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TITANIUM AND ZIRCONIUM ORGANIC COMPOUNDS

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This invention relates in general to titanium and zirconium organic compounds and more specifically to titanium-carbon or zirconium-carbon bonded compounds.

A number of metal-carbon bonded compounds have previously been prepared and among these are bis-cyclopentadienyl titanium and bis-cyclopentadienyl titanium dihalide and zirconium dihalide. The latter compound, i.e. the dihalide of both titanium and zirconium and its method of preparation is more fully described and claimed in co-pending application Serial No. 443,956, filed July 16, 1954, by Daniel F. Herman, said application being assigned to the same assignee as the instant application.

Such compounds are of interest as catalytic agents and as reagents in various organic reactions for the preparation of other organic compounds. It is desirable therefore to produce derivatives of such compounds so that these compounds may have wider applications in various organic systems.

An object of the instant invention therefore is to produce derivatives of bis-cyclopentadienyl titanium and zirconium compounds. A further object is to produce derivatives of bis-cyclopentadienyl titanium and zirconium dihalide. Another object is to produce derivatives which will have applications other than those of the bis-cyclopentadienyl titanium and zirconium dihalides themselves. A still further object is to produce derivatives which under certain conditions are more reactive than either bis-cyclopentadienyl titanium or zirconium dihalide. A further object is to provide a method for producing derivatives of bis-cyclopentadienyl titanium and zirconium dihalide. These and other objects will become more apparent from the following more complete description of the instant invention.

Broadly, this invention contemplates a compound comprising a derivative of bis-cyclopentadienyl metal dihalide, said metal selected from the group consisting of titanium and zirconium, said dihalide selected from the group consisting of fluorine, chlorine, bromine and iodine, said derivative containing one cyclopentadienyl group, one aliphatic group and 2 halogens attached to each metal atom, said aliphatic group being a 5 membered carbon ring and containing from 2 to 4 halogens selected from the group consisting of chlorine, bromine and iodine, said halogens attached to said ring.

This invention further contemplates a method for the preparation of derivatives of bis-cyclopentadienyl metal dihalide, said metal selected from the group consisting of titanium and zirconium, said dihalide selected from the group consisting of fluorine, chlorine, bromine and iodine, which comprises reacting bis-cyclopentadienyl metal dihalide with a halogen selected from the group consisting of chlorine, bromine and iodine. A preferred embodiment of the instant invention is to suspend the bis-cyclopentadienyl metal dihalide in an inert solvent and react the suspension with the halogen.

Bis-cyclopentadienyl titanium or zirconium dihalide

is not very soluble in most inert solvents and therefore it is convenient, but not necessary, to form a suspension. Most any inert solvent may be employed and among the most readily available are CCl_4, $CHCl_3$, hexane, cyclohexane, petroleum ether and tetrachloroethane.

The reaction is simple and straightforward. The halogen is merely reacted with the bis-cyclopentadienyl metal dihalide and the derivatives are formed. Usually a large excess of the halogen is used to permit a more complete reaction to take place. The reaction is usually run under atmospheric pressure but may be run under pressure if desired. The reaction is usually carried out at room temperature, however, the temperature employed is dependent upon either the solvent or pressure used.

In carrying out the reaction between the bis-cyclopentadienyl titanium or zirconium dihalide and the halogen, two derivatives may be formed. Apparently only one of the cyclopentadienyl rings is attached and the halogen is attached thereto in multiples of two. The first derivative which is formed, and is isolable if desired, is cyclopentadienyl (dihalocyclopentenyl) metal dihalide. This derivative is then further halogenated if desired to produce another isolable derivative which contains 4 halogens, that is, cyclopentadienyl (tetrahalocyclopentanyl) metal dihalide.

As bis-cyclopentadienyl metal dihalide is reacted with chlorine, bromine or iodine, the derivatives are formed stepwise, i.e. cyclopentadienyl (dihalocyclopentenyl) metal dihalide is formed first and then as more halogen is added cyclopentadienyl (tetrahalocyclopentanyl) metal dihalide is produced. The reaction may be stopped at anytime if desired and the particular derivatives produced are directly dependent upon the amount of chlorine, bromine or iodine added. Since chlorine is most conveniently added as a gas by bubbling the gas through the suspension, a large excess is usually employed to obtain sufficient contact between the chlorine gas added and the bis-cyclopentadienyl metal dihalide employed. Both bromine and iodine are most conveniently employed in solution and therefore a much better contact is obtained between the bromine or iodine added and the bis-cyclopentadienyl metal halide employed and only a slight excess over the theoretical quantity of bromine or iodine is required to produce either one of the derivatives desired.

