United States Patent Office

3,285,946

Patented Nov. 15, 1966

3,285,946

MONO- AND DI-(LOWER ALKYL SUBSTITUTED) DICYCLOPENTADIENYL IRON

Earl G. De Witt, Royal Oak, and Jerome E. Brown and Hymin Shapiro, Detroit, Mich., assignors to Ethyl Corporation, New York, N.Y., a corporation of Virginia

No Drawing. Filed Nov. 23, 1955, Ser. No. 548,755
2 Claims. (Cl. 260—439)

This application is a continuation-in-part of our prior co-pending applications Serial No. 417,919, filed March 22, 1954, and now abandoned, and Serial No. 297,392, filed July 5, 1952.

This invention relates to alkylated dicyclopentadienyl iron compounds and their use as antiknock materials.

It is an object of this invention to provide new compositions of matter. A further object is to provide liquid hydrocarbon fuel containing these new compositions of matter wherein the fuels possess superior antiknock qualities. A further object is to provide new antiknock agents and antiknock fluids.

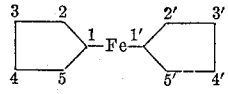
We have discovered new compositions of matter which comprise alkyl dicyclopentadienyl iron wherein the cyclopentadiene radicals are substituted with 1 to 10 alkyl groups containing 1 to 10 carbon atoms, the total number of the carbon atoms in the alkyl groups being 1 to 32. An outstanding example of this new class of compounds is bis-(methylcyclopentadienyl) iron. We have also discovered that by blending these new compositions of matter with liquid hydrocarbon fuels to obtain a liquid hydrocarbon fuel containing alkyl cyclopentadienyl iron wherein the cyclopentadiene radicals are substituted with 1 to 10 alkyl groups of 1 to 10 carbon atoms, the total number of the carbon atoms in the alkyl groups being 1 to 32, we obtain fuels of superior antiknock characteristics. We have also discovered new antiknock fluids comprising organolead antiknock agents, scavengers for these antiknock agents, and alkyl dicyclopentadienyl iron of the type described.

The new compounds of this invention are superior as antiknock agents because they not only possess exceptional antiknock activity but they also combine to a high degree the ancillary properties necessary for a successful commercial antiknock. Thus, for example, our compounds are superior because of their favorable solubility, volatility, and state of aggregation characteristics (e.g. melting point). Being liquids or low melting solids or semi-solids soluble to a high degree in liquid hydrocarbons, they are easily blended with gasoline and are readily and smoothly inducted with the gasoline into the combustion chamber of the engine where they exert their antiknock effect. Because of their good volatility characteristics they are also distributed equitably among the cylinders of a multi-cylinder engine.

The compounds of this invention all contain iron as the central metallic atom, and to this iron atom are attached two cyclopentadiene rings. These rings contain 1 to 10 alkyl groups of 1 to 10 carbon atoms, the total number of the carbon atoms in the alkyl groups being 1 to 32. The alkyl groups included within this invention are therefore the methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, and all the isomeric amyl, hexyl, heptyl, octyl, nonyl, and decyl groups.

In one embodiment of our invention one of the cyclopentadiene rings contains 1 to 5 alkyl groups of 1 to 10 carbon atoms, the total number of the carbon atoms in the alkyl groups being 1 to 32, and the other cyclopentadiene ring is unsubstituted. This embodiment includes the mono-, di-, tri-, tetra-, and pentaalkyl cyclopentadienyl irons where all the alkyl groups are on one cyclopentadiene ring. Using for convenience the generic

term "ferrocene" to represent bis-(cyclopentadienyl) iron, numbered as illustrated,



it will be seen that this embodiment includes monomethyl ferrocene, monoethyl ferrocene, monobutyl ferrocene, monodecyl ferrocene, 1,2-dimethyl ferrocene, 1,3-dihexyl ferrocene, 1,2,3-triisopropyl ferrocene, 1,2-dimethyl-4-octyl ferrocene, 1,2,3,4-tetraethyl ferrocene, 1,2,3,4-tetraheptyl-5-butyl ferrocene, and the like. According to present understanding of the ferrocene molecule, all the positions of any one cyclopentadiene ring in ferrocene are equivalent to each other with respect to the iron atom so that there is only one monoalkyl ferrocene. In the case of the di- and trialkyl ferrocenes, positional isomerization is possible. In our nomenclature, this is indicated by numerical prefixes to the names of the compounds.

