oxide oxidizes platinum(II) complexes to platinum(IV) compounds with the added OH groups occupying *trans* positions. Assuming this is the case with the above oxidation the reaction should proceed through the following route to form the product with the indicated structure (Scheme II).

The infrared spectrum of the compound shows that the assignment of the structure (V) is correct. It is interesting to note that by shortening the reaction time the ring closure reaction shown above may be stopped at a point where only one carboxyl group has reacted to close the ring. The infrared spectrum of the product shows a sharp band at 3410 cm.$^{-1}$ which is interpreted as O–H stretching of a coordinated hydroxyl group. The two bands at 1710 and 1650 cm.$^{-1}$ are assumed to be un-ionized and coordinated COO stretching bands, respectively. On the basis of these data the assignment of structure VI to the compound is quite obvious.

Of particular interest is the oxidation of II by $[PtCl_6]^{-2}$. Since the products obtained are shown to have structures V and VI, the incoming chloride groups are situated *cis* to each other. This is quite unlike other oxidations involving Pt(II) complexes where the incoming groups generally occupy *trans* positions in the resulting Pt(IV) compounds. It is quite possible that a different mechanism is operative in the present case.

When VI is heated at 130° a product is obtained in which all the carboxyl groups are coordinated and there are no coordinated OH groups. The elemental analyses confirm the simple formula of $Pt(C_6H_{10}N_2O_4)Cl_2$. It is likely the third isomer of dichloro(ethylenediamine-N,N′-diacetic acid)platinum(IV), the structure of which is depicted by VII in Scheme I. It is also possible that a polymer is formed in the heating process.

Acknowledgment.—The investigator wishes to thank the National Science Foundation for the support of this study.

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Biscyclopentadienyl Titanoxane Polymers

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Received October 30, 1963

A novel sequential reduction–oxidation process was used to prepare the biscyclopentadienyl titanoxane polymers from bis(cyclopentadienyl)titanium dichloride (I). The formation of the polymers was accompanied by a loss of one cyclopentadienyl ring for each metal atom, leading to materials of lower solubility and thermal stability than expected. The dimeric intermediate $TiCp_2Cl–O–TiCp_2Cl$ was isolated by reduction of I with zinc followed by air oxidation.

Introduction

Titanoxane polymers obtained by the controlled hydrolysis of tetraalkoxytitanium compounds have been studied extensively by Bradley and co-workers.[1,2] In other studies, Rust and co-workers[3] utilized monomers containing two univalent bidentate chelate groups (8-hydroxyquinoline and acetylacetonates) and two labile groups in an effort to prepare linear polymers. Consideration was then given to converting the known soluble and stable dichloride, bis(cyclopentadienyl)titanium dichloride (I), to the polymer $(–TiCp_2–O–)_n$ (II). Dipole moment measurements[4] were recently used to deduce the tetrahedral nature of I. The tetrahedral arrangement does not preclude polymer formation as evidenced by the existence of silicone and carbon resins. Furthermore, the expected Ti–O–Ti bond angle of 180°, which has been shown for $CpCl_2Ti–O–TiCl_2Cp$,[5] should promote chain growth with respect to cyclization.

An obvious route to the proposed polymer II, similar to the preparation of siloxane linear polymers, would be reaction with hydroxide ion, but treatment with aqueous base cleaves metal–cyclopentadienyl bonds.[6] The bis(cyclopentadienyl)titanium dialkoxides might also be effective precursors for titanoxane polymers but obvious attempts at their synthesis were not successful.[7]

The reduction of I by metallic zinc has been reported[8] in oxygen-containing solvents such as acetone and tetrahydrofuran. It was considered that oxidation of the reduced species should afford a dimer with an oxo bridge as demonstrated by Nöth and Hartwimmer

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[1] D. C. Bradley, R. Gaze, and W. Wardlaw, *J. Chem. Soc.*, 469 (1957).

[2] D. C. Bradley, R. Gaze, and W. Wardlaw, *ibid.*, 3977 (1955).

[3] J. B. Rust, U. S. Dept. of Commerce, AD262707 (1961).

[4] S. A. Giddings and R. J. Best, *J. Am. Chem. Soc.*, **83**, 2393 (1961).

[5] G. Allegro, P. Ganis, L. Porri, and P. Corradini, *Atti Accad. Naz. Lincei*, **30**, 44 (1961).

[6] G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.*, **76**, 4281 (1954).

[7] A. N. Nesmeyanov, O. V. Nogina, and A. M. Berlin, *Dokl. Akad. Nauk SSSR*, **134**, 607 (1960).

[8] J. M. Birmingham, A. K. Fischer, and B. Wilkinson, *Naturwissenschaften*, **42**, 96 (1955).

with the bromo analog.[9] A novel polymerization process was visualized involving the reduction of IV, with the loss of the chloro group on each titanium atom, followed by oxidation to the desired polytitanoxane.

$$\underset{\text{I}}{TiCp_2Cl_2} \xrightarrow{\text{red.}} \underset{\text{III}}{[TiCp_2Cl]} \xrightarrow{[O]} \underset{\text{IV}}{(TiCp_2Cl)_2O} \xrightarrow[\text{2, [O]}]{\text{1, red.}} \underset{\text{II}}{(\text{-}TiCp_2\text{-}O\text{-})_n}$$

This method offered the advantages of avoiding basic conditions and subsequent ring–metal cleavage and could possibly be extended to other systems.

Results and Discussion

(A) Formation of Polymers.—The preparation of polymer II by hydrolysis of I under neutral or slightly acid conditions was not successful. Refluxing I in water for 3 hr. resulted in recrystallization of starting material (53%) along with an insoluble precipitate primarily titanium dioxide (20%). The hydrolytic stability of I contrasts sharply with that of titanium tetrachloride, which is hydrolyzed completely by cold water.

Efforts were then directed at forming the desired polymer in a nonaqueous system.

Reduction of I was carried out with zinc in acetone or tetrahydrofuran under argon and anhydrous conditions. The unreacted zinc was removed by filtration, and weighing showed that reduction of Ti(IV) to Ti(III) was complete. Slow ingress of oxygen to the green filtrate afforded the orange crystalline product IV (60%), soluble in acetone, dimethylformamide, tetrahydrofuran, and chloroform.

Refluxing IV in tetrahydrofuran with sodium borohydride gave a sudden change to a purple then blue-green solution after an initiation period of 1 day. The characteristic green to blue color was evidence of reduction to a lower valence state of titanium. Addition of a small amount of diborane gas was found to trigger the reduction. Apparently the sodium borohydride reduction is dependent on formation of traces of diborane which, once the reaction starts, is self-regenerative. Subsequently it was found that diborane gas could be used solely in the reduction. The reduced species was not examined but no cyclopentadiene was detected, suggesting that each Ti atom was still bound to two cyclopentadienyl groups. The complete understanding of the reduction of IV was beyond the scope of this study but the desired Ti–Cl bond cleavage must have occurred, as reduction of only the Ti–O bond would give the pure green color of III and reoxidation would regenerate IV. Hence the two possible intermediates must have been $TiCp_2$ or $[TiCp_2]_2O$, solvated and/or complexed with boron compounds.

A preliminary examination of the polarographic reduction of the "oxy dimer" IV showed reduction at approximately −0.9 volt *vs.* s.c.e. compared to −0.44 volt for I. No definite evidence for the existence of a stepwise reduction was obtained, nor was it possible to determine the number of electrons involved in the reduction per molecule of IV. A variety of metallic reducing agents (zinc, magnesium, lithium, and sodium) caused no reduction even after long periods of exposure at the reflux temperature of the solvents employed.

It was also of interest that molten sodium (a stronger reducing agent than zinc) in boiling xylene did not reduce I after a reaction period of 1 week. Treatment of the blue-green solution with dry oxygen gave a yellow insoluble product. Infrared demonstrated the presence of cyclopentadienyl rings and Ti–O–Ti bonds.

In addition, a solution of I in acetone or THF when stirred with zinc in an atmosphere of dry air was converted completely to the same yellow insoluble product. Thus, as one would expect, IV is formed by reduction and reoxidation of I and apparently the mechanism of polymer formation in this case is a consequence of the following disproportionation reaction

$$\underset{\text{IV}}{2n(TiCp_2Cl)_2O} \longrightarrow \underset{\text{I}}{nTiCp_2Cl_2} + \underset{\text{II}}{(\text{-}TiCp_2\text{-}O\text{-})_n}$$

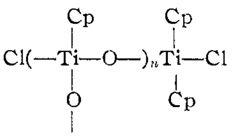
The insolubility of the eventual polymeric product appears to be the driving force in the above reaction. To observe the disproportionation reaction, nuclear magnetic resonance examination of a solution of IV in acetone showed a single proton magnetic resonance peak at τ 3.65 but on standing a second peak at τ 3.41 appeared. After 2 weeks the intensities of the two peaks were identical, and a small amount of yellow solid II separated. Titanocene dichloride has a single absorption band at τ 3.39 which is within experimental error for the value τ 3.41 developed above.

