

[54] **PREPARATION OF DIARENE CHROMIUM COMPOUNDS**

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[57] **ABSTRACT**

Diarene chromium compounds where each arene separately is an alkyl benzene or optionally alkyl substituted diphenyl, tetralin or indane molecule are prepared substantially pure by condensing gaseous chromium atoms with the arene or mixture thereof at a pressure of less than  $10^{-2}$  torr and at a temperature compatible with maintaining that pressure. The diarene chromium compounds may be thermally decomposed to deposit a layer comprising chromium.

**15 Claims, 2 Drawing Figures**

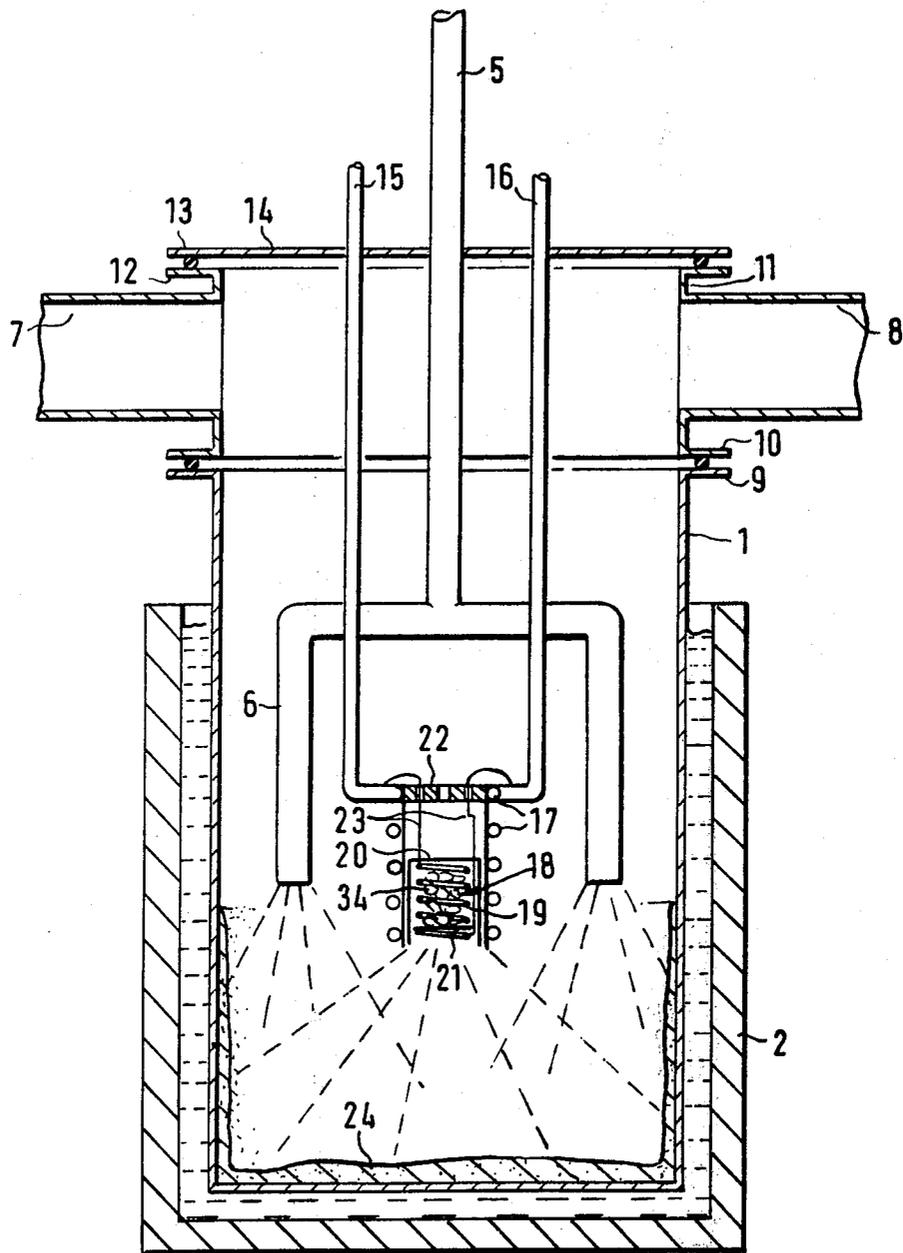
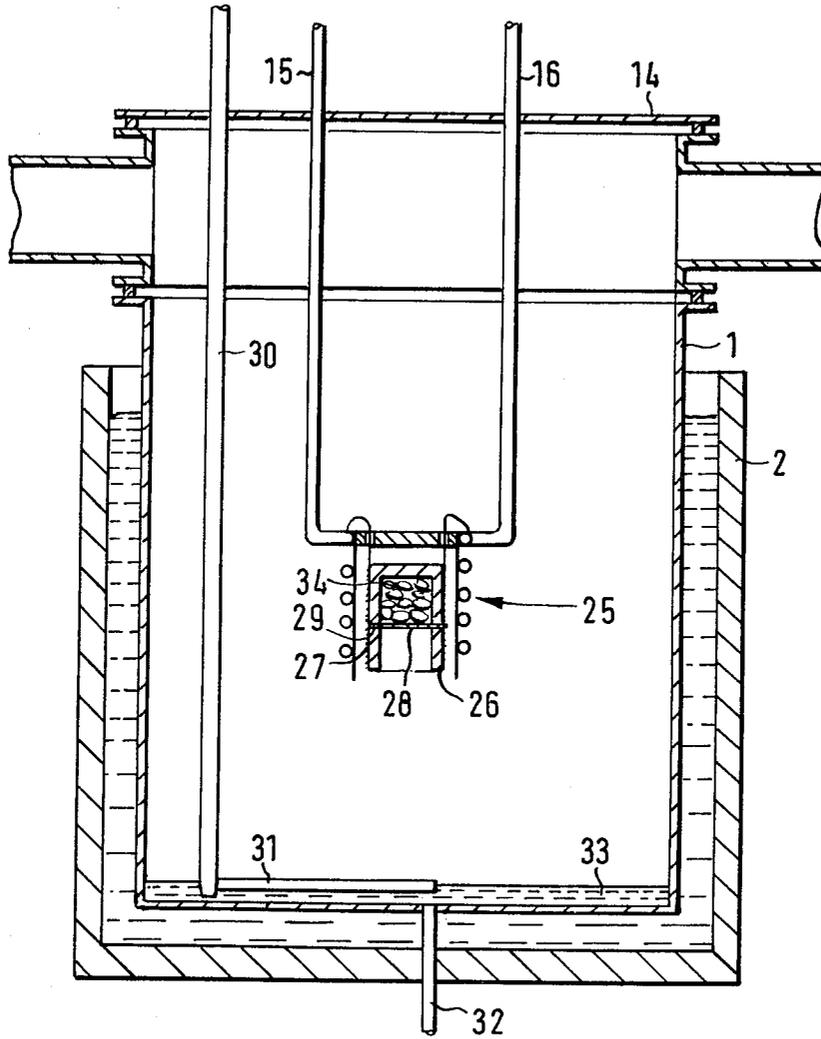


FIG. 1



## PREPARATION OF DIARENE CHROMIUM COMPOUNDS

The present invention relates to complexes of aromatic compounds with chromium, and to methods for producing them.

Complexes of alkyl benzenes with chromium such as dicumene chromium are known. Such compounds are normally prepared by a reaction between chromium chloride, aluminium and the alkyl benzene, normally under the influence of an aluminium chloride catalyst. Unfortunately, however, this route tends to bring about the rearrangement of isomerisation of the alkyl benzene species by a Friedel Craft reaction so that for example the product typically obtained when employing cumene as the alkyl benzene comprises a liquid mixture having the apparent composition 7% dibenzene chromium, 43% dicumene chromium, 34% mixed bis (diisopropyl benzene) chromium, and 16% bis (triisopropyl benzene) chromiums. With ethyl benzene as the alkyl benzene, a mixture of diarene chromiums is obtained, each compound having as the arene part, two ethylbenzene, diethylbenzene or triethylbenzene molecules, one benzene and one ethylbenzene molecule, or one ethylbenzene and one diethylbenzene molecule. It has been reported (Metody Poluch. Anal. Veshchestv. Osobvi. Chist. Tr. Vses, Konf. 1968, p.116; Chem. Abs. 1971,75 63925) that under very carefully controlled conditions it is possible to make pure bis(ethyl benzene) chromium by the Friedel-Crafts route, but the process is completely unsuitable for industrial application.