Both of these derivatives contain one cyclopentadienyl group and one aliphatic 5 membered carbon ring attached to each metal atom. Both derivatives also have 2 halogens attached to each metal atom. In addition these derivatives contain either 2 or 4 halogens selected from the group consisting of chlorine, bromine and iodine, said halogens are attached to the aliphatic 5 membered carbon ring.

In carrying out the process of this invention, any of the bis-cyclopentadienyl titanium or zirconium dihalides may be used. All of the titanium dihalide compounds are colored solids which vary from a yellow color for the difluoride to a deep red for the diiodide. The dichloride and dibromide lie in between as shades of red. All of the zirconium dihalide salts are white. Any of these dihalides are reacted with a halogen selected from the group consisting of chlorine, bromine and iodine and the titanium derivatives formed are all solids varying in color in various shades of orange while the solids are white for zirconium derivatives.

In order to describe more fully the instant invention, the following examples are presented.

Example 1

0.69 gram of bis-cyclopentadienyl titanium dichloride was dissolved in 100 ml. hot CCl_4. Chlorine gas was

bubbled through the solution at a rate of approximately 50 ml./min. for one hour. The chlorine addition was stopped when the red colored solution became orange in color. The solution was filtered and the yellow filtrate was vacuum stripped to remove the solvent and excess chlorine, leaving an orange colored solid. 0.25 gram of cyclopentadienyl dichlorocyclopentenyl titanium dichloride was recovered. Theoretical Ti=15.0%, found Ti=15.1%.

Example 2

0.6 gram of bis-cyclopentadienyl titanium dichloride and 2 ml. liquid bromine were added to 200 ml. CCl_4 and the mixture was allowed to stand overnight in a refrigerator at 0° C. The mixture was then heated to boiling on a hot plate to remove the bulk of the excess bromine. The solution was cooled and filtered prior to vacuum stripping. 1.20 grams of yellow-orange crystals of cyclopentadienyl tetrabromocyclopentanyl titanium dichloride were recovered. Theoretical Ti=8.44%; found Ti=8.21%.

It should be noted that the second derivative, i.e. cyclopentadienyl tetrabromocyclopentanyl titanium dichloride, was produced instead of the first, i.e. cyclopentadienyl dibromocyclopentenyl titanium dichloride, since an excess of bromine was employed. If the amount of bromine were limited to substantially the theoretical amount to form cyclopentadienyl dibromocyclopentenyl titanium dibromide, only the first derivative would have been formed.

Example 3

0.15 gram of bis-cyclopentadienyl zirconium dichloride was placed in a flask with 250 ml. CCl_4 and chlorine gas was bubbled through the mixture for 1 hour at the rate of 50 ml./min. The flask was stoppered and placed in a refrigerator overnight. Upon filtering, a white camphoraceous smelling solid weighing 0.1 gram was obtained after drying under vacuum for 2 hours. The cyclopentadienyl tetrachlorocyclopentanyl zirconium dichloride was identified by comparison of its infrared spectra with the analogous titanium compound.

It should be noted that the second derivative, i.e. cyclopentadienyl tetrachlorocyclopentanyl zirconium dichloride was formed instead of the first derivative. It should be further noted that this example differs from that of Example 1 in the amounts of reagents used. The amount of bis-cyclopentadienyl zirconium dichloride employed was considerably less than the amount of bis-cyclopentadienyl titanium dichloride used in Example 1 while the amount of chlorine used was the same, therefore, the ratio of chlorine to the bis-cyclopentadienyl metal dichloride was much greater in Example 3 than in Example 1 which results in the formation of the second derivative instead of the first.

Example 4

0.5 gram of bis-cyclopentadienyl titanium dichloride and 1.0 gram I_2 was mixed in a flask with 50 ml. CCl_4. The mixture was heated for one hour under gentle refluxing conditions and was cooled and permitted to stand overnight. The reaction mixture was stripped of the solvent and the excess iodine was sublimed off from the product. The material was recrystallized from CCl_4 and identified as cyclopentadienyl tetraiodocyclopentanyl titanium dichloride.

Example 5

0.5 gram of bis-cyclopentadienyl titanium dibromide was mixed with 200 ml. CCl_4 and chlorine gas was bubbled through the mixture for one hour at the rate of 50 ml./min. The flask containing the mixture was stoppered and placed in a refrigerator overnight. The solution was vacuum stripped to remove the solvent and excess chlorine leaving an orange colored solid. The product was identified as cyclopentadienyl tetrachlorocyclopentanyl titanium dibromide.