The metathetical reaction between I and silver oxide was attempted. Conversion took place readily but

$$\underset{\text{I}}{nTiCp_2Cl_2} + nAg_2O \longrightarrow 2nAgCl + \underset{\text{II}}{(\text{-}TiCp_2\text{-}O\text{-})_n}$$

it was not possible to separate II from the silver chloride by-product. The odor of cyclopentadiene was detected over the reaction mixture, and the insolubility of the yellow material suggested that this product was similar to those prepared by the reduction and oxidation processes.

(B) Properties and Structure of Polymeric Products.—Elemental analysis (Table I) of the yellow polymeric products obtained by the three methods discussed demonstrate that in all cases approximately one cyclopentadienyl ring was lost from each titanium atom. The formula which best fits the analyses of the products is



$$Cl(\text{—}\overset{\displaystyle Cp}{\underset{\displaystyle \overset{|}{O}\atop |}{Ti}}\text{—}O\text{—})_n\overset{\displaystyle Cp}{\underset{\displaystyle Cp}{Ti}}\text{—}Cl$$

Also there is a correlation between the carbon to titanium ratio and the Cl content. Apparently, the materials with the greatest degree of polymerization (based on lowest percentages of chlorine end groups)

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[9] H. Nöth and R. Hartwimmer, *Ber.*, **93**, 2246 (1960).

TABLE I

ANALYSIS OF PRODUCTS

Method of prepn.	Analysis, %	Atom ratio[a]
Redn. of IV and reoxidn.	C 38.16	5.93
	H 4.25	
	Ti 25.5	1
	Cl 3.35	0.17
Simultaneous redn. and oxidn. of I	C 37.75	4.88
	H 3.73	
	Ti 30.8	1
	Cl 2.01	0.083

[a] Theoretical ratio of C:Ti in $(-TiCp_2-O-)_n$ is 10:1.

are the materials more prone to split out cyclopentadiene.

The materials obtained were not thermally stable and hydrolyzed easily. They darkened in a capillary melting point apparatus between 200 and 220° with no evidence of fusion. Thermogravimetric analysis in air and nitrogen showed that the samples lost weight slowly from 40 to 200° (9–10%) and then rapidly at 450° in air and 400° in nitrogen. At 400° the weight loss was 18% in both air and nitrogen. After 500° no further weight loss was observed up to 650°. The total weight loss was 41.6% in air and 27.8% in nitrogen. The former quantity corresponds to the theoretical conversion to TiO_2. Consistent with the weight loss at low temperature was the odor of cyclopentadiene which developed when the materials were stored at room temperature in closed vials. The yellow polymeric products also exhibited poorer hydrolytic stability than their precursor, I. Cyclopentadiene was given off after prolonged contact with cold water and much more rapidly in hot water whereas, as shown earlier, I can be recrystallized from boiling water. The poor over-all hydrolytic and thermal stability of the products is also consistent with the known lower stability of monocyclopentadienyl compounds.

There was some evidence that the desired polymer II, with two cyclopentadienyl groups flanking each titanium atom, existed in solution. Evaporation of the yellow to orange solutions, obtained after oxidation of the diborane reduction product of IV and removal of the precipitated product, gave materials of similar properties to the yellow polymers. They could not be redissolved and this may possibly be due to loss of cyclopentadienyl groups and cross linking through multiple titanium to oxygen links.

Throughout this investigation no evidence as to the formation of oligomeric cyclic structures was obtained. However, these occurrences in solution could not be discounted. It may also be possible that the insoluble yellow products contain structural groups, cyclic in character, which could be cross linked by loss of one cyclopentadienyl group from a titanium atom.

Presuming that the desired polymer was formed and then suffered metal–cyclopentadienyl bond cleavage, there appear to be two possible causes of such bond rupture, steric and electronic. Models were not available to test steric effects but considering a tetrahedral disposition of ligands around the metal atom, and a linear arrangement at the bridging oxygen atoms, it can be visualized that spatial considerations may be important in polymer formation. Also the linearity of the oxygen presupposes a partial Ti–O double bond character arising from donation of the electrons from the p_y and p_z oxygen orbitals to the empty titanium d-orbitals. Bond shortening would result from the increased bond order and magnify the steric problem. This postulate is consistent with the finding[5] that the Ti–O bond distance in $(TiCl_2Cp)_2O$ is 1.78 Å., which is clearly shorter than the expected single bond distance of 1.92 Å. The cause of titanium–ring bond weakening by electronic effects is not known precisely, but the difficulty encountered in preparing the dialkoxides of bis(cyclopentadienyl)titanium suggests that the moiety is less stable when flanked by two oxygen atoms rather than two chloro groups.