Timms (Chem. Comm. 1969, 1033) has described a process of reacting gaseous chromium atoms with benzene vapour at a low pressure and collecting the bis benzene chromium product on a cooled surface.

As further described below, compounds of this type are mainly used for depositing chromium on a substrate. We have now found that if the process described in the Timms article is applied to alkyl benzenes and unsubstituted and alkyl substituted diphenyls, tetralins and indanes di arene chromiums can be obtained in a substantially pure form. This is surprising since it would have been expected that the chromium atoms would have decomposed the alkyl substituted hydrocarbons or at least caused disproportionation or rearrangement. The process is simple and easy and is carried out in a single stage without the use of expensive materials (e.g. chromium chloride) or hazardous materials.

The present invention provides a process for preparing diarene chromium compounds, which process comprises condensing gaseous chromium atoms with at least one aromatic compound of formula Ar' or Ar'', or a mixture thereof, at a pressure of less than  $10^{-2}$  torr and at a temperature compatible with maintaining said pressure, Ar' representing an alkyl benzene molecule, in which the benzene ring is substituted by one or more alkyl groups, preferably 1 - 3 groups, each preferably of 1 - 6 carbon atoms, especially branched chain alkyl groups of at least 3 carbon atoms, and Ar'' representing a diphenyl tetralin or indane molecule, each of which is unsubstituted or substituted by one or more alkyl groups, each preferably of 1 - 6 carbon atoms. This process enables arene chromium compounds to be formed without substantial isomerization or disproportionation and is particularly applicable when the arene

contains at least one alkyl group of 2 or more, usually 3 or more carbon atoms.

The pressure in the system should be less than  $10^{-2}$  torr; preferably it is below  $10^{-3}$  torr and optimally below  $2 \times 10^{-4}$  torr. If high speed pumping is employed this dynamic pressure will be below the equilibrium pressure for the system. It is of course the dynamic pressure in the system which is the pressure referred to herein. It is necessary to keep the pressure in the system at these low levels in order to prevent the reaction of the chromium atoms with themselves or other undesired species which might be present if a high vacuum were not maintained.

The reaction is carried out in a reactor having walls maintained at a temperature compatible with the need to maintain the pressure at less than  $10^{-2}$  torr and stop volatilization of the aromatic compound. Thus with volatile aromatic compounds such as toluene, the wall temperature is less than for less volatile aromatic compounds such as diphenyl for a constant pressure. Of course if the pressure can be greater and still less than  $10^{-2}$  torr in the case of the volatile compound then it may be possible for the wall temperature to be the same in both cases.

Chromium atoms for condensing with the aromatic compound may be obtained by any convenient means of which many are known - for example by volatilisation (typically as sublimation) of massive chromium or from a chromium arc or other plasma, or by the action of an electron or laser beam on massive chromium. If volatilisation techniques are employed it may be possible to employ not only pure chromium metal as the source but also ferrochrome or certain compounds such as chromium carbide. Normally such material will be heated by conventional electrical resistance heating in a molybdenum or tungsten crucible.

Normally a substantial excess of the aromatic compound or compounds will be employed in the process of the invention. For example a molar excess of 10 : 1 is typical and one of 20 : 1 is often preferred.

The process can be carried out by a cocondensation route by passing gaseous chromium atoms and vapour of the aromatic compound or compounds in a reactor on to the chilled surface of the reactor, preferably one chilled to at least  $-60^{\circ}\text{C}$ , such as  $-60^{\circ}\text{C}$  to  $-100^{\circ}\text{C}$ , but especially  $-160^{\circ}\text{C}$  to  $-200^{\circ}\text{C}$ . A temperature of about  $-80^{\circ}\text{C}$  can be maintained with a mixture of solid carbon dioxide and an organic solvent such as ethanol or acetone. A temperature of  $-180^{\circ}\text{C}$  to  $-200^{\circ}\text{C}$  can be maintained with liquid air or liquid nitrogen (b.p.  $-196^{\circ}\text{C}$ ). Slightly lower temperature from the values of about  $-80^{\circ}\text{C}$  and  $-190^{\circ}\text{C}$  can be obtained by forced cooling. Alternatively any other temperature and method of cooling can be used so long as the chilled surface can be maintained at a temperature compatible with maintaining the pressure of less than  $10^{-2}$  torr. The actual temperature of the cooling bath surrounding the reactor needed to maintain the inner surface of the reactor at the necessary temperature depends on the wall thickness, heat losses and other similar parameters. The temperature of the inner surface is less, preferably  $20^{\circ}\text{C}$  to  $60^{\circ}\text{C}$  less, than that necessary to keep the vapour pressure of the aromatic compound or compounds sufficiently low to avoid any substantial volatilization under the pressure employed.