Another embodiment of the invention comprises alkyl dicyclopentadienyl irons or alkyl ferrocenes wherein the cyclopentadienyl radicals are substituted with 2 to 10 alkyl groups of 1 to 10 carbon atoms, the total number of the carbon atoms in the alkyl groups being 1 to 32, and wherein each of the cyclopentadienyl rings has at least one alkyl group. The nomenclature we have adopted for these compounds, except for the very simplest ones, is to designate alkyl groups on one cyclopentadiene ring by unprimed numerals and to designate those on the other ring by primed numerals (see the illustrative formula above).

In this embodiment of the invention are included

bis-(methylcyclopentadienyl) iron,
bis-(ethylcyclopentadienyl) iron,
bis-(decylcyclopentadienyl) iron,
1,2,1'-trimethyl ferrocene,
1,2-dimethyl-1',2'-diethyl ferrocene,
1,3-dimethyl-1',2'-didecyl ferrocene,
1,3,1'-trimethyl ferrocene,
1,2,3-tri-n-propyl-1'-octyl ferrocene,
1,2-dimethyl-3-amyl-1',2'-dimethyl ferrocene,
1,2,3,1',3'-pentamethyl ferrocene,
1,2-diethyl-4-methyl-1'-n-heptyl ferrocene,
1,2,4,1',2'-pentaethyl ferrocene,
1,2,4-tridecyl-1',3'-dimethyl ferrocene,
1,2,4-tripropyl-1',2',3'-triethyl ferrocene,
bis-(1,2,4-trimethylcyclopentadienyl) iron,
1,2,3,4,1'-pentahexyl ferrocene,
1,2-dimethyl-3,4,1',2'-tetraethyl ferrocene,
1,2,3,4,1',3'-hexamethyl ferrocene,
1,2,3,4,1',2',3'-heptaethyl ferrocene,
1,2,3,4,1',2',4'-heptamethyl ferrocene,
bis-(tetraethylcyclopentadienyl) iron,
1,2,3,4,5,1'-hexamethyl ferrocene,
1,2,3,4,5,1',2'-heptaethyl ferrocene,
1,2,3,1'-tetramethyl-4,3'-dipropyl ferrocene,
1,2,3,4,5-pentamethyl-1',2',3'-trinonyl ferrocene,
1,2,3,4,5-pentamethyl-1',2',4'-triethyl ferrocene,
nonamethyl ferrocene,
decamethyl ferrocene,
decaethyl ferrocene,

and the like. Other compounds within this embodiment will now be apparent to those skilled in the art. For availability and for optimum qualities leading to good antiknock usage, we prefer to use those compounds wherein both cyclopentadienyl rings are substituted with alkyl groups, preferably of 1 to 4 carbon atoms, one on each ring, as these represent the most mobile liquids among our compounds. Therefore, a preferred mode

of this invention comprises liquid hydrocarbon fuels containing a lower alkyl dicyclopentadienyl iron in an amount sufficient to increase the antiknock characteristics of said fuel. We especially prefer such compounds wherein all the alkyl groups are the same. We have had especially good results with bis-(methylcyclopentadienyl) iron and bis-(ethylcyclopentadienyl) iron.

The compounds of this invention can be prepared in a variety of ways. One convenient method is the condensation of the alkali metal derivative of the appropriate alkylated cyclopentadiene with an iron salt. The alkali metal derivative of the alkylated cyclopentadiene can in turn be made by reaction of the alkylated cyclopentadiene with alkali metal, preferably in dispersed form or with an active alkali metal derivative such as an alkyl sodium or lithium compound.

Our compounds may also be prepared by condensation of Grignard reagents derived from alkylated cyclopentadienes with iron salts or other iron compounds, by Friedel-Craft alkylation of ferrocene, etc. Other means for preparation of our compounds will be apparent to those skilled in the art.

Preparation of our compounds is exemplified in the following examples.

EXAMPLE I

Bis-(ethylcyclopentadienyl) iron

In a stirred reaction vessel provided with a reflux condenser and liquid feed means ethyl magnesium bromide (1 mole) is prepared in diethyl ether by the usual method. To the ether solution of Grignard reagent is added 1 mole of ethyl cyclopentadiene, resulting in the formation of ethylcyclopentadienyl magnesium bromide. A solution of 0.5 mole of anhydrous ferric chloride in 200 parts of diethyl ether is then added to the reaction mixture over a period of approximately 30 minutes. The reaction mixture is then maintained at reflux temperature of about 40° C. for one hour. The mixture is then cooled and treated by adding 10 percent aqueous ammonium chloride solution to the reaction mixture. The ether layer which contains the desired bis-(ethylcyclopentadienyl) iron is separated from the aqueous layer and the ether dried and removed by distillation. The crude product which is obtained as the residue from this distillation is purified by vacuum distillation to yield pure bis-(ethylcyclopentadienyl) iron in good yield. This product corresponds to the formula $C_{14}H_{18}Fe$. This compound boils at 130–131° C./9 mm., melts at −35° C., has a refractive index n_D^{25} 1.5760, and is a mobile, deep amber colored liquid with a mild camphoraceous odor.

The same technique is used to obtain other compounds of this invention, such as 1,2,3,4,1′,2′,3′,4′-octamethyl ferrocene, 1,3,1′,3′-tetrahexyl ferrocene, and the like.

EXAMPLE II

Bis-(methylcyclopentadienyl) iron

Methylcyclopentadienyl lithium is prepared according to the method of "Organic Reactions," vol. VI, pp. 352–353, John Wiley and Sons, Inc., New York (1951). An ether solution of this material (1 mole) is slowly added with agitation to 0.5 mole of anhydrous ferric chloride which is completely dissolved in anhydrous diethyl ether. The reaction is carried out in a vessel equipped with mechanical agitator and reflux condenser. The reaction is vigorous and exothermic. After addition of the lithium compound is complete, 500 parts of saturated aqueous ammonium chloride solution is added to the reaction mixture with vigorous agitation. Three-hundred parts of benzene are then added to extract the bis-(methylcyclopentadienyl' iron product. The ether-benzene layer is separated from the aqueous layer and the ether and benzene removed under vacuum. The residue is distilled under vacuum to yield bis-(methylcyclopentadienyl) iron in good yield. The product is isolated as a dark orange to red liquid boiling at 240° C./760 ml.

The above technique is applicable to other compounds of this invention, such as 1,2,3,4,1′,2′,3′,4′-octapropyl ferrocene, bis-(decylcyclopentadienyl) iron, and the like.

EXAMPLE III

Monomethyl ferrocene

A 20 percent dispersion of sodium in toluene is prepared by conventional methods. To this is added a mixture of 70 percent of tetramethylcyclopentadiene and 30 percent of cyclopentadiene. The total amounts of mixed cyclopentadienes amount to 1 mole for every gram atom of sodium in dispersion form. This mixture is reacted for 10 minutes at a temperature of 40° C. under a blanket of dry nitrogen, and then 0.9 mole of ferric chloride, completely dissolved in tetrahydrofuran, is added. After reacting for 15 minutes at 40° C., the reaction mixture is worked up as described in the preceding examples, and a good yield of monomethyl ferrocene is obtained.

The procedure of Example III can be used with good results to obtain other mixed ferrocenes of this invention, both those in which there is one unsubstituted cyclopentadiene nucleus and those in which both cyclopentadiene nuclei are substituted but with different alkyl groups or with the same alkyl groups in different orientation on the cyclopentadiene ring. Thus, this method can be used for the preparation of 1,3-dinonyl ferrocene, 1,2,3,4,5-pentaethyl ferrocene, 1,2,4,1′,2′,3′-hexaethyl ferrocene, 1,2,3-trimethyl-1′-isopropyl ferrocene, and the like. Generally an excess of the more highly alkylated cyclopentadiene is used to overcome its slower reaction rate. A mixture of products is normally obtained, and this may be resolved by conventional means, usually vacuum fractionation.

EXAMPLE IV

Decamethyl ferrocene

A 20 percent dispersion of sodium in mineral oil is prepared by conventional methods. To this is added pentamethylcyclopentadiene in amount corresponding to 1 mole for every weight-atom of sodium present in the dispersion. To the sodio pentamethylcyclopentadiene thus prepared is added a solution of 0.5 mole of ferric chloride dissolved in tetrahydrofuran. Reaction is carried out under anhydrous conditions for 15 minutes at 40° C., and a good yield of decamethyl ferrocene is obtained.

EXAMPLE V

Tetraoctyl ferrocene

Tetraoctyl ferrocene is prepared in a manner identical with that of Example IV, except that 1,3-dioctylcyclopentadiene is used as the starting material.

The new compounds of this invention find their greatest utility when used as antiknock agents. To take advantage of this outstanding utility, we blend our new compounds with gasoline to obtain liquid petroleum hydrocarbon fuels containing alkyl cyclopentadienyl iron where the cyclopentadiene groups are substituted with 1 to 10 alkyl groups containing 1 to 10 carbon atoms, the total number of the carbon atoms in the alkyl groups being 1 to 32, in amount sufficient to exert antiknock effect. In so doing, we find that we achieve outstanding antiknock activity and that the fuel blends are such that the antiknock agent is readily blended, inducted, and distributed to the cylinders of the engine. We, in many instances, obtain best results when mixtures of our iron compounds are blended with fuels according to the invention. Many of the fuels so produced which contain mixtures of our alkyl dicyclopentadienyl iron compounds possess superior inductibility and distributability properties.

The fuel with which the antiknock agent of this invention can be blended may be any of the liquid hydrocarbon fuels of the gasoline boiling range. These fuels are usually blends of two or more components and can contain all types of hydrocarbons, including paraffins, both straight and branched chain, olefins, cycloaliphatics containing

paraffin or olefin side chains, and aromatics containing aliphatic side chains. The fuel type depends on base stock from which it is obtained and on the method of refining. For example, it can be a straight run or processed hydrocarbon, including thermally cracked, catalytically cracked, reformed, hydroformed, etc. The boiling range of the components of the gasoline can vary from 0 to about 430° F., although the boiling range of the fuel blend is often found to be between an initial boiling point of from about 80° F. to 100° F. and a final boiling point of about 430° F. While the above is true for ordinary gasoline, the boiling range is a little more restricted in the case of aviation gasoline. Specifications for the latter often require that the boiling range be from about 82° F. to about 338° F., with certain fractions of the fuel boiling away at a particular intermediate temperature.

The hydrocarbon fuels in which the antiknock agent of this invention can be employed often contain minor quantities of various impurities. One such impurity is sulfur, which can be present either in a combined form as an organic or inorganic compound, or as the elemental sulfur. The amounts of such sulfur can vary in various fuels from about 0.003 percent to about 0.30 percent by weight. Fuels containing quantities of sulfur both lesser and greater than the range of amounts referred to above are also known. Our antiknock agents are less sensitive to fuel impurities than are prior antiknock agents such as organolead compounds.

The amount of alkyl dicyclopentadienyl iron used to provide a finished fuel of the desired octane number can be determined by one of the accepted octane rating methods, such as the Research or Motor methods of the American Society for Testing Materials (ASTM) or various road rating methods. In general, however, we prefer to employ amounts not greatly exceeding about 10 grams of iron per gallon of fuel. For most fuels for use in automotive engines, the required amount will be substantially below the maximum, while for fuels or aircraft engines where the octane number requirement is considerably higher, the amount of iron employed may approach this maximum. Thus, the amount of iron in the form of alkyl dicyclopentadienyl iron that can be added to a hydrocarbon fuel of the type described above is from about 0.01 gram to about 10 grams per gallon of the fuel. When the fuel is employed in an ordinary automobile engine, an especially preferred range of concentrations of alkyl dicyclopentadienyl iron in the fuel is from about 0.1 to about 4.0 grams of the metal per gallon of fuel. Because of the high degree of effectiveness of our materials, these amounts give results comparable to or better than those obtained with substantially greater amounts of previous antiknocks.

In addition to the alkyl dicyclopentadienyl iron antiknock agent and sulfur impurities, other components may also be present in the hydrocarbon fuel. Such other components may be antioxidants, stabilizers, dyes, and the like, specific examples of which are N,N'-di-sec-butyl-p-phenylene diamine, 2,4-dimethyl-6-tert-butylphenol, and the like.

Our antiknock agents can be employed with or without scavengers. Although we have found that satisfactory results are obtained without the use of scavengers, they do aid in removing decomposition products from the combustion chamber and thus are desirable. Among the scavengers which may be used are phosphorus and arsenic compounds, especially organic phosphates such as trialkyl and triaryl phosphates (tributyl phosphate, tricresyl phosphate, and the like), and also organic compounds of boron, such as borate esters. When we use scavengers of the above types, we find that they perform best in amount such that there is from 0.4 to about 1 atom of phosphorus, arsenic, or boron present for each atom of iron in the fuel. Halogenated organic compounds may also be used as scavengers. The types and amounts specified in Barthol-omew Patent 2,398,281 are very satisfactory for this purpose.

The following illustrates typical fuels within the scope of the present invention.

EXAMPLE VI

To a motor fuel consisting of a blend of straight run, catalytically cracked, and polymer stocks, having an initial boiling point of 98° F. and an end point of 402° F., is added monomethyl ferrocene in amount so that there is 0.01 gram of iron present as monomethyl ferrocene per gallon of the fuel. This liquid hydrocarbon fuel possesses superior antiknock qualities.

EXAMPLE VII

To a motor fuel consisting of 100 percent catalytically cracked gasoline having an initial boiling point of 105° F. and an end point of 425° F. is added 1,2,1',2'-tetraoctyl ferrocene in amount corresponding to 0.1 gram per gallon of fuel. Also added to this mixture is triphenyl phosphate in amount so that there is one phosphorus atom present for every atom of iron in the fuel. This liquid hydrocarbon fuel possesses outstanding antiknock qualities.

EXAMPLE VIII

To an aviation gasoline of grade 100/130, comprising isopentane, alkylate, aromatics, and straight run gasoline, and having an initial boiling point of 82° F. and an end point of 330° F., is added bis-(methylcyclopentadienyl) iron in amount so that 10 grams of iron are present per gallon of fuel. To this blend is also added tributyl borate in amount so that one atom of boron is present for every two atoms of iron in the fuel. This liquid hydrocarbon fuel has high antiknock value.

EXAMPLE IX

To a liquid hydrocarbon fuel consisting of a blend of light catalytically cracked naphtha, polymer stock, catalytic reformate, and light straight run naphtha, containing butane and having an initial boiling point of 90° F. and an end point of 360° F., is added monoamyl ferrocene in amount corresponding to 4.0 grams of iron per gallon of fuel. This liquid hydrocarbon fuel possesses outstanding antiknock activity.

To illustrate the outstanding antiknock effectiveness of our new compounds, we performed tests according to the Research method for determining antiknock activity (ASTM No. D-908). This test, which is generally accepted as a method giving a good indication of fuel and antiknock behavior in commercial multi-cylinder engines, is conducted in a single-cylinder engine especially designed for the purpose and referred to as the CFR engine. This engine has a variable compression ratio, and during the test the temperature of the jacket water is maintained at 212° F. The engine is operated at a speed of 600 r.p.m. with a spark advance of 131° before top dead center. In such a test, we rated bis-(methylcyclopentadienyl) iron in a fuel which consisted of 20 volume percent diisobutylene, 20 volume percent toluene, 20 volume percent isooctane, and 40 volume per cent n-heptane. The amount of iron compound was chosen so as to give a concentration of 1.1 grams of iron as the bis-(methylcyclopentadienyl) compound per gallon of fuel. At this concentration, it was found that this amount of the iron compound raised the octane number of the fuel the same amount that required 1.7 ml. of tetraethyllead. Expressed in another manner, it was found that at this concentration one gram of iron as the above compound was equivalent in antiknock effectiveness to 1.6 grams of lead as tetraethyllead. It was not necessary to heat the induction system of the engine to induct the iron compound into the engine.

In a further test in which bis-(methylcyclopentadienyl) iron was used at a concentration of 3.3 grams of metal per gallon of fuel, the antiknock effectiveness was such that one gram of iron as the above compound was equivalent to 1.7 grams of lead as tetraethyllead.

When the Research method antiknock rating is applied to other compounds of this invention such as decamethyl ferrocene, 1,2,3-triethyl-1',3'-dipropyl ferrocene, monomethyl ferrocene, 1,2,4-trioctyl ferrocene, 1,2,3,4,1',2',3',4'-octamethyl ferrocene, and the like, good antiknock effectiveness is likewise demonstrated.

When we tested bis-(cyclopentadienyl) iron under these circumstances, we found that it had undesirable inductibility characteristics and that in order to overcome these characteristics which resulted in stoppage of the carburetion system, it was necessary to preheat the induction system to a temperature of 125° F. In contrast, when compounds of this invention were used, no heating of the induction system was necessary. Our compounds were smoothly inducted into the engine with an unheated induction system.

A use to which the present compounds are particularly adapted is that of a supplementary antiknock. In other words great benefits are obtained when we blend our antiknocks and organolead antiknocks with gasoline to obtain a liquid hydrocarbon fuel containing an alkyl cyclopentadienyl iron wherein the cyclopentadiene radicals are substituted with 1 to 10 alkyl groups of 1 to 10 carbon atoms, in an amount sufficient to increase the antiknock characteristics of said fuel, and containing an organolead compound in an amount sufficient to increase the antiknock characteristics of said fuel.

When we utilize our compounds in such a manner, we obtain fuels which give a greater antiknock response than does the same fuel containing an equivalent amount of lead as an organolead compound, and at the same time we achieve economical and technical advantages.