Experimental

All glass apparatus was thoroughly dried and reactions were carried out under dry argon unless noted. (Solvents were also dried by standard procedures.)

Analytical Procedures.—Molecular weight was determined by the vapor pressure thermistor method in methylene chloride. Titanium was determined by wet oxidation, zinc amalgam reduction, and titration with standard Fe^{3+}, chlorine by Schoniger combustion and titration with mercuric perchlorate, and carbon–hydrogen by microcombustion techniques.

(A) **Preparation of Bis(cyclopentadienyl)titanium Dichloride (I).**—Fifty ml. of a solution of magnesium cyclopentadienide (2.10 *M*, 0.105 mole) in tetrahydrofuran was transferred to a dry flask and 100 ml. of xylene was added. Titanium tetrachloride (20.4 g., 0.110 mole) and 50 ml. of xylene were mixed in the dropping funnel and were added over a period of 30 min. with vigorous stirring. The temperature rose approximately 20° during the reaction. (In one experiment it was found that when the reaction mixture was heated, extensive decomposition occurred, depressing the yield). Stirring was continued for 30 min. after completion of the addition. The red solid which precipitated was filtered and then was recrystallized from xylene to afford 13 g. (50%) of product, m.p. 285–287°. *Anal.* Calcd. for $C_{10}H_{10}TiCl_2$: C, 48.23; H, 4.05; Cl, 19.24. Found: C, 48.31; H, 4.10; Cl, 19.2.

The infrared spectrum shows C–H stretch (3105 cm.$^{-1}$), in-plane, in-phase rock (1020, 1030 cm.$^{-1}$), out-of-plane, in-phase rock (822, 875 cm.$^{-1}$), and weak bands at 930, 958, and 1133 cm.$^{-1}$.

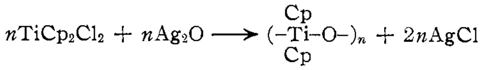
(B) **Preparation of Titanium Oxybis(chlorodicyclopentadienyl) (IV).**—I (5 g., 0.020 mole) and powdered zinc (1 g., 0.0153 g.-atom) were introduced into the reaction vessel. Reagent grade acetone (25 ml.) was deaerated by passing argon through a sintered glass gas dispersion stick immersed in the solvent and was added to the reactants. As the mixture was stirred, the red solution turned green in less than 5 min. Stirring was continued for 1 hr. to ensure complete reaction. The green solution was removed by filtration and the reaction vessel rinsed with 10 ml. of dry deaerated acetone. The combined filtrates were transferred rapidly to a desiccator, which was fitted with a drying tower, and allowed to oxidize slowly. The solution turned orange-red, and orange crystals separated which were filtered and recrystallized from acetone in 60% yield (2.65 g.), m.p. 230° dec. *Anal.* Calcd. for $C_{20}H_{20}Ti_2Cl_2O$: C, 54.21; H, 4.55; Cl, 16.04; ash (TiO_2), 34.67; mol. wt., 443.1. Found: C, 53.84; H, 4.43; Cl, 16.49; ash, 34.65; mol. wt., 427.

The infrared spectrum of IV in mineral oil showed the normal C–H stretch at 3085 cm.$^{-1}$. A triplet at 1006, 1016, and 1024 cm.$^{-1}$ was assigned to the in-plane, in-phase rock; the out-of-plane, in-phase rock has a strong band at 810 cm.$^{-1}$ with satellites at 845, 831, and 795 cm.$^{-1}$ and possibly 867 and 753 cm.$^{-1}$, caused by crystal effects. A broad strong band at 720 cm.$^{-1}$ was assigned to the Ti–O–Ti stretch.

(C) **Reduction and Oxidation of IV.**—IV (2 g., 0.0045 mole) was dissolved in 100 ml. of tetrahydrofuran in a 250-ml. round bottom, three-necked flask. Argon was swept through the solution to remove the last traces of oxygen in the system. Diborane was then passed into the solution slowly by means of argon and a diborane generator, which was operated by the dropwise addition of boron trifluoride etherate, diluted with diglyme, into a rapidly stirred suspension of sodium borohydride in diglyme. A purple color appeared almost instantaneously, followed by a gradual development of blue-green solution in 3 hr. The reaction was allowed to proceed at room temperature for 16 hr. Dry air was then passed slowly through the reaction mixture causing an exothermic reaction to occur which was accompanied by a color change to bright green and then to yellow with separation of a yellow solid. All of the solvent was removed with the flow of dry air. The solid residue was suspended in 30 ml. of cold de-ionized water, filtered, and washed with a small amount of water and ether, to give 0.54 g. of a yellow solid, m.p. 230° dec. The analysis is shown in Table I. The infrared spectrum showed C–H stretch (3100 cm.$^{-1}$), cyclopentadienyl bands at 1018 cm.$^{-1}$ and a broad band at 855 cm.$^{-1}$; broad bands at 795 and 720 cm.$^{-1}$ were considered to arise from Ti–O–Ti bands. Some evidence for –OH group was seen in the 3050 cm.$^{-1}$ region.