Alternatively, as we have discovered, the process of the invention can be carried out in a liquid phase route

by condensing gaseous chromium atoms in a reactor on to a continually regenerated surface of a liquid, which comprises the aromatic compound or compounds and is maintained at a temperature compatible with the need to keep the pressure in the reactor of less than  $10^{-2}$  torr. The temperature is usually  $-60^{\circ}\text{C}$  to  $-150^{\circ}\text{C}$ , preferably  $-70^{\circ}\text{C}$  to  $-100^{\circ}\text{C}$ , especially  $-80^{\circ}\text{C}$  to  $-90^{\circ}\text{C}$  e.g. about  $-80^{\circ}\text{C}$  with cooling by a bath of solid carbon dioxide and an organic solvent such as acetone or ethanol. The same general criteria governing the temperature as in the cocondensation process apply here too but the lower limit for the temperature of the liquid is its melting point while the upper limit depends on the volatility of the liquid. The liquid phase can be the aromatic compound (or compounds) alone or diluted with a solvent having itself a sufficiently low vapour pressure at the temperature of the liquid. Examples of such solvents for use with temperatures of the order of  $-60^{\circ}\text{C}$  to  $-100^{\circ}\text{C}$  and 0 to  $25^{\circ}\text{C}$  respectively are di-isooctyl ether and hydrocarbon vacuum pump oils such as "Apiezon BW". The liquid phase is preferably agitated e.g. with a rotating or oscillating stirrer or an oscillatable paddle in order to expose continually a fresh surface for reaction with the chromium atoms, and, where the source of chromium atoms radiates heat in the direction of the liquid, ensures that the surface of the liquid is not heated sufficiently to volatilize substantial amounts of it. The liquid may also be stirred by magnetic or ultrasonic means. Alternatively external agitation can be avoided if desired, by passing the liquid through at least one port in the side wall of the reactor and thence down the wall and out through an exit port in the base, or the liquid can be fed in at the upper side of a sloping base to the reactor and out at the lower side of the base. The liquid entering the reactor is pre-chilled to enable the necessary pressure of less than  $10^{-2}$  torr to be retained. The entry and exit ports to the reactor are provided with vacuum locks to keep the reduced pressure in the reactor. The liquid phase route is very suitable for use on an industrial scale with continuous feeding and withdrawal of the liquid as mentioned above.

The diarene chromium compounds prepared by the process of the invention generally and by both of its preferred embodiments can be separated from the unreacted aromatic compound in any convenient manner, for example in the case of the cocondensation route by solvent extraction followed by distillation. An alternative method which we have found useful is simply to permit the walls of the reactor to heat up to room temperature and simply to pump off the unreacted aromatic compound. The desired chromium compound can be obtained either directly from the walls of the reactor by solvent extraction or by heating the reactor whilst keeping the pressure very low. The chromium compound sublimates under these conditions and may be collected by means of a cold finger in the vacuum system line.

In the case of the liquid phase reaction the product is a mixture of the desired chromium compound, colloidal chromium and massive chromium as well as unreacted aromatic compound. The techniques described above of evaporation of the unreacted aromatic compound followed by sublimation or distillation of the chromium compound can be used to work up the liquid phase product, as can initial evaporation followed by solvent extraction and then evaporation of solvent, if