Among the organolead compounds we use in our leaded iron-containing fuels are tetraalkyllead compounds, such as tetramethyllead, tetraethyllead, tetraisopropyllead, dimethyldipropyllead, tetraoctyllead, and the like. We also use tetraaryl compounds, such as tetraphenyllead, tetratolyllead, and so forth. We have unexpectedly found that when we use our iron compounds along with organolead antiknocks in liquid hydrocarbon fuels, we obtain a greater antiknock effect from the iron than we do when we use our iron compound in liquid hydrocarbon fuel in the absence of lead. We normally regulate the amount of organolead antiknock compound so as to be equivalent to 1.05 to 6.34 grams of lead per gallon of fuel.

To illustrate this facet of our invention, we perform tests according to the Research method (ASTM No. D-908) as described above. For example, we blended with the fuel described in the above tests 1 ml. of tetraethyllead per gallon of fuel and 1.1 grams of iron as bis-(methylcyclopentadienyl) iron per gallon. When this was tested according to the Research method, it was found that the iron compound had an antiknock activity such that each gram of iron was equivalent to 2.7 grams of lead as tetraethyllead.

Thus, a valuable aspect of our invention consists of providing antiknock fluids which comprise organolead antiknock, a scavenger for the organolead antiknock, and an alkyl dicyclopentadienyl iron wherein the cyclopentadiene radicals are substituted with 1 to 10 alkyl groups of 1 to 10 carbon atoms, the total number of carbon atoms in said alkyl groups being 1 to 32. In such fluids the amount of the iron antiknock agent ranges between 20 to 80 percent of the combined amounts of iron and lead antiknock agents. The preferred type of scavenger for the organolead antiknock agent is an organic halogen compound such as ethylene dibromide, ethylene dichloride, trichlorobenzene, dibromotoluene, dibromopentanes and butanes, and mixtures of the above and other halogenated organic compounds. Such fluids may also contain a scavenger for the iron antiknock compound. Such scavengers may be of the type mentioned previously (phosphorus, arsenic, and boron compounds, etc.). The amount of such scavenger generally ranges from 0 to 1 atom per atom of iron in the fluid.

The following examples illustrate leaded fluids and fuels of this invention.

EXAMPLE X

An antiknock fluid is prepared by blending 80 parts by weight of bis-(ethylcyclopentadienyl) iron with 20 parts by weight of tetraethyllead. To this mixture is added ethylene dibromide in amount equivalent to one theory based on the lead present. This mixture is found to be an outstanding antiknock fluid.

When blended with the gasoline of Example VI such that the amount of tetraethyllead is equivalent to 1.05 grams of lead per gallon of fuel, a liquid hydrocarbon fuel having superior antiknock properties is obtained.

EXAMPLE XI

We prepare an antiknock fluid which is composed of 20 parts by weight of bis-(isopropylcyclopentadienyl) iron, 80 parts of tetraisopropyllead, 1.0 theory of ethylene dichloride, and 0.5 theory of ethylene dibromide based on the tetraisopropyllead employed, and sufficient tricresyl borate to give one atom of boron for every atom of iron in the fluid. This fluid possesses superior antiknock properties.

When blended with the aviation gasoline of Example VIII in amount so that the amount of lead present is 6.34 grams per gallon, a superior antiknock liquid hydrocarbon fuel is obtained.

We claim:

1. An unsymmetrical di(lower alkyl substituted cyclopentadienyl) iron compound wherein each lower alkyl cyclopentadienyl radical, by virtue of dissimilar alkyl substitution, differs from the other lower alkyl cyclopentadienyl radical.

2. A (lower alkyl-substituted dicyclopentadienyl) iron in which only one cyclopentadienyl group is substituted, said lower alkyl group being the sole substituent.

References Cited by the Examiner

UNITED STATES PATENTS

2,398,281	4/1946	Bartholomew	252—386
2,680,758	6/1954	Thomas	260—439

FOREIGN PATENTS

1,080,357	5/1954	France.

OTHER REFERENCES

Kealey et al., Nature, vol. 168, Dec. 15, 1951, pp. 1039, 1040.

Rosenblum, The Structure and Chemistry of Ferrocene, thesis deposited in Harvard University Library, Feb. 19, 1954.

TOBIAS E. LEVOW, *Primary Examiner.*

LEON D. ROSDOL, ARTHUR WINKELSTEIN, J. C. LANGSTON, T. L. IAPALUCCI, A. P. DEMERS, *Assistant Examiners.*