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PREPARATION OF CYCLOMATIC NICKEL NITROSYLS

Thomas H. Coffield, Heidelberg, Germany, and Kryn G. Ihrman, Farmington, Mich., assignors to Ethyl Corporation, New York, N.Y., a corporation of Delaware

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This invention relates to a new chemical process. More specifically, this invention relates to a novel process for forming cyclomatic nickel nitrosyl compounds which have great utility as antiknock additives in gasoline.

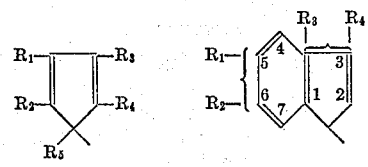
An object of this invention is to provide a new and useful process for forming organometallic coordination compounds. A further object of this invention is to provide a process for forming cyclomatic nickel nitrosyl compounds. Further objects will become apparent from a reading of the specification and claims which follow.

The above objects are accomplished by providing a novel process for the formation of cyclomatic nickel nitrosyl compounds. This process involves the reaction of a tricyclomatic trinickel dicarbonyl compound with nitric oxide. Although we are not bound by any theory as to the reaction mechanism, it is believed that our process can be represented by the following reaction:

$$Cy_3Ni_3(CO)_2 + 3NO \rightarrow 3CyNiNO + 2CO$$

As shown by the above, our process is represented as the reaction of one mole of a tricyclomatic trinickel dicarbonyl compound with three moles of nitric oxide to form three moles of a cyclopentadienyl nickel nitrosyl compound and two moles of carbon monoxide.

The tricyclomatic trinickel dicarbonyl compound employed as a reactant in our process may contain cyclomatic hydrocarbon groups containing from five to about 13 carbon atoms. In general, such cyclomatic hydrocarbon groups can be represented by the formulae:



where the R groups are selected from the group consisting of hydrogen and univalent hydrocarbon radicals. The cyclomatic groups are represented by Cy in the above equation. Typical of the cyclomatic groups which may be contained in the tricyclomatic trinickel dicarbonyl reactant are cyclopentadienyl, indenyl, methylcyclopentadienyl, propylcyclopentadienyl, diethylcyclopentadienyl, phenylcyclopentadienyl, tert-butyl cyclopentadienyl, p-ethylphenyl cyclopentadienyl, 4-tert-butyl indenyl and the like. These radicals are contained in the reactants tricyclopentadienyl trinickel dicarbonyl, triindenyl trinickel dicarbonyl, tris(methylcyclopentadienyl) trinickel dicarbonyl, tris(propylcyclopentadienyl) trinickel dicarbonyl, tris(diethylcyclopentadienyl) trinickel dicarbonyl, tris(phenylcyclopentadienyl) trinickel dicarbonyl, tris(tert-butyl cyclopentadienyl) trinickel dicarbonyl, tris(p-ethylphenyl cyclopentadienyl) trinickel dicarbonyl and tris(4-tert-butyl indenyl) trinickel dicarbonyl. These reactants, when employed in our process, yield respectively cyclopentadienyl nickel nitrosyl, indenyl nickel nitrosyl, methylcyclopentadienyl nickel nitrosyl, propylcyclopentadienyl nickel nitrosyl, diethylcyclopentadienyl nickel nitrosyl, phenylcyclopentadienyl nickel nitrosyl, tert-butyl cyclopentadienyl nickel nitrosyl, p-ethylphenyl cyclopentadienyl nickel nitrosyl and 4-tert-butyl indenyl nickel nitrosyl.

A preferred tricyclomatic trinickel dicarbonyl reactant

is tricyclopentadienyl trinickel dicarbonyl. This reactant is preferred since the cyclopentadienyl moiety present in the reactant is derived from cyclopentadiene, a readily available chemical of commerce. Further, the product, cyclopentadienyl nickel nitrosyl, formed when using tricyclopentadienyl trinickel dicarbonyl as the reactant, is an extremely potent antiknock having great utility as a gasoline additive.

Our process may be readily carried out as essentially a liquid phase reaction. When so carried out, it is preferably conducted in an autoclave. The autoclave is equipped with inlet and outlet ports, pressure controls connected with said ports so that the pressure can be regulated in the autoclave, temperature controls and agitation means which disperse the reactants so that they intimately contact each other. The autoclave temperature in our process is maintained between about zero to about 100° C. A preferred temperature range is from about 20 to about 40° C. since within this range the reaction goes readily with a minimum of said reactions. In general, the pressure employed in the reaction vessel is not critical. Pressures ranging from one to about 50 atmospheres may be employed. Normally, however, the process is conducted at pressures ranging from about one to about five atmospheres.