Example 6

0.5 gram of bis-cyclopentadienyl titanium diiodide and 1.0 gram of I_2 was mixed in a flask with 50 ml. of CCl_4. The mixture was heated for one hour under gentle refluxing conditions and was cooled and permitted to stand overnight. The reaction mixture was stripped of the solvent and the excess iodine was sublimed off the product. The material was recrystallized from CCl_4 and was identified as cyclopentadienyl tetraiodocyclopentanyl titanium diiodide.

Example 7

0.4 gram of bis-cyclopentadienyl titanium difluoride was admixed with 2 ml. liquid bromine and 200 ml. of CCl_4. The mixture was allowed to stand overnight in a refrigerator at 0° C. The mixture was then heated on a hot plate to remove the bulk of the excess bromine. The mixture was cooled and filtered prior to vacuum stripping. The yellow-orange crystals obtained were identified as cyclopentadienyl tetrabromocyclopentanyl titanium difluoride.

Example 8

0.5 gram of bis-cyclopentadienyl titanium dibromide and 2 ml. of liquid bromine were added to 200 ml. of CCl_4 and the mixture was allowed to stand overnight at 0° C. The mixture was then heated to remove the bulk of the bromine. The solution was cooled and filtered prior to vacuum stripping. The orange-colored crystals were identified as cyclopentadienyl tetrabromocyclopentanyl titanium dibromide and had the following analysis.

	C	H	Ti	Br
Theory	18.2	1.5	7.3	72.8
Found	18.0	2.5	6.5	71.2

From the above description and by the examples presented, a new type of derivative of bis-cyclopentadienyl titanium or zirconium dihalide has been produced. The derivatives formed contain an entirely new and novel type of bond, that is, a stable aliphatic carbon-metal bond for both the titanium and zirconium compounds. Such a new bond is far more reactive than the cyclopentadienyl metal bond and therefore is more useful in free radical type reactions in the production of various polymers and in other organic systems.

One particular type of reaction which utilizes the product of the instant invention is in the polymerization of styrene which uses the instant product as a catalyst. Styrene is polymerized as follows:

0.05 gram of the cyclopentadienyl dichlorocyclopentenyl titanium dichloride prepared in Example 1 was dissolved in 50 grams of an inhibitor-free styrene. This solution was then added under nitrogen atmosphere with stirring to 100 ml. H_2O containing 1 gram of ethyl sulfonate, which is a surface active agent, and 0.0159 gram of tartaric acid. After 2½ hours heating at 80–90° C. a white emulsion was formed which was added to 500 ml. methyl alcohol to precipitate a finely divided white polystyrene which was filtered, dried and recovered. This polymer was tested and found to be superior to known grades of polystyrene in that the polymer prepared by the catalyst of this invention was tougher and had a higher molecular weight. The method was repeated using cyclopentadienyl tetrabromocyclopentanyl titanium dichloride prepared in Example 2 and a similar polystyrene was obtained.

This application is a continuation-in-part of Serial No. 540,167 filed October 12, 1955, now abandoned.

While this invention has been described and illustrated by the examples shown, it is not intended to be strictly

limited thereto, and other variations and modifications may be employed within the scope of the following claims.

I claim:

1. A compound comprising a derivative of bis-cyclopentadienyl metal dihalide, said metal selected from the group consisting of titanium and zirconium, said dihalide selected from the group consisting of fluorine, chlorine, bromine and iodine, said derivative having one cyclopentadienyl group, one aliphatic group and two halogens directly attached to each metal atom, said aliphatic group selected from the group consisting of dihalocyclopentenyl and tetrahalocyclopentanyl.

2. Compound according to claim 1 in which 2 chlorines are attached to each metal atom.

3. Compound according to claim 1 in which 2 bromines are attached to each metal atom.

4. Compound according to claim 1 in which 2 iodines are attached to each metal atom.

5. Compound according to claim 1 in which 2 fluorines are attached to each metal atom.

6. Compound according to claim 1 in which the metal in said compound is titanium.

7. Compound according to claim 1 in which the metal in said compound is zirconium.

8. Compound according to claim 1 in which said aliphatic group is dihalocyclopentenyl.

9. Compound according to claim 1 in which said aliphatic group is tetrahalocyclopentanyl.

No references cited.