necessary after filtration. Alternatively an inert gas e.g. nitrogen can be admitted to the reactor to bring the pressure back to atmospheric and then the liquid phase filtered to remove massive chromium and probably some of the colloidal chromium. The filtrate is treated with water containing an oxidizing agent such as oxygen (e.g. as air) or hydrogen peroxide to convert the chromium compound into its cation and form a chromium containing sludge which is then separated. The diarene chromium cation in the water can then be converted into an insoluble salt e.g. the tetra phenyl boron salt and separated, or can be reduced to the diarene chromium (O) compound with an appropriate reducing agent e.g. sodium dithionite or stannous chloride, the chromium (O) compound being extracted into an organic solvent at least partially immiscible with water, such as aromatic hydrocarbons e.g. benzene, toluene, and chlorinated hydrocarbons. Evaporation of the organic solvent leaves the chromium arene compound. The present invention also provides bis arene chromium compounds of the formula  $\text{Ar}'\text{CrAr}'$ ,  $\text{Ar}''\text{CrAr}''$ , or  $\text{Ar}'\text{CrAr}''$  wherein  $\text{Ar}'$  and  $\text{Ar}''$  are as defined above except that both  $\text{Ar}''$  are not diphenyl molecules, and both  $\text{Ar}'$  are not ethyl benzene molecules, in the substantial absence of any disproportionation or rearrangement product thereof in the case of the compounds of formula  $\text{Ar}'\text{CrAr}'$ .

Examples of the alkyl benzene molecules represented by  $\text{Ar}'$ ,  $\text{Ar}''$  or  $\text{Ar}'''$  are toluene, *o*-, *m*- and *p*-xylene, ethylbenzene, mesitylene (and isomers thereof), cumene, *m*-di-isopropyl benzene, *cymene* (*p*-isopropyl toluene) and *tert.* butyl benzene. A particularly important compound is di cumene chromium, which when pure is a solid of melting point about  $46^{\circ}\text{C}$  in contrast to its mixture with its rearrangement or disproportionation products as a result of the Friedel-Crafts reaction process which mixture is a liquid of freezing point  $-21.8^{\circ}\text{C}$  and boiling point  $297^{\circ}\text{C}$ . Another important compound is bis *m*-(*di*-isopropyl) benzene chromium which is a solid of melting point about  $55^{\circ}\text{C}$ .

The diarene chromium compounds of the invention or produced by the process of the invention can be used as reactive intermediates and also in the wide range of uses to which the presently available impure compounds may be put. Thus they may be used as components of Ziegler Natta catalysts, but their main use lies in their thermal decomposition to deposit a layer comprising chromium on a heated surface of a substrate. When they are passed in the gaseous phase over a surface heated e.g. to about  $300^{\circ}\text{C}$ , a layer comprising chromium is deposited on the surface; this layer also contains free carbon, enhancing the corrosion resistance to acids of the layer over that obtained from electrolytic or vacuum deposited chromium. Alternatively to the thermal decomposition of the gaseous chromium compound, thermal decomposition in the liquid phase at about  $200^{\circ}\text{C}$  in the presence of a catalyst can also be used.

The invention is illustrated with reference to the accompanying drawings in which

FIG. 1 is a diagrammatic section through an apparatus suitable for carrying out the cocondensation process and

FIG. 2 is a diagrammatic section through an apparatus suitable for carrying out the liquid phase process.

The apparatus of FIG. 1 has a reaction vessel made of e.g. stainless steel surrounding which is a cooling

jacket 2 into which coolant e.g. liquid nitrogen can be put. Mounted on vessel 1 by means of flanges 9 and 10 is a middle member 11 having a vacuum exit line 7 and line 8, line 7 being connected to a vacuum pump directly and line 8 being connected to a vacuum pump by way of a cold trap (not shown). Mounted on middle member 11 by means of flanges 12 and 13 is lid 14, in which are held vapour inlet pipe 5 and water pipes 15 and 16. Vapour pipe 5 divides into three equally spaced limbs 6 (only two of which are shown). Water pipes 15 and 16 are formed at their lowest point into a cooling jacket 17 centrally located in the reactor and in which jacket is mounted a furnace 18. Furnace 18 consists of an open ended coil 19 of tungsten wire, which, in use contains chromium source 34, and which has two molybdenum heat shields 20 loosely fitting thereover. Chromium 34 is retained in the coil by a molybdenum strip 21 across the bottom of coil 19. The water pipes 15 and 16 are separated by an insulated joint of alumina tube 22 and electrical leads 23 pass from the coil 19 to each of the pipes 15 and 16 as power conductors. FIG. 1 also shows product 24 collecting on the inside of reactor 1.

In operation the reactor is first evacuated to the desired degree of vacuum using line 7. Liquid nitrogen is then introduced into the jacket 2. Chromium metal in chip form is heated in the furnace 18 by resistance heating to e.g. 1600°C, evaporates and by means of heat shields 20 the atoms are directed downwards towards the reactor. The desired aromatic compound is volatilised elsewhere, for example by heating, and introduced to the reactor via pipe 5. The vapour of the aromatic compound condenses on the liquid nitrogen-cooled walls of the reactor in the vicinity of the outlets of the limbs 6. After the reaction has run for the desired period, the heating is switched off and the liquid nitrogen pumped from the jacket 2. When room temperature is reached the unreacted aromatic compound may be separated by simply pumping it off at low pressure. If desired it may be collected in a liquid nitrogen trap which replaced the cold trap in line 8. The desired product may be obtained by heating the reactor whilst maintaining the pressure at a low value by pumping through line 8, the product being collected by condensation on the cold finger.

For the liquid phase route, the apparatus shown in FIG. 2 can be used. The apparatus is basically the same as that shown in FIG. 1, the differences lying in the different furnace assembly, the absence of inlet pipe 5 and limbs 6, and the presence of a stirrer and valve closed outlet in the base of the reactor. Otherwise the remaining features of the apparatus are the same and will not be further described. The furnace 18 present in FIG. 1 is unsatisfactory in the liquid phase route because it does not give a sufficiently collimated beam of chromium atoms. The furnace 25 in FIG. 2 has an inverted alumina crucible 26 wound with molybdenum wire 27 and coated with alumina cement. Chromium 34 is held in the crucible 26 by molybdenum strip 28 slotted into slits 29 in the crucible walls. The bottom part of crucible 26 provides a degree of collimation for the beam of chromium atoms. A stirrer shaft 30 having a paddle 31 is mounted off centre on lid 14 and is reciprocated by means of a motor (not shown). The reactor 1 has in its base an outlet 32, closed by a valve (not shown). The paddle 31 is immersed in liquid 33 in the bottom of the reactor 1. In use the liquid phase is placed in the bot-

tom of the reactor 1, outlet 32 being closed. The reactor is closed and its walls cooled to the necessary temperature e.g. -190°C or about -80°C by cooling medium in the jacket 2. The reactor is then evacuated to the desired pressure, the stirrer reciprocated and the heating of the chromium started. At the end of the reaction period, the heating is switched off, jacket 2 removed and an inert gas e.g. nitrogen passed into the apparatus. The liquid phase is then passed out through outlet 32, the valve being opened, and the liquid worked up to isolate the arene chromium compound. Alternatively in a continuous process the prechilled liquid may be fed into the reactor continuously in the presence or absence of the stirrer with continuous withdrawal of reaction liquid through outlet 32.

The invention is illustrated in the following examples.

#### EXAMPLE 1

2.1 parts by weight of chromium were placed in the furnace of the apparatus shown in FIG. 1 and the apparatus was then sealed for evacuation. The pressure in the reactor was reduced to less than  $2 \times 10^{-4}$  torr. The crucible was heated by passing a current of 40 amps at 9 volts, m-Di-isopropyl benzene (30.2 parts by weight) was volatilised by heating to about 70°C and drawn into the reactor over a period of 20 minutes. After completion of the reaction a black solid was obtained, which on vacuum sublimation gave bis - m - di isopropyl benzene with a melting point of about 55°C. Analysis of the iodide derived from the product showed Cr 10.0 % I 25.7% C 56.5% H 7.30% (expected for bis (m-di isopropyl benzene) chromium iodide Cr. 10.3, I 25.2, C 57.2, H 7.15%).

The product of Example 1 was mixed with a water-hexane mixture, followed by reaction with nitric acid, which results in freeing the alkyl benzene compound from the chromium components, and then solution of the alkyl benzene compound in hexane. Gas chromatography on the hexane extract after removal of hexane showed only one peak identified as m - di - isopropylbenzene.

Similarly mass spectroscopy of the product showed only one peak corresponding to a parent compound, the m/e value of which peak was 376 as expected.