A solvent is preferably used as a dispersant for the reactants in our process. The solvent is preferably free of air or oxygen, and one means by which this may be conveniently accomplished is by bubbling carbon monoxide through it or by heating it so as to expell any absorbed gases.

The nature of the solvent which may be used in our process is not critical. In general, any solvent can be utilized which does not react with the reactants employed in our process. Typical of applicable solvents are hydrocarbon and ether solvents. The hydrocarbon solvents may be aliphatic hydrocarbons such as n-hexane, n-octane, isooctane, n-heptane, various positional isomers of hexane, octane and heptane, or mixtures of the above. The solvent may also be a cycloaliphatic hydrocarbon such as cyclohexane or methylcyclohexane. Further applicable solvents are cyclic olefins such as cyclohexene and methylcyclohexene. Straight and branched-chain olefins such as isoheptene, n-hexene, isooctene, isoheptene and the like are also applicable. Aromatic hydrocarbon solvents such as benzene, toluene, ethylbenzene and xylenes, either mixed or pure, may also be used.

Typical of the ether solvents are the cyclic ethers such as tetrahydrofuran, 1,4-dioxane and 1,3-dioxane. Non-cyclic monoethers such as diethylether, diisopropylether and diphenylether are good solvents for use in our process. Non-cyclic polyethers such as the dimethylether or ethyleneglycol, the diethylether of ethyleneglycol, the dibutylether of ethyleneglycol, the dimethylether of diethyleneglycol, the diethylether of diethyleneglycol and the dibutylether of diethyleneglycol are also excellent solvents for use in our process.

A preferred group of solvents for use in our process are the highly polar ethers such as tetrahydrofuran, ethyleneglycol dimethylether, ethyleneglycol diethylether, ethyleneglycol dibutylether, diethyleneglycol dimethylether, diethyleneglycol diethylether, diethyleneglycol dibutylether and the like.

Our solvents should preferably have a normal boiling point which varies by at least 25° C. from the normal boiling point of the product. A variation of at least 25° C. between the normal boiling points of the product and solvent aids greatly in separation of the product from the solvent by means of distillation.

Ordinarily, excess nitric oxide is employed in our process. This excess is preferably in the order of 100 percent. Therefore, for each mole of tricyclomatic tri-

nickel dicarbonyl reactant, there are generally about six moles of nitric oxide. Greater or lesser quantities of nitric oxide can be used, although in general such use decreases the efficiency of our process. The use of at least 100 percent excess of nitric oxide helps to insure that the tricyclomatic trinickel dicarbonyl reactant is most completely consumed in the reaction. This is desirable since it is the more expensive reactant.

In conducting our process, it is preferable that air be excluded from the reaction mixture. Otherwise, some deterioration is likely to occur. This may be accomplished by using in the system a blanketing gas of nitric oxide. Since carbon monoxide is a product of the reaction, the blanketing gas will also contain some carbon monoxide. The out gases containing nitric oxide and carbon monoxide may be recycled to the autoclave.

The reaction mixture is preferably agitated so as to insure homogeneity of the reaction mass. In the autoclave, there are generally present both gases and liquids, and agitation insures that these phases are well dispersed. Without agitation, the gaseous reactants may tend to collect in the upper portion of the autoclave, while tthe liquid reactants settle to the bottom of the autoclave. When this occurs, the reaction rate is diminished. Agitation is, therefore, desirable in insuring a constant reaction rate.

Tricyclomatic trinickel dicarbonyl compounds are reported in the literature and may be made by the reaction of nickel tetracarbonyl with a dicyclomatic nickel compound. Typical of such preparation is that of tricyclopentadienyl trinickel dicarbonyl as illustrated by the following example in which all parts and percentages are by weight unless otherwise indicated.

Example I

Twenty parts of dicyclopentadienyl nickel, 87.9 parts of benzene and 25.3 parts of nickel tetracarbonyl were heated at reflux for 24 hours during which time the solution became black. The solvent and unreacted nickel tetracarbonyl were removed by distilling the mixture into two cold traps maintained at about −70° C. in which unreacted nickel tetracarbonyl was removed. Sublimation of the residues at 60° C. gave 1.0 part of nickelocene contaminated with cyclopentadienyl nickel carbonyl dimer. Further, sublimation at 100° C. for three hours gave 1.0 part of cyclopentadienyl nickel carbonyl dimer. The remaining residues were transferred to a Soxhlet extractor and extracted for about 400 hours with cyclohexane to give 19.7 parts of green crystalline tricyclopentadienyl trinickel dicarbonyl. Calculated for $C_{17}H_{15}Ni_3O_2$: C, 47.6; H, 3.54; Ni, 41.2. Found: C, 47.9; H, 3.78 and Ni, 40.8. The structure of the product was confirmed by comparing its infrared spectrum with that of an authentic sample of tricyclopentadienyl trinickel dicarbonyl.