(D) **Simultaneous Oxidation and Reduction of I.**—I (3 g., (0.012 mole) was dissolved in 50 ml. of acetone. Granular zinc (2.00 g., 0.030 g.-atom) was added and the mixture stirred for 4 hr. in dry air. A light yellow precipitate was obtained and removed from the unreacted zinc by decantation and filtering. The precipitate was washed with two 10-ml. and one 5-ml. portions of cold de-ionized water and then dried under vacuum at room temperature to give 1.20 g. of product, m.p. 230° dec. More product was obtained by longer treatment of the acetone solution with the granular zinc followed by a similar work-up (see analysis, Table I). The infrared spectrum was almost identical with that of material obtained in (C).

(E) **Reaction of I and Silver(I) Oxide.**—Equimolar quantities of I and silver oxide were stirred for 16 hr. in acetone in an attempt to obtain the reaction



$$n\mathrm{TiCp_2Cl_2} + n\mathrm{Ag_2O} \longrightarrow (-\underset{\mathrm{Cp}}{\overset{\mathrm{Cp}}{\mathrm{Ti}}}-\mathrm{O}-)_n + 2n\mathrm{AgCl}$$

A yellow precipitate and pale red solution were obtained. The yellow material was insoluble and could not be separated from the silver chloride. Evaporation of the solution gave a gummy material whose infrared spectrum exhibited cyclopentadienyl and Ti–O–Ti bands. It was concluded that this material was mainly the dimer or oligomers.

(F) **Attempted Hydrolysis of I.**—I (1 g.) was refluxed in 50 ml. of de-ionized water for 3 hr. A small amount (0.08 g.) of a pale insoluble material precipitated. Infrared examination of this material shows little or no cyclopentadienyl groups present. The filtrate was reduced in volume and red crystals appeared on cooling (0.23 g.) which were shown by melting point and infrared to be I. A further 0.30 g. of I also was obtained by further reduction in volume. It was also noted in a subsequent experiment that the filtrate obtained after refluxing 3 hr. could be boiled for a further 3 hr. without any signs of decomposition.

Contribution from the Department of Chemistry,
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The Reaction Product of Bis(2,4-pentanediono)titanium(IV) Dichloride with Anhydrous Iron(III) Chloride

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Received October 8, 1963

The reaction of anhydrous ferric chloride with bis(2,4-pentanediono)titanium(IV) dichloride in glacial acetic acid is shown to lead to the formation of tris(2,4-pentanediono)titanium(IV) tetrachloroiron(III). This species has been characterized by its ultraviolet spectrum and is shown to be a 1:1 electrolyte in nitrobenzene, nitromethane, and acetonitrile. Mössbauer studies have suggested the presence of the tetrahedral $\mathrm{FeCl_4^-}$ species in the solid state. An interesting apparent correlation is observed between the size of the cation in the $\mathrm{M[FeCl_4]}$ complexes that have been studied and the Mössbauer half-width for absorption by $\mathrm{FeCl_4^-}$.

The reaction of titanium tetrachloride with acetylacetone (H-acac) in anhydrous solvents[1–5] leads to the formation of $\mathrm{Ti(acac)_2Cl_2}$. This material originally was formulated[2–4] as $\mathrm{[Ti(acac)_3]_2TiCl_6}$ by analogy with the formation of cationic species of the type $\mathrm{M(acac)_3^+}$ with other group IV elements.[6] In addition, Dilthey[2] was able to prepare a crystalline material which appeared to be $\mathrm{Ti(acac)_3FeCl_4}$.

Mehrotra and co-workers[5,7,8] recently re-investigated the reaction of titanium tetrachloride with acetylacetone. Molecular weight and other studies showed quite conclusively that the product is monomeric[7] and corresponds to the simple formula $\mathrm{Ti(acac)_2Cl_2}$. Based on these results, Pande and Mehrotra[5] suggested the reaction product of $\mathrm{Ti(acac)_2Cl_2}$ with $\mathrm{FeCl_3}$ in glacial acetic acid[2] could be formulated as a $\mathrm{TiCl_4}$ adduct of iron(III) acetylacetone. Additional studies by Puri and Mehrotra[8] suggested that this material has a low conductivity in nitrobenzene (molar conductance values

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