

1

3,138,625

CYCLOPENTADIENYL METAL COMPOUNDS

Michael Cais, % Technion Israel Institute of Technology, Haifa, Israel, assignor of three-fourths to Technion Research & Development Foundation, Limited, a corporation of Israel

No Drawing. Filed Apr. 2, 1962, Ser. No. 184,570

Claims priority, application Israel Apr. 4, 1961

8 Claims. (Cl. 260-429)

This invention relates to cyclopentadienyl metal compounds, i.e. organometallic compounds in which a transition metal is bound to a cyclopentadienyl nucleus through a π -bond.

Some compounds of this kind have technical uses in various fields, for example, as antiknock additives to fuels, additives to lubricants, for producing metal coatings on metallic or non-metallic substrates, as drying agents to be incorporated in drying paints, varnishes, oils, resins or the like, and as intermediate in the manufacture of metal-containing polymers.

However, of the comparatively large number of cyclopentadienyl metal compounds known as a result of fundamental research, few only have been found to be suitable for technical use.

The present invention provides new cyclopentadienyl metal compounds particularly suitable for various technical uses, especially as antiknock agents and for the preparation of metal coatings. More particularly the compounds according to the invention are related on the one hand to the known cyclopentadienyl manganese tricarbonyl, and on the other hand to the known dicyclopentadienyl metal compounds of which the iron compound is known as ferrocene. Ferrocene-type compounds containing a transition metal other than iron are also known, e.g. cobalt, nickel, ruthenium. Moreover, compounds are known in which two ferrocene-type groups are interconnected by a $-\text{CO}-$ bridge.

For the purposes of the invention the cyclopentadienyl manganese tricarbonyl group will be referred to hereinafter for short as "manganese tricarbonyl" components, and the dicyclopentadienyl metal group as "ferrocene-type component," the latter irrespective of the metal it contains.

The invention consists in cyclopentadienyl metal compounds wherein the cyclopentadienyl nucleus of a manganese tricarbonyl component is linked through a single-carbon-atom bridge to the cyclopentadienyl nucleus of a second manganese tricarbonyl component, or to one of the cyclopentadienyl nuclei of a ferrocene-type component.

The single-carbon-atom bridge may be a methylene group, a hydroxymethylene group or a carbonyl group.

Where the compounds according to the invention contain a ferrocene-type component, the two cyclopentadienyl nuclei thereof may be so linked each to a manganese tricarbonyl component.

In all compounds according to the invention, any of the cyclopentadienyl nuclei may contain substituents.

Compounds according to the invention whose components contain different metals can be used for the manufacture of metal coatings in which the two metals are disposed in a substantially atomic mixture so that the coatings can be regarded as consisting of alloys.

For the preparation of the compounds according to the invention, the manganese tricarbonyl and ferrocene-type compounds, whose preparation has been described in the literature, can be used as starting materials. For the creation of the carbon-atom bridge one of the two components is converted into the corresponding formed formyl chloride which is linked up with the other component by a Friedel-Crafts type reaction. The immediate

2

product of this synthesis is the compound in which the bridge has the constitution



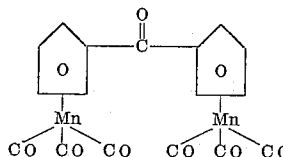
i.e. of a carbonyl group. The bridge can be converted into a hydroxymethylene or methylene group by reduction, e.g. catalytical reduction with hydrogen, or chemical reduction by means of zinc and hydrochloric acid, lithium-aluminium hydride or in any other suitable manner.

The invention is illustrated by the following examples to which it is not limited.

EXAMPLE 1

Di-(Cyclopentadienyl Manganese Tricarbonyl)-Ketone

To a mixture of 1.15 g. of cyclopentadienyl manganese tricarbonyl and 1.2 g. of anhydrous AlCl_3 in 35 ml. of methylene chloride a solution of 1.5 g. of (chloroformylcyclopentadienyl) - manganese tricarbonyl in 20 ml. methylene chloride was added dropwise. After refluxing for 5 hours, the mixture was cooled and poured into acidified iced water. The organic layer was separated from the aqueous layer and the solvent was evaporated. The residue was chromatographed over basic alumina. Elution with hexane/benzene (1:1) yielded 0.7 g. of crystals of di-(cyclopentadienyl manganese tricarbonyl)-ketone of the Formula A



M.P. 145-145.5° (from hexane/benzene).

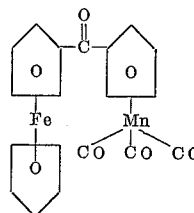
Analysis.—Calculated for $\text{C}_{17}\text{H}_{10}\text{O}_7\text{Mn}_2$: C, 46.81; H, 2.31; Mn, 25.19%. Found: C, 46.84; H, 2.10; Mn, 24.94%.

EXAMPLE 2

(Cyclopentadienyl Manganese Tricarbonyl) - (1-Ferrocenyl)-Ketone and Di-(Cyclopentadienyl Manganese Tricarbonyl)-(1,1'-Ferrocenyl)-Diketone

To a mixture of 0.93 g. of ferrocene and 1 g. of anhydrous AlCl_3 in 30 ml. of methylene chloride, a solution of 1.33 g. of (chloroformylcyclopentadienyl)-manganese tricarbonyl in 15 ml. of methylene chloride was added dropwise. The mixture was stirred at room temperature for 1 hour, then refluxed for 1 hour, then cooled and poured into acidified iced water. The organic layer was separated from the aqueous layer and the solvent evaporated. The residue was chromatographed over 110 g. of basic alumina.

Benzene elution yielded 0.142 g. of unreacted ferrocene and then 1.25 g. of red crystals of (cyclopentadienyl manganese tricarbonyl)-(1-ferrocenyl)-ketone of the Formula B

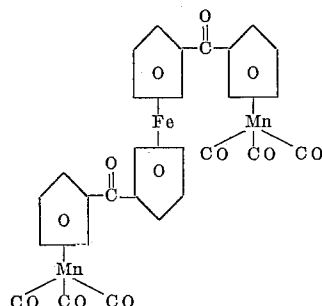


M.P. 148-149° (from hexane).

Analysis.—Calculated for $\text{C}_{19}\text{H}_{13}\text{O}_4\text{MnFe}$: C, 54.84; H, 3.15%. Found: C, 55.15; H, 3.43%.

3

Further elution with chloroform yielded 0.127 g. of red-violet crystals of di-(cyclopentadienyl manganese tricarbonyl) (1,1'-ferrocenyl)-diketone of the formula C



M.P. 230–232°.

Analysis.—Calculated for $C_{28}H_{16}O_8FeMn_2$: C, 52.05; H, 2.49%. Found: C, 52.29; H, 2.50%.

The same compound, i.e. the diketone was obtained in a 82% yield when a second Friedel-Crafts reaction was carried out on the monosubstituted ferrocene, $C_{19}H_{13}O_4MnFe$, of Formula B.

EXAMPLE 3

Di-(Methylcyclopentadienyl Manganese Tricarbonyl)-(1,1'-Ferrocenyl)-Diketone

When the reaction described in Example 2 was carried out with (chloroformyl-methylcyclopentadienyl)-manganese tricarbonyl, a diketone was obtained that was similar to that according to Formula C above but contained a methyl group as a substituent in the cyclopentadienyl nuclei of both manganese tricarbonyl components.

Analysis.—Calculated for $C_{30}H_{20}O_8FeMn_2$: C, 53.44; H, 2.99%. Found: C, 53.78; H, 3.25%.

EXAMPLE 4

Di-(Cyclopentadienylmanganese Tricarbonyl)-Methane

A mixture of 0.172 g. of di-(cyclopentadienyl manganese tricarbonyl)-ketone (as prepared in accordance with Example 1) in 50 ml. of ethanol and zinc amalgam (prepared from 4 g. of zinc, 0.4 g. of mercuric chloride, 0.2 ml. of hydrochloric acid and 6.4 ml. of water) was refluxed for 72 hours, with the addition of 1 to 2 ml. of hydrochloric acid every 12 hours. Then the mixture was cooled and poured into water and the mixture was extracted with ether. The ether extract was separated from the aqueous liquid, the ether evaporated and the residue was distilled in vacuo (140°/0.01 mm. Hg). The product consisted of crystals M.P. 106°, being di-(cyclopentadienyl manganese tricarbonyl)-methane.

Analysis.—Calculated for $C_{17}H_{12}O_6Mn_2$: C, 48.60; H, 2.40%. Found: C, 49.43; H, 2.51%.

EXAMPLE 5

(Ferrocenyl)-(Cyclopentadienyl Manganese Tricarbonyl)-Methane

0.116 of (cyclopentadienyl manganese tricarbonyl)-(1-ferrocenyl)-ketone (prepared in accordance with Ex-

4

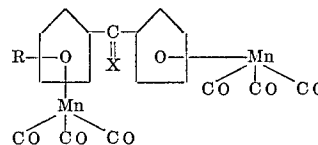
ample 2) was reduced by the Martine-Chemmenson method. The residue was worked up in the usual manner and chromatographed over basic alumina to yield 0.047 g. (42.3%) of orange crystals M.P. 121.5–122°, being (ferrocenyl)-(cyclopentadienylmanganese tricarbonyl)-methane.

Analysis.—Calculated for $C_{19}H_{17}O_3FeMn$: C, 56.75; H, 3.76%. Found: C, 56.80; H, 3.85%.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:

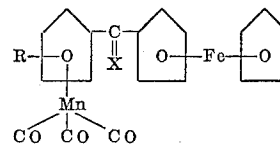
1. Cyclopentadienyl metal compounds selected from the group consisting of di-(cyclopentadienyl manganese tricarbonyl)-ketone; cyclopentadienyl manganese tricarbonyl-(1-ferrocenyl)-ketone; di-(cyclopentadienyl manganese tricarbonyl)-(1,1'-ferrocenyl)diketone; di-(methylcyclopentadienyl manganese tricarbonyl)-(1,1'-ferrocenyl)-diketone; di-(cyclopentadienylmanganese tricarbonyl)-methane.

2. Cyclopentadienyl metal compounds having the following structural formula:



wherein R is selected from the group consisting of H and CH_3 , and X is selected from the group consisting of H_2 and O.

3. Cyclopentadienyl metal compounds having the following structural formula:



wherein R is selected from the group consisting of H and CH_3 , and X is selected from the group consisting of H_2 and O.

4. Di-(cyclopentadienyl manganese tricarbonyl)-ketone.

5. Cyclopentadienyl manganese tricarbonyl-(1-ferrocenyl)-ketone.

6. Di-(cyclopentadienyl manganese tricarbonyl)-(1,1'-ferrocenyl)-diketone.

7. Di-(methylcyclopentadienyl manganese tricarbonyl)-(1,1'-ferrocenyl)-diketone.

8. Di-(cyclopentadienyl manganese tricarbonyl)-methane.

References Cited in the file of this patent

Cais et al.: "Tetrahedron Letters," 440–443 (August 1961) as abstracted in Chem. Abst. 5997–5998, March 19, 1962.