



Bis-cyclopentadienyl compounds of iron and vanadium
by Norman J Birkholz

A THESIS Submitted to the Graduate Committee in partial fulfillment of the requirements for the degree of Master of Science in Chemistry
Montana State University
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Abstract:

In an attempt to produce bridged-ring ferrocenes and substituted ferrocenes and "vanadocenes", the following results were obtained: A green crystalline adduct from n-BuMgBr and VOCl_3 in Bu_2O was found to be unidentifiable.

Cyclopentadienyl, β -carboxypropionylcyclopentadienyl iron, m.p. 155°C , and bis- β -carboxypropionylcyclopentadienyl iron, m.p. $187.5\text{--}188.5^\circ\text{C}$, were prepared by reaction of AlCl_3 , ferrocene, and succinic anhydride. Attempted cyclization of cyclopentadienyl, β -carboxypropionylcyclopentadienyl iron with polyphosphoric acid resulted in the formation of a black, iron containing acid which was not identified.

Di-phenyl, bis-cyclopentadienyl vanadium (red-brown, d. above 139°C) was believed formed by reaction of ethereal phenyl lithium and bis-cyclopentadienyl vanadium dichloride.

Several unsuccessful preparations of substituted iron and vanadium compounds are also described.

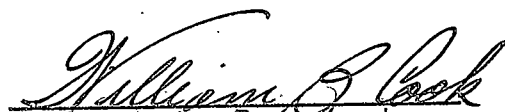
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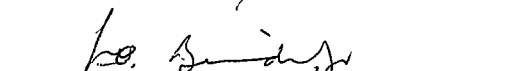
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OF
IRON AND VANADIUM

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A B S T R A C T

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Several unsuccessful preparations of substituted iron and vanadium compounds are also described.

OBJECTIVES

The objectives of this research were as follows:

1. Investigation of the compounds formed when VOCl_3 reacts with Grignard reagents.
2. Preparation of a substituted bis-cyclopentadienyl vanadium dichloride.
3. Substitution of the chlorine moiety of bis-cyclopentadienyl vanadium dichloride.
4. Preparation of bis-fluorenyl iron and bis-fluorenyl vanadium dichloride.
5. Preparation of a substituted ferrocene in which the two rings are bridged by a carbon chain.

INTRODUCTION

At the time this research was begun, the only organo-vanadium compounds known were Wilkinson's bis-cyclopentadienyl vanadium dichloride (36) and Vernon's VOCl_3 - Phenyl magnesium bromide adduct (32). By this time also, several experimenters had concentrated their efforts on the elucidation of bis-cyclopentadienyl metal structures, following Kealy and Pauson's discovery (20) of bis-cyclopentadienyl iron in 1951.

It was originally intended to limit this investigation to vanadium compounds, but poor and meager results forced the research to be extended to iron compounds in the hope of obtaining material for a positive thesis.

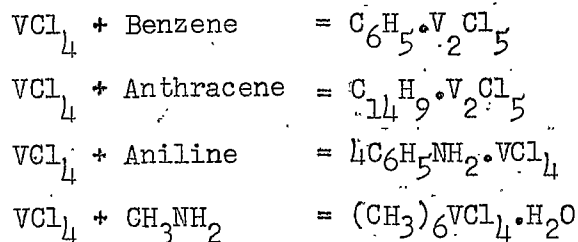
Since no substituted bis-cyclopentadienyl vanadium compounds had been prepared by other investigators, and since no one had yet investigated the possibility of creating bridged-ring ferrocenes, the major part of the work was directed toward their preparation.

It is believed that synthesis of substituted vanadium compounds would be an important extension of present knowledge, and that the preparation of a bridged-ring ferrocene might pave the way to a new class of compounds.

L I T E R A T U R E S U R V E Y

Organo-vanadium compounds:

Mertes (22) made the earliest known attempt at synthesis of organo-vanadium compounds in 1912. He studied the addition compounds of VCl_4 with such compounds as benzene, gasoline, kerosene, and various amines. Empirical formulae from his analyses led him to postulate such compounds as the following, which were all black amorphous solids which could not be recrystallized:



The only known solvent with which VCl_4 does not form a precipitate is CCl_4 .

A series of reactions of phenyl magnesium bromide with VCl_2 , VCl_3 , VOCl_3 , V_2O_3 , V_2O_4 , and V_2O_5 is reported by Vernon (32). He reports no reaction in all cases except VOCl_3 , from which he obtained a dull greenish precipitate described as rapidly decomposing in air or on warming. The substance could not be purified.

Bis-cyclopentadienyl metals and related compounds:

In 1951 Kealy and Paulson (20) reported the preparation of bis-cyclopentadienyl iron, $(\text{C}_5\text{H}_5)_2\text{Fe}$, which was not only the first true organo-iron compound, but was also the first known compound containing the "sandwich bond", in which the iron atom lies directly between the two rings, which lie in parallel planes. These authors prepared the compound by reaction

of anhydrous FeCl_3 with an ethereal solution of cyclopentadienyl magnesium bromide. The compound has since been prepared by reacting FeCl_2 and cyclopentadienyl sodium in tetrahydrofuran solution (35), and by passing vapors of cyclopentadiene and its dimer over hot iron in presence of alumina and Mo_2O_3 . (23)

Since the time of this discovery, many similar compounds have been prepared using other transition metals. Mass spectra have been recorded (13) for the bis-cyclopentadienyl compounds of iron, cobalt, nickel, chromium, ruthenium, vanadium, manganese, and magnesium, and for $(\text{C}_5\text{H}_5)_2\text{ReH}$.

Fischer and Hafner (7) prepared bis-cyclopentadienyl chromium by forming $\text{Cr}(\text{NH}_3)_6(\text{C}_5\text{H}_5)_3$ in liquid ammonia, then heating it to 80-120 °C in a high vacuum. The $(\text{C}_5\text{H}_5)_2\text{Cr}$ is described as red needles, m.p. 173 °C, soluble in organic solvents, and stable to light in absence of oxygen.

Fischer and Jira (9) prepared green, volatile $\text{Ni}(\text{C}_5\text{H}_5)_2$ by vacuum pyrolysis of the precipitate formed by reaction of cyclopentadienyl potassium and $\text{Ni}(\text{NH}_3)_6(\text{SCN})_2$ in liquid ammonia.

This method of preparation was extended to include indenyl metals when Fischer, Seus, and Jira (12) reacted indenyl potassium and $\text{Co}(\text{NH}_3)_4(\text{SCN})_2$ in liquid ammonia to form a yellow-brown precipitate of $\text{Co}(\text{NH}_3)_6(\text{C}_9\text{H}_7)_2$, which yielded bis-indenyl cobalt upon pyrolysis. The compound was black and melted at 178-181 °C.

Fischer and Seus (11) also reported bis-indenyl iron, prepared from FeCl_3 and indenyl magnesium bromide in an ether-benzene solvent.

Bis-indenyl iron was made by Pauson and Wilkinson (27) by reaction of indenyl lithium and FeCl_3 in ether-benzene. They describe the comp-

ound as being deep purple, crystalline, m.p. