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PREPARATION OF CYCLOPENTADIENE METAL COMPOUNDS

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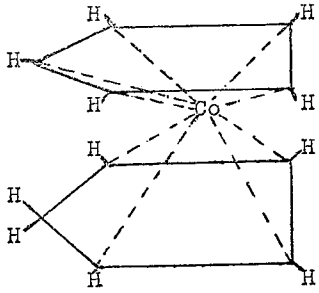
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This invention relates to a new and improved process for the preparation of organometallic compounds. More specifically this invention relates to a process for forming organometallic compounds in which a bis(cyclopentadienyl) metal compound is reduced to form a compound in which one or more cyclopentadiene molecules are bonded to the metal atom.

An object of this invention is to provide a process for forming organometallic compounds. A further object is to provide a new process in which a bis(cyclopentadienyl) metal compound is reacted with a reductant to form compounds in which one or more cyclopentadiene molecules are bonded to the metal atom. A more specific object is to provide a process in which are produced organometallic compounds of the metals selected from the group consisting of cobalt, rhodium, iridium, and nickel having one or more cyclopentadiene molecules coordinated with the metal atom. Further objects will become apparent by a reading of the specification and claims which follow.

The invention involves formation of organometallic compounds in which one or more cyclopentadiene molecules are coordinated with the metal atom, by reacting a bis(cyclopentadienyl) compound of a metal selected from the group consisting of cobalt, rhodium, iridium and nickel with a reducing agent. When the starting material is a bis(cyclopentadienyl) metal compound of cobalt, rhodium, or iridium, the resulting product is a compound in which both a cyclopentadienyl radical and a cyclopentadiene molecule are coordinated with the metal atom. When the starting material is a bis(cyclopentadienyl) compound of nickel, the product is a bis(cyclopentadiene) nickel compound.

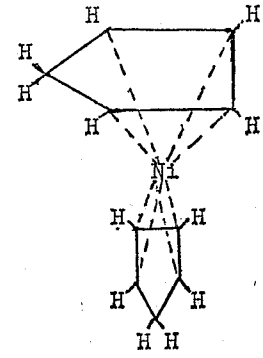
The compounds produced by our process are electronically neutral, reasonably stable compounds. This is so because the central metal atom present in the compounds has attained the configuration of the next higher rare gas above it in the periodic table by virtue of the donated electrons from the cyclopentadienyl radical and cyclopentadiene molecule. To illustrate, the compound cyclopentadienyl cobalt cyclopentadiene produced by our process has the following structural configuration:



As shown the cyclopentadienyl radical contributes five electrons to the cobalt atom and the cyclopentadiene molecule contributes four electrons to the cobalt atom. This gives a total of nine coordinated electrons and results in the cobalt atom having the electronic configuration of krypton which is the next higher inert gas above cobalt in the periodic table.

A somewhat different type of compound produced by the process results from the reaction of a reducing agent with a bis(cyclopentadienyl) nickel compound. As an

example, the compound bis(cyclopentadiene) nickel produced by the process has the structural configuration:



As shown, two cyclopentadiene molecules are coordinated with the nickel atom. Each cyclopentadiene molecule donates four electrons to the nickel atom for bonding, thereby giving it the electronic configuration of krypton which is the next higher rare gas above nickel in the periodic table.

I am not bound by any theory regarding the nature of my process. However, in order to explain the fact that my process produces cyclopentadienyl metal cyclopentadiene compounds of cobalt, rhodium, and iridium and conversely produces bis(cyclopentadiene) compounds of nickel, it is assumed that the metal atoms have a driving force toward attainment of rare gas configuration. Reduction of a single cyclopentadienyl radical leads to rare gas configuration when the starting material is a bis(cyclopentadienyl) metal compound of cobalt, rhodium, and iridium. Thus, the reduction stops at this point. On the other hand it is necessary that both cyclopentadienyl radicals be reduced when the starting material is a bis(cyclopentadienyl) nickel compound in order that the nickel atom attains rare gas configuration. Therefore, reduction in this case does not stop until both cyclopentadienyl radicals have been reduced.

My process involves the reduction of a compound having the formula Cy_2M. M in the above formula is a metal selected from the group consisting of cobalt, rhodium, iridium and nickel. Cy represents a cyclopentadienyl radical which may be substituted with various substituents and preferably contains from 5 to about 13 carbon atoms. Typical of the substituents which may be present on the cyclopentadienyl radical are alkyl groups such as methyl, ethyl, propyl, n-butyl, tert-butyl, hexyl and the like. The substituent groups may be aryl groups such as benzyl, p-methyl phenyl, and the like. Also, the substituent groups may be cycloaliphatic such as cyclohexyl, cyclopentyl; alkenyl groups such as propenyl, butenyl, pentenyl and the like, and cycloalkenyl radicals such as cyclohexenyl, cyclopentenyl and the like. In addition the cyclopentadienyl radical may be substituted with groups containing hetero atoms such as halogens, amines and the like. Typical of such groups are trichloromethyl, fluoro, dimethylamino, dihexylamino and the like.

Typical of the bis(cyclopentadienyl) metal compounds utilized as reactants in our process are bis(cyclopentadienyl) cobalt, bis(cyclopentadienyl) nickel, bis(methylcyclopentadienyl) rhodium, bis(propylcyclopentadienyl) iridium, bis(diethylcyclopentadienyl) nickel, bis(phenylcyclopentadienyl) cobalt, bis(trichloromethylcyclopentadienyl) nickel, bis(dimethylaminocyclopentadienyl) cobalt, bis(p-chlorobenxylcyclopentadienyl) nickel, and the like. When reduced according to my process these compounds yield respectively cyclopentadienyl cobalt cyclopentadiene, bis(cyclopentadiene) nickel, methylcyclopentadienyl rhodium methylcyclopentadiene, propylcyclopentadienyl iridium propylcyclopentadiene, bis(diethylcyclopentadiene)

nickel, phenylcyclopentadienyl cobalt phenylcyclopentadiene, bis(trichloromethylcyclopentadiene) nickel, dimethylaminocyclopentadienyl cobalt dimethylaminocyclopentadiene and bis(p-chlorobenxylcyclopentadiene) nickel.

My process takes the form of several embodiments. The first embodiment involves the reaction of a bis(cyclopentadienyl) metal compound as defined above with an alkali metal amalgam in the presence of a hydrolytic solvent. A preferred form of this embodiment involves the preparation of compounds as defined above in which the cyclopentadiene moiety is substituted only with hydrogen or a hydrocarbon substituent. The alkali metal amalgam may comprise, for example, sodium, lithium, or potassium amalgamated with mercury. The solvent is hydrolytic; that is, it contains a replaceable hydrogen atom. In this embodiment it is essential that the solvent contain a replaceable hydrogen atom since in the reduction of the bis-(cyclopentadienyl) compound a source of hydrogen is required to convert the cyclopentadienyl radical to cyclopentadiene. Typical of such hydrolytic solvents are the alcohols. Preferably, the alcohol solvent contains from one to four carbon atoms. Examples of such alcohols are methyl alcohol, ethyl alcohol, propyl alcohol and butyl alcohol.

The process embodiment defined above involving the use of an alkali metal amalgam in the presence of a hydrolytic solvent is preferred to other of my process embodiments as defined later. This embodiment is preferred since it gives in general better yields of product with less occurrence of undesirable side reactions than do the other embodiments.

In conducting my process according to the first process embodiment, the temperature employed may range between about −20° C. to about 100° C. Preferably the temperature is maintained between about zero to about 35° C. during the reaction, since within this range good yields of product are obtained with a minimum of undesirable side reactions occurring. The pressure employed is not critical and pressures up to 100 atmospheres of inert gas can be used. Preferably, however, the pressure is maintained between about atmospheric pressure and about five atmospheres. A protective atmosphere is preferably employed in the reaction vessel since this prevents decomposition of the reactants or products. Typical of the inert gases which may be used as a protective atmosphere are nitrogen, argon, helium, krypton, and neon. The reaction mixture is preferably agitated so that the reactants are intimately dispersed. This is extremely desirable since without agitation the reactants cannot contact each other sufficiently to maintain an even reaction rate.

In general the time required for the reaction varies between about 30 minutes and about 12 hours. The time requirement is not critical, however, since the time required will vary with the reaction temperature and the quantities of reactants used. Thus, if the reaction temperature is high and certain of the reactants are used in excess, the reaction time will be relatively short. Conversely, if a low temperature is employed and the reactants are used in stoichiometric quantities, the reaction time will be longer.

In general, an excess of alkali metal amalgam is utilized in the process. For each mole of bis(cyclopentadienyl) metal reactant, there are preferably employed from about three to about six moles of alkali metal as amalgam. Greater or lesser quantities of alkali metal amalgam can be employed although in general this decreases the efficiency of the process.

The composition of the alkali metal amalgam generally comprises between about two to about 5 percent by weight of alkali metal. Greater or lesser quantities of alkali metal can be employed in the amalgam but the use of such quantities may reduce the effectiveness of the reaction. For example, if the concentration of alkali metal is less than two percent, the reaction rate may be decreased because of the decreased contact between the alkali metal and the bis(cyclopentadienyl) reactant. When the alkali metal content in the amalgam is higher than five percent, some alkali metal may be present in unamalgamated form. At such concentrations the alkali metal may, in a free form, react with explosive violence if water is present in the system. This result is undesirable since in some instances water is employed in the process.

As stated above, the preferred solvent for use in the process is an alcohol containing from about one to about four carbon atoms. Such alcohols are hydrolytic and supply hydrogen for the reacton. Other solvents may be employed, however. For example, a mixed solvent comprising up to about 10 percent by weight of water admixed with alcohol can be employed. A mixed solvent can be employed containing up to about 10 percent by weight of water admixed with a highly polar ether such as tetrahydrofuran, ethylene glycol dimethylether, ethylene glycol diethylether, ethylene glycol dibutylether, diethylene glycol dimethylether, diethylene glycol diethylether, diethylene glycol dibutylether, and the like.

Other mixed solvents which can be employed are those comprising 10 percent or more by weight of an alcohol containing from about one to about four carbon atoms and a neutral hydrocarbon or ether solvent. Typical of the solvents with which the alcohol can be admixed are the aliphatic hydrocarbons such as n-hexane, n-octane, isooctane, n-heptane, various isomers of hexane, octane and heptane, or mixtures of the above. Other suitable neutral solvents are the cycloaliphatic hydrocarbons such as cyclohexane or methylcyclohexane. Straight and branched chain olefins such as isoheptene, n-hexene, isooctene, and n-octene are also applicable. Aromatic hydrocarbon solvents such as benzene, toluene, ethylbenzene and xylene, either mixed or pure, may also be used.

Other solvents which can be employed are mixtures comprising 10 percent or more by weight of an alcohol, as defined above, admixed with an ether solvent. Typical of such ether solvents are the cyclic ethers such as tetrahydrofuran, and 1,3-dioxane. Non-cyclic monoethers such as diethylether, diisopropylether and diphenylether are also applicable. Other ethers which may be admixed with an alcohol are ethylene glycol dimethylether, ethylene glycol diethylether, diethyleneglycol dimethylether, diethylene glycol diethylether, and the like.

The amount of solvent used in the process is not critical. Generally, however, sufficient solvent is employed to dissolve the dicyclopentadienyl metal reactant. Use of less solvent than this amount is permissible so long as a fluid reaction mass is maintained. Use of a great excess of solvent does not unduly hinder the process but its use generally achieves no purpose. Also, the use of a large excess of solvent dilutes the reaction mass and thereby diminishes the reaction rate; extra process equipment is required to handle increased solvent throughput, and more valuable solvent is lost through evaporation, leakage, etc.

The other process embodiments involve use of a reductant other than an alkali metal amalgam. A second process embodiment involves the use of a simple or complex alkali metal hydride as the reductant. Examples of such hydrides are sodium borohydride, lithium aluminum hydride, lithium borohydride, potassium borohydride, magnesium bis(aluminum hydride), sodium trimethoxy borohydride, sodium hydride, lithium hydride, cesium hydride, rubidium hydride, potassium hydride and the like. The complex alkali metal borohydrides are preferred hydrides for reducing bis(cyclopentadienyl) metal compounds, as defined above, in which the cyclopentadienyl moiety contains hetero substituents that are easily reduced. The borohydrides are milder reducing agents than other alkali metal hydrides. Their use thereby enables reduction of the bis(cyclopentadienyl)metal compound without reducing the hetero substituents.

When using a simple or complex alkali metal hydride as the reductant, the same solvents may be employed as

previously set forth for the alkali metal amalgam embodiment. Certain alkali metal hydrides are extremely reactive, however, and in some cases it is not desirable to use water in a weight concentration up to 10 percent of the solvent mixture. For example, when using sodium hydride as the reductant, I prefer to maintain the water concentration at less than two percent by weight. Selection of a solvent that is not too reactive with the alkali metal reductant is within the skill of the art when practicing my process. In my process, therefore, the water concentration can be adjusted to suit the reactivity of the alkali metal reductant.

The temperature at which reaction may be carried out when using an alkali metal hydride ranges from about zero to about 100° C. Preferred temperatures are about zero to about 50° C. since within this range yields are maximized and undesirable side reactions are minimized. The process is preferably carried out under an inert atmosphere of, for example, nitrogen, argon, krypton or neon. Agitation is preferably employed in the process since it insures intimate contacting of the reactants and a steady reaction rate. The process pressures are not critical and up to 100 atmospheres of inert gas pressure can be used. Preferably pressures ranging from about one to about five atmospheres are employed.

From about one to about six moles of alkali metal hydride are generally employed for each mole of bis(cyclopentadienyl)metal compound. Greater or lesser quantities of alkali metal hydride can be used but in general the reaction works best within the above specified range. The amount of solvent employed is not critical but in general sufficient solvent is employed to dissolve the cyclopentadienyl metal reactant. Use of a large excess of solvent does not greatly hinder the reaction but in general is avoided. It may result in solvent loss and a slower reaction rate due to decreased contact between the reactants.

Another embodiment of my process involves the use of an alkali metal as the reductant. In using an alkali metal as reductant, a preferred form of my process involves reduction of a bis(cyclopentadienyl)metal compound in which the cyclopentadienyl moieties are substituted only with hydrogen or a hydrocarbon substituent. This embodiment is closely related to the previous embodiment utilizing an alkali metal hydride reductant. In general, the same conditions apply to this embodiment as apply to reduction via an alkali metal hydride. Since the alkali metals, e.g., sodium, potassium, lithium, cesium, and rubidium are somewhat more reactive than the alkali metal hydrides, precautions must be taken as to the composition of the solvent employed. The alkali metals react vigorously with water and relatively high concentrations of water in the solvent should therefore be avoided. Water concentration in the solvent when using an alkali metal reductant should generally not exceed one percent by weight. Higher concentrations can be used but their use may make the reaction rate hard to control. In many cases, it is, therefore, desirable to dilute the solvent containing water or an alcohol as previously defined, with additional inert solvent. Since many of the alkali metals react rapidly with alcohols, high alcohol concentrations should be avoided since they will make the reaction difficult to control. Use of higher alcohols, e.g., butyl or propyl, is frequently advantageous in the process since higher alcohols are less reactive with respect to the alkali metal. They can be employed with less risk of letting the reaction rate get out of hand.

A further process embodiment differing slightly from previous embodiments involves the reaction of a cyclopentadienyl metal compound as previously defined with hydrogen in the presence of a neutral solvent and a hydrogenation catalyst. Typical hydrogenation catalysts such as Raney nickel, platinum, palladium, and copper chromite can be used. The catalyst is generally employed in a small amount ranging up to a maximum concentration of about 30 percent by weight of the bis(cyclopentadienyl)metal compound to be reduced. Ordinarily, excess hydrogen is employed. Use of excess hydrogen tends to force the reaction to completion and thereby results in higher product yields in a shorter time period. In order to insure an excess of hydrogen, the reaction is preferably conducted under at least about one atmosphere of hydrogen pressure. Higher pressures up to about five atmospheres of hydrogen can be employed but in general pressures in the order of one atmosphere are preferred. Excess hydrogen which is not consumed in the reaction can be readily recovered and recycled to the reaction vessel. In this process embodiment a preferred species is the reduction of a bis(cyclopentadienyl) metal compound in which the cyclopentadienyl moieties are substituted only with hydrogen or a hydrocarbon substituent.

During the process the reaction mixture is preferably agitated. This results in intimate contacting of reactants and a smooth and even reaction rate. Process temperatures can range from between about zero to about 100° C. Preferably the temperature ranges between about 25 to about 50° C. Within this latter range maximum yields of product are obtained with a minimum of undesirable side reactions. The pressure is not critical and may range between about one to about 150 atmospheres of an inert gas. Higher pressures may be used although this is generally not advantageous.

Unlike preceding process embodiments this embodiment does not require a solvent which is hydrolytic. Hydrogen is added directly to the reaction mixture and it is, therefore, not necessary that the solvent contain active hydrogen. Hydrolytic solvents may be employed however without adversely affecting the reaction. Typical of the solvents which may be employed are aliphatic hydrocarbons such as hexane, heptane, n-octane, n-nonane and isomeric forms of the preceding hydrocarbons. Also cycloaliphatic hydrocarbons are applicable such as cyclohexane, methyl cyclohexane and the like. Aromatic solvents such as toluene, benzene and xylenes either pure or mixed, can be used.

Ether solvents such as ethyl octylether, ethyl hexylether, diethylene glycol diethylether, diethylene glycol dimethylether, diethylene glycol dibutylether, ethylene glycol dimethylether, ethylene glycol diethylether, ethylene glycol dibutylether, dioxane and the like are suitable. Silicone oils such as the dimethyl polysiloxanes, methyl phenyl polysiloxanes, di-(chlorophenyl)polysiloxanes, hexapropyl disilane and diethyldipropyldiphenyldisilane may also be employed. Included also are pentyl butanoate, ethyl decanoate, ethyl hexanoate and ester solvents derived from poly acids such as succinic, malonic, glutaric, adipic, pimelic, suberic, azelaic, sebacic and pinic acids. Specific examples of the diesters are di-(2-ethylhexyl) adipate, di-(2-ethylhexyl) azelate, di-(2-ethylhexyl) sebacate, di-(methyl cyclohexyl) adipate and the like. Also applicable, as previously stated, are hydrolytic solvents as defined previously. Such solvents include the alcohols, e.g., methyl, ethyl, propyl and butyl alcohol, water admixed with one of the foregoing alcohols, or a mixture of water and/or an alcohol with an inert organic solvent.

To further illustrate our process, there are presented the following examples in which all parts and percentages are by weight unless otherwise indicated.

Example 1

A mixture of 3.2 parts of nickelocene and 38.6 parts of a five percent sodium amalgam in 79 parts of absolute ethanol was stirred at 0° C. under nitrogen atmosphere for 2.5 hours. During the reaction period, the nickelocene reacted to give a red-brown reaction mixture. The ethanol suspension was decanted from the mercury into a separatory funnel and about 200 parts of water and about 64 parts of petroleum ether were added. The or-

ganic phase was washed twice with water and dried rapidly over magnesium sulfate at a reduced temperature. It was then concentrated by heating in vacuo to dryness to give 2.12 parts of a red-crystalline residue. The residue was recrystallized from petroleum ether at —78° C. to give 0.6 part of bis(cyclopentadiene) nickel having a melting point of 38–42° C. Sublimation of this product at room temperature and 0.2 mm. pressure gave an analytical sample of bis(cyclopentadiene) nickel having a melting point of 43–44.5° C. *Analysis.*—Calculated for $C_{10}H_{12}Ni$: C, 62.91; H, 6.31; Ni, 30.75. Found: C, 63.0; H, 6.52; Ni, 30.5. The mother liquors of the crystallization were sublimed and yielded an additional 0.95 part of semi-pure bis(cyclopentadiene) nickel having a melting point of 40–43° C. The compound is sensitive to air and decomposes under nitrogen at 175° C. The compound is diamagnetic and its structure was further supported by infrared analysis.

Example 2

A mixture comprising 3.1 parts of freshly sublimed cobaltocene, 57.6 parts of 5 percent sodium amalgam and 79 parts of absolute alcohol were stirred at 0° C. for three hours under a nitrogen atmosphere. During the reaction period, the sodium amalgam reacted completely and the color of the mixture changed from purple to red-brown. The solvent was removed at 20 mm. pressure and room temperature to give a red semi-solid mixed with mercury metal. This mixture was subjected to sublimation at 75° C. and 20 mm. causing the separation of 1.05 parts of crude cyclopentadienyl cobalt cyclopentadiene as long, dark-red needles having a melting point of 107–115° C. The product was further purified by chromatographing through a column packed with alumina and eluting with petroleum ether. A brick-red band, which separated first, was concentrated to a red crystalline solid. Sublimation of the solid at 90° C. and 20 mm. gave 0.46 part of red crystals (cyclopentadienyl cobalt cyclopentadiene) having a melting point of 94–95° C. The structure of the product was further confirmed by infrared analysis.

Example 3

A mixture of 6.32 parts of nickelocene and about 2.5 parts of Raney nickel in 197 parts of absolute ethanol was stirred and treated with hydrogen at atmospheric pressure and room temperature. When slightly more than two equivalents of hydrogen were taken up, the hydrogenation was stopped and the reaction product was discharged. The reaction product was then filtered and concentrated to dryness. The residues were chromatographed through an alumina-packed column. The product was eluted with petroleum ether. Two bands, one green and one red, were observed. The red band was separated and dried to give 0.2 part of bis(cyclopentadiene)nickel. The green band, when separated and dried, gave 0.8 part of unreacted nickelocene.

Example 4

To a stirred solution comprising 1.88 parts of nickelocene in 19.7 parts of absolute ethanol under a nitrogen atmosphere were added 0.37 part of sodium borohydride. The sodium borohydride was added all at once. On warming the reaction vessel in a water bath for a few minutes at 50. C. an exothermic reaction was initiated. The reaction mixture rapidly turned black and hydrogen gas was evolved. After about 15 minutes, vigorous reaction had ceased and the mixture was stirred at room temperature for an additional 45 minutes. Two hundred parts of water and 158 parts of ethylether were added to give two phases which contained a black suspension. The mixture was filtered and the phases were separated. The ether phase was washed with water, dried over magnesium sulfate and concentrated in vacuo to a green-brown partially crystalline mass. This was placed in a column containing finely divided alumina. Elution with petroleum ether gave first an orange band which on concentration gave a red semi-solid. Crystallization of the solid from petroleum ether gave 0.1 part of bis(cyclopentadiene) nickel as dark red prisms. Their melting point was 38–40° C. A second band, eluted with petroleum ether, was nickelocene. When concentrated and recrystallized from petroleum ether the nickelocene gave dark green crystals having a melting point of 166–170° C. with decomposition.

Example 5

One mole of bis(methylcyclopentadienyl) nickel is dissolved in butyl alcohol and six moles of potassium as a two percent potassium amalgam are charged to an evacuated autoclave. The autoclave is pressurized to five atmospheres with argon. The mixture is heated with stirring for 30 minutes at 35° C. after which the autoclave is cooled and the contents are discharged. The product, bis(methylcyclopentadiene) nickel is separated from the solvent by means of chromatography. A good yield is obtained.

Example 6

Two moles of bis(octylcyclopentadienyl) rhodium dissolved in a solvent comprising 10 percent water and 90 percent tetrahydrofuran is charged to an autoclave along with three moles of lithium in the form of a three percent lithium amalgam. The autoclave is pressurized with helium to 100 atmospheres. The autoclave is cooled to —20° and maintained at this temperature for 12 hours while the reaction mixture is stirred. It is then vented and the product is discharged. A good yield of octylcyclopentadienyl rhodium octylcyclopentadiene is obtained by separation of the product from the solvent through chromatography.

Example 7

One mole of bis(methylcyclopentadienyl) cobalt dissolved in a solvent comprising 50 percent propyl alcohol and 50 percent benzene is charged to an evacuated autoclave along with one mole of lithium aluminum hydride. The vessel is pressurized to one atmosphere of nitrogen. The reaction mixture is stirred for three hours at 0° C. whereupon the autoclave is discharged. The product methylcyclopentadienyl cobalt methylcyclopentadiene is recovered in good yield from the solvent by chromatography.

Example 8

Two moles of bis(trichloromethylcyclopentadienyl) nickel dissolved in methyl alcohol is charged to an evacuated autoclave along with two moles of sodium borohydride. The vessel is pressurized with nitrogen to one atmosphere. The mixture is stirred for two hours at 20° C. and the vessel is discharged. The product bis(trichloromethylcyclopentadiene) nickel is recovered in good yield by chromatography.

Example 9

One mole of bis(cyclopentadienyl) iridium dissolved in a solvent comprising two percent water and 98 percent dioxane is charged to an evacuated autoclave along with six moles of sodium hydride. The autoclave is pressurized to 100 atmospheres with argon and stirred for 30 minutes at 30° C. The vessel is then discharged and water is added to the reaction mixture. The mixture is filtered and the solids are dissolved in petroleum ether. A good yield of cyclopentadienyl iridium cyclopentadiene is recovered from the ether by means of fractional crystallization.

Example 10

One mole of bis(dimethylcyclopentadienyl) nickel dissolved in absolute ethanol is charged to an evacuated autoclave along with two moles of lithium. The autoclave is then pressurized to one atmosphere with nitrogen and stirred for three hours at 15° C. The contents are then discharged and a good yield of bis(dimethylcyclo-

pentadiene) nickel is separated from the reaction product by means of chromatography.

Example 11

One mole of bis(methylcyclopentadienyl) cobalt dissolved in sec-butyl alcohol is charged to an evacuated autoclave along with three moles of potassium. The autoclave is pressurized to 75 atmospheres with argon. The mixture is then stirred for four hours at 20° C. whereupon the vessel is discharged. A good yield of methylcyclopentadienyl cobalt methylcyclopentadiene is recovered by distilling the reaction product under reduced pressure.

Example 12

Two moles of bis(cyclopentadienyl) cobalt dissolved in ethylether is charged to an autoclave which is pressurized to one atmosphere with hydrogen. One-tenth mole of platinum catalyst is added to the autoclave and stirring of the reaction mixture is commenced. The pressure in the autoclave is maintained at one atmosphere by feeding in hydrogen as the reaction progresses. When one mole of hydrogen has been fed to the autoclave, stirring is ceased and the autoclave is discharged. The product is filtered and the filtrate is reduced to dryness by heating under reduced pressure. The residues are sublimed to give a good yield of cyclopentadienyl cobalt cyclopentadiene.

Example 13

One mole of bis(methylcyclopentadienyl) nickel dissolved in benzene is charged to an autoclave pressurized to five atmospheres with hydrogen. Copper chromite is then added to the autoclave in an amount equal to 10 percent by weight of the bis(methylcyclopentadienyl) nickel reactant. The reaction mixture is stirred at 50° C. until a pressure drop is noted which is equivalent to one mole of hydrogen being consumed in the reaction. Agitation is then stopped and the reaction vessel is discharged. A good yield of bis(methylcyclopentadienyl) nickel is obtained by distillation from the reaction product.

Example 14

One mole of bis(phenylcyclopentadienyl) rhodium dissolved in diethylene glycol dimethylether is charged to an autoclave pressurized with hydrogen to one atmosphere. Finely divided palladium catalyst is added which is equal to two weight percent of the bis(phenylcyclopentadienyl) rhodium. The reaction mixture is stirred at 40° C. Pressure in the reaction vessel is maintained constant at one atmosphere by slowly adding hydrogen to the system as hydrogen is consumed in the reaction. When ½ mole of hydrogen has been added to the system in maintaining the pressure at one atmosphere, stirring is ceased and the reaction vessel is discharged. A good yield of phenylcyclopentadienyl rhodium phenylcyclopentadiene is obtained from the reaction product by means of chromatography.

The compounds made according to the process are useful antiknocks when added to a petroleum hydrocarbon. They may be used as primary antiknocks in which they are the major antiknock component in the fuel or also as supplemental antiknocks. When used as supplemental antiknocks, they are present as the minor antiknock component in the fuel in addition to a primary antiknock such as tetralkyllead compound. Typical alkyllead compounds are tetraethyllead, tetrabutyllead, tetramethyllead and various mixed lead alkyls such as dimethyldiethyllead, diethyldibutyllead and the like. When used as either a supplemental or primary antiknock the compounds produced by the process may be present in the gasoline in combination with typical scavengers such as ethylene dichloride, ethylene dibromide, tricresylphosphate and the like.

The compounds produced by my process are further useful in many metal plating applications. In order to effect metal plating using the compounds produced by my process, they are decomposed in an evacuated space containing the object to be plated. On decomposition, they lay down a film of metal on the object. The gaseous plating may be carried out in the presence of an inert gas so as to prevent oxidation of the plating metal or the object to be plated during the plating operation.

The gaseous plating technique described above finds wide application in forming coatings which are not only decorative but also protect the underlying substrate material. When the metal laid down is a conductor such as nickel this technique enables the preparation of plated circuits which find wide application in the electrical arts.

Deposition of metal on a glass cloth illustrates the applied process. A glass cloth band weighing one gram is dried for one hour in an oven at 150° C. It is then placed in a tube which is devoid of air and there is added to the tube 0.5 gram of bis(cyclopentadiene) nickel. The tube is heated at 400° C. for one hour after which time it is cooled and opened. The cloth has a uniform metallic grey appearance and exhibits a gain in weight of about 0.02 gram. The cloth has greatly decreased resistivity and each individual fiber proves to be a conductor. An application of current to the cloth causes an increase in its temperature. Thus a conducting cloth is prepared which can be used to reduce static electricity, for decorative purposes, for thermal insulation by reflection or as a heating element.

Having fully described my novel process, I desire to be limited only within the scope of the appended claims.

I claim:

1. Process for preparing a cyclopentadiene metal compound selected from the class consisting of cyclopentadienyl cobalt cyclopentadienes, cyclopentadienyl iridium cyclopentadienes, cyclopentadienyl rhodium cyclopentadienes, and bis(cyclopentadiene) nickels wherein the cyclopentadiene and cyclopentadienyl groups are hydrocarbon groups having from 5 to about 13 carbon atoms; said process comprising reacting the corresponding neutral bis(cyclopentadienyl) metal compound at a temperature within the range of about −20° C. to about 100° C. with a reducing agent selected from the class consisting of

A. alkali metals, alkali metal amalgams and simple and complex alkali metal hydrides,

wherein said process is conducted in the presence of a hydrolytic solvent and

B. hydrogen, in the presence of a catalytic quantity of a catalyst selected from the class consisting of Raney nickel, platinum, palladium and copper chromite,

wherein said process is conducted in the presence of a solvent selected from the class consisting of hydrolytic and non-hydrolytic solvents.

2. The process of claim 1 wherein the reducing agent is an alkali metal amalgam and a hydrolytic reaction solvent is employed.

3. The process of claim 1 wherein the reducing agent is an alkali metal hydride selected from the group consisting of complex alkali metal hydrides and simple alkali metal hydrides and a hydrolytic reaction solvent is employed.

4. The method of claim 1 wherein the reducing agent is an alkali metal and a hydrolytic reaction solvent is employed.

5. The process of claim 1 wherein the reducing agent is hydrogen.

6. The process of claim 5 wherein the reduction reaction is carried out in the presence of a hydrogenation catalyst.

7. The process of claim 1 wherein the bis(cyclopentadienyl) metal compound is selected from the group consisting of cobalt, rhodium and iridium and the product produced is a cyclopentadienyl metal cyclopentadiene compound in which the metal is selected from the group consisting of cobalt, rhodium and iridium.

8. The process of claim 1 wherein the bis(cyclopenta-

dienyl) metal compound is a bis(cyclopentadienyl) nickel compound and the product produced is a bis(cyclopentadiene) nickel compound.

9. The process of claim 2 wherein the alkali metal amalgam contains between about 2 to about 5 percent by weight of alkali metal.

10. Process comprising reacting bis(cyclopentadienyl) nickel with an alkali metal amalgam containing from about two to about 5 percent by weight of alkali metal in the presence of a hydrolytic solvent at a temperature within the range of about —20° C. to about 100° C. and under an atmosphere of an inert gas to yield bis(cyclopentadiene) nickel.

11. Process comprising reacting bis(cyclopentadienyl) cobalt with an alkali metal amalgam containing from about two to about 5 percent by weight of alkali metal in the presence of a hydrolytic reaction solvent at a temperature within the range of about —20° C. to about 100° C. and under an atmosphere of an inert gas to yield cyclopentadienyl cobalt cyclopentadiene.

12. Process comprising reacting bis(cyclopentadienyl) nickel with hydrogen in the presence of absolute ethanol and a catalytic quantity of Raney nickel at a temperature within the range of about 0° C. to about 100° C. to yield bis(cyclopentadiene) nickel.

13. Process comprising reacting bis(cyclopentadienyl) nickel with sodium borohydride in the presence of a hydrolytic solvent at a temperature within the range of about 0° C. to about 100° C. and under an atmosphere of an inert gas to yield bis(cyclopentadiene) nickel.

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