To further illustrate our process involving essentially a liquid phase reaction, there are presented the following examples. All parts and percentages are by weight unless otherwise indicated.

Example II

To a reaction vessel equipped with stirring means, a gas inlet, temperature control means and a condenser with a nitrogen T were added 311 parts of tetrahydrofuran. With the system under nitrogen, 5.16 parts of tricyclopentadienyl trinickel dicarbonyl were added. Nitric oxide was bubbled through the system for four hours. The volume of the reaction mixture was reduced by removal of most of the solvent through heating under vacuum, the mixture was filtered and the residue was fractionated. A total of 4.43 parts of cyclopentadienyl nickel nitrosyl having a boiling point of 62–63° C. at 30 millimeters was recovered. The structure of the product was confirmed by comparison of its infrared spectrum and melting point with that of an authentic sample of cyclopentadienyl nickel nitrosyl.

Example III

Forty-two and five-tenths parts of tricyclopentadienyl trinickel dicarbonyl, 18 parts of nitric oxide and 1000 parts of diethyleneglycol dibutylether are charged to an evacuated autoclave equipped with inlet and discharge ports, temperature control means, pressure control means and an agitator. The autoclave is maintained at a temperature of 30° C. and a pressure of one atmosphere. The reaction mixture is agitated for two hours whereupon the autoclave is discharged. The reaction mixture is distilled to give a good yield of cyclopentadienyl nickel nitrosyl in the distillate. The residual solvent is filtered and recycled to the autoclave.

Example IV

Forty-two and five-tenths parts of tricyclopentadienyl trinickel dicarbonyl, 13.5 parts of nitric oxide and 1600 parts of benzene are charged to an evacuated reaction vessel equipped as in Example III. The reaction mixture is agitated for four hours at a temperature of 40° C. and a pressure of one atmosphere. The autoclave is then cooled and discharged, and the reaction mixture is filtered. The filtrate is distilled to give a good yield of crude cyclopentadienyl nickel nitrosyl in the residue. The benzene filtrate is recycled to the reaction vessel. The residues are further distilled to give essentially pure cyclopentadienyl nickel nitrosyl.

Example V

Forty-two and five-tenths parts of tricyclopentadienyl trinickel dicarbonyl, 20 parts of nitric oxide and 1200 parts of ethyleneglycol dimethylether are charged to an evacuated autoclave equipped as in the previous examples. The reaction mixture is agitated for one hour at a pressure of five atmospheres and a temperature of 20° C. The autoclave is then discharged, and the contents are filtered. The filtrate is distilled to give a good yield of crude cyclopentadienyl nickel nitrosyl in the residue. The ethyleneglycol dimethylether filtrate is recycled to the reaction vessel. The crude cyclopentadienyl nickel nitrosyl is further purified by flash distillation to give a good yield of essentially pure cyclopentadienyl nickel nitrosyl.

Example VI

Forty-seven parts of tris(methylcyclopentadienyl) trinickel dicarbonyl, 13.5 parts of nitric oxide and 600 parts of tetrahydrofuran are charged to an evacuated autoclave. The mixture is agitated for three hours at a temperature of 30° C. and a pressure of two atmospheres. The autoclave is then discharged, and its contents are filtered. The filtrate is distilled to give a good yield of crude methylcyclopentadienyl nickel nitrosyl in the residue which is purified by further distillation. The tetrahydrofuran distillate is recycled to the autoclave.

Example VII

Fifty-seven and five tenth parts of tris(indenyl) trinickel dicarbonyl, 30 parts of nitric oxide and 2500 parts of n-octane are charged to a reaction vessel equipped as in the preceding examples. The reaction mixture is agitated at a temperature of 50° C. and a pressure of 10 atmospheres for six hours. The autoclave is then cooled and discharged. The reaction product is purified by distillation to give a good yield of crude indenyl nickel nitrosyl in the residue. The filtrate comprising the n-octane solvent is recycled to the autoclave.

