for  $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{NO}_2)_2][\text{Co}(\text{C}_2\text{H}_8\text{N}_2)(\text{C}_3\text{H}_2\text{O}_4)_2]$ : C, 24.25; H, 4.75; N, 18.86. Found: C, 24.30; H, 4.66; N, 18.2.

The diastereoisomer dissolved in the minimum volume of warm water was treated with potassium iodide (5 g.), the mixture cooled in ice and the  $[\text{Coen}_2(\text{NO}_2)_2]l$  filtered off. The *dextro* potassium salt was precipitated with a large volume of cold ethanol and recrystallized from a little water by adding ethanol. The optical isomers were less soluble than the racemate. A 0.02% solution in water gave  $\alpha_D = +0.32^\circ$ ,  $\alpha_{5780} = +0.45^\circ$ ,  $\alpha_{5461} = +0.24^\circ$ , whence  $[\alpha]_D = +1550^\circ$ ,  $[\alpha]_{5780} = +2250^\circ$ ,  $[\alpha]_{5461} = +1200^\circ$ . The substance racemized rapidly in 0.04% solution at 99°, (*t*/2 = 1.25 hr.), with about 10% decomposition. Complete decomposition ensued in 15 hr. at 20° in 0.1 *N* sodium hydroxide solution. It was stable in cold hydrochloric acid (1 *N*) over 24 hr. but decomposed rapidly at 99°. Photo-racemization did not occur in solution, nor in the solid state.

*Anal.* Calcd. for  $\text{K}[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ : C, 24.12; H, 4.05; N, 7.03. Found: C, 23.95; H, 4.0; N, 6.93.

*l*-Potassium Bis-(malonato)-ethylenediamine-cobaltate (III) 2-Hydrate.—The filtrate from the separation of the diastereoisomer above was evaporated at 50° in a stream of air to a volume of 35 ml., potassium iodide (5 g.) added and the mixture cooled in ice. The yellow  $[\text{Coen}_2(\text{NO}_2)_2]l$  was removed and the *dextro* potassium salt was caused to crystallize by the addition of ethanol (200 ml.). It was crystallized to a constant rotation from a little water by adding ethanol. A 0.02% solution gave  $[\alpha]_{5461} = -1150^\circ$ .

*Anal.* Found: C, 23.97; H, 3.98; N, 6.93.

*dl*-Oxalatobisethylenediamine-cobalt(III) Chloride 1-Hydrate.—A solution of cobalt(II) acetate 4-hydrate (20 g.) in water (100 ml.) at 60° was added to a mixture of oxalic acid 2-hydrate (15 g.) in water (100 ml.) containing ethylenediamine (15 ml., 99%) at 70°. The mixture, while being stirred mechanically, was then heated rapidly to 80°. Some pink cobalt(II) complex sometimes separated at this stage. Lead(IV) oxide (10 g.) was added and the heating continued to boiling. The mixture was boiled gently for 0.5 hr., adding more lead(IV) oxide (2 g.) after 10 minutes and again after 20 minutes. It was then cooled to room temperature, sulfuric acid (10 ml., 10 *N*) added and filtered. Hydrochloric acid (25 ml., 10 *N*) was added to the deep red filtrate, which was then evaporated on the steam-bath in a current of air to a volume of 100 ml., and finally cooled in ice. The red crystals were washed with 80% aqueous methanol, then methanol and air dried (yield, 21 g., 86%). The substance was recrystallized by dissolution in hot water (150 ml.), adding concentrated hydrochloric acid (25 ml.) and cooling in ice.

*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  $[\text{Co}(\text{C}_2\text{H}_5\text{N}_2)_2(\text{C}_2\text{O}_4)][\text{Co}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)]\cdot 3\text{H}_2\text{O}$ : 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.

**Acknowledgment.**—The authors are indebted to Dr. J. Fildes of the Department of Medical Chemistry for analyses.

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

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

BY JAMES G. MURRAY<sup>2</sup>

RECEIVED SEPTEMBER 23, 1960

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).