#### EXAMPLE 2

The process was carried out as in Example 1 using cumene (volatilised at about 50°C) as the alkylbenzene compound. In this case the crucible was heated using 34 amps at 0.8 volts. The cumene was fed in for 30 minutes enabling 62.3 g. of cumene to be employed. The product obtained was a dark solid which on vacuum sublimation gave bis cumene chromium having a melting point of about 46°C. The product was decomposed with acid and extracted as in Example 1 and gas liquid chromatography showed only one peak. Mass spectroscopy on the bis - cumene - chromium showed only one peak corresponding to a parent compound, which peak had a m/e of 292 as expected.

#### EXAMPLE 3

A saturated solution of diphenyl in m - di isopropyl benzene was placed in the bottom of the reactor of an apparatus as shown in FIG. 2 and cooled to -80°C to -85°C by means of an acetone/solid carbon dioxide bath in jacket 2. The reactor was then evacuated to a pressure of  $10^{-3}$  torr, the stirrer started and the chro-

mium in the crucible heated to 1500° - 1600°C. The reaction was carried out for 30 mins, after which the heating and stirring were stopped, the jacket removed and the reactor filled with nitrogen. The liquid was passed through outlet 32 and massive chromium separated by filtration anaerobically. A diphenyl m - di isopropyl benzene chromium compound can be isolated by evaporation of the hydrocarbons from the filtrate and distillation of the residue. Alternatively the liquid filtrate is evaporated to remove the hydrocarbons and the residue distributed between hexane and dilute nitric acid and the hexane extract evaporated. Gas liquid chromatography of the residue showed only diphenyl and m - di isopropyl benzene peaks, showing that the residue from the filtrate contained both these molecules combined with chromium.

Similar results are obtained when the solution of diphenyl in m - diisopropyl benzene was replaced by 5% (by weight) solutions of cumene or tertiary butyl benzene in m - diisopropylbenzene.

We claim:

1. A process for preparing diarene chromium compounds, comprising condensing gaseous chromium atoms with at least one aromatic compound of formula Ar' or Ar'', or a mixture thereof, at a pressure of less than 10<sup>-2</sup> torr and at a temperature compatible with maintaining said pressure, wherein Ar' is an alkylbenzene molecule in which the benzene ring is substituted by one or more alkyl groups, and Ar'' is a diphenyl, tetralin or indane molecule, each of which is unsubstituted or substituted by at least one alkyl group.
2. A process according to claim 1 wherein each alkyl group has at least 3 carbon atoms.
3. A process according to claim 2 wherein the alkylbenzene is cumene or m - di - isopropyl benzene.
4. A process according to claim 1 wherein the temperature is not more than -60°C.
5. A process according to claim 2 which comprises passing gaseous chromium atoms and vapour of the aromatic compound or compounds in a reactor onto a chilled surface of the reactor.
6. A process according to claim 5 wherein the tem-

perature is -160°C to -200°C.

7. A process for producing a diarene chromium compound comprising

contacting in a reactor gaseous chromium atoms with a continually regenerated surface of a liquid aromatic at a pressure of less than 10<sup>-2</sup> torr at a temperature compatible with maintaining said pressure in the reactor,

said liquid aromatic being at least one aromatic compound of formula Ar' or Ar'', or a mixture thereof, wherein Ar' is an alkylbenzene molecule in which the benzene ring is substituted by one or more alkyl groups, and Ar'' is a diphenyl, tetralin or indane molecule, each of which is unsubstituted or substituted by at least one alkyl group,

whereby a reaction product comprising said diarene chromium compound in said liquid aromatic are produced.

8. A process according to claim 7 wherein said liquid aromatic has the formula Ar' and wherein said diarene chromium compound has the formula Ar'CrAr'.

9. A process according to claim 7 wherein said liquid aromatic has the formula Ar'' and wherein said diarene chromium compound has the formula Ar''CrAr''.

10. A process according to claim 7 wherein the temperature is -60°C to -100°C.

11. A process according to claim 10 wherein the liquid is m - di - isopropyl benzene or a mixture thereof with another alkylbenzene having at least 3 carbon atoms in the alkyl group and is maintained at a temperature of -80°C to -90°C.

12. A process according to claim 8 wherein said liquid aromatic having the formula Ar' contains at least one alkyl group of at least two carbon atoms.

13. A process according to claim 7 wherein each alkyl group contains at least two carbon atoms.

14. A process according to claim 10 wherein each alkyl group contains at least two carbon atoms.

15. A process according to claim 1 wherein each alkyl group contains at least two carbon atoms.

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