As shown by the preceding examples, our process goes readily over a wide range of process conditions when using a variety of tricyclomatic trinickel dicarbonyl reactants. For example, when tris(phenylcyclopentadienyl) trinickel dicarbonyl is utilized as a reactant in the above process, the product, phenylcyclopentadienyl nickel nitrosyl, is obtained. Likewise, when tris(di-tert-butylcyclopentadienyl) trinickel dicarbonyl, tris(n-hexylcyclopentadienyl) trinickel dicarbonyl or tris(tetramethylcyclopen-

tadienyl) trinickel dicarbonyl are utilized as reactants in the above process, the compounds di-tert-butylcyclopentadienyl nickel nitrosyl, n-hexylcyclopentadienyl nickel nitrosyl and tetramethylcyclopentadienyl nickel nitrosyl are obtained in good yield.

Our process may also be carried out as essentially a gas phase reaction. In this embodiment, a gaseous tricyclomatic trinickel dicarbonyl compound and nitric oxide are fed through a heated tube reactor. The reactor is packed with suitable particulate material to insure intimate mixing of the components. The cyclomatic nickel nitrosyl product may be separated from the out gases by conventional means such as passing the gases through a cooling system and condensing out the product together with unreacted tricyclomatic trinickel dicarbonyl. The product is separated from the nickel reactant by conventional means such as extraction or distillation. The separated tricyclomatic trinickel dicarbonyl is recycled to the reactor. The out gases from the condenser may also be recycled to the reactor.

The cyclomatic nickel nitrosyl compounds produced by our process are excellent antiknocks. They have been tested by the Research Method to determine their antiknock effect in a hydrocarbon fuel. The Research Method of determining octane number of the fuel is generally accepted as a test method which gives a good indication of fuel behavior in full-scale automotive engines under normal driving conditions. It is the method most used by commercial installations in determining the value of a gasoline additive.

The Research Method is conducted in a single cylinder engine especially designed for this purpose and referred to as the CFR engine. This engine has a variable compression ratio and during the test the temperature of the water jacket is maintained at 212° F., and the inlet air temperature is controlled at 125° F. The engine is operated at a speed of 600 r.p.m. with a spark advance of 13° before top dead center. This test method is more fully described in Test Procedure D–908–55 contained in the 1956 edition of "ASTM Manual of Engine Test Methods for Rating Fuels."

The fuel employed in these tests was a mixture representative of commercial gasolines in present production. It consisted of 20 volume percent diisobutylene, 20 volume percent toluene, 20 volume percent isooctane and 40 volume percent n-heptane. This fuel, when rated without an antiknock additive, had a research octane number of 91.3. When the fuel contained one gram of nickel per gallon as cyclopentadienyl nickel nitrosyl, it had a research octane number of 93.8. Two grams of nickel per gallon as cyclopentadienyl nickel nitrosyl raised the octane number of the base fuel to 95.0.

In addition, a typical compound produced by our process, cyclopentadienyl nickel nitrosyl, was tested as a supplemental antiknock. In this test, one gram of nickel per gallon as cyclopentadienyl nickel nitrosyl was added to a base fuel which contained three milliliters of tetraethyllead per gallon. The presence of the nickel additive resulted in an increase of 3.4 octane numbers over that obtainable with the tetraethyllead alone. This increase represents an outstanding improvement in antiknock effectiveness.

Although the process of our invention has been illustrated only with respect to the production of cyclomatic nickel nitrosyl compounds, it works equally as well in producing similar compounds of platinum and palladium.

Having fully described our novel and inventive process by the foregoing examples and discussion, we desire that our invention be limited only within the scope of the appended claims.

We claim:

1. Process for the formation of a cyclomatic nickel nitrosyl compound in which the cyclomatic group is a hydrocarbon radical containing from 5 to about 13 carbon atoms and is selected from the class consisting of the cyclopentadienyl radical, the indenyl radical, and hydrocarbon substituted cyclopentadienyl and indenyl radicals, wherein the hydrocarbon substituents are selected from the class consisting of alkyl, phenyl and alkylphenyl radicals, said process comprising reacting the tricyclomatic trinickel dicarbonyl compound containing the corresponding cyclomatic radical with nitric oxide.

2. The process of claim 1 wherein the reaction is carried out in essentially the liquid phase.

3. The process of claim 1 wherein the tricyclomatic trinickel dicarbonyl compound is tricyclopentadienyl trinickel dicarbonyl, and the product formed is cyclopentadienyl nickel nitrosyl.

References Cited in the file of this patent

Fischer et al.: Z. Naturfarsh 10b, pages 598, 599 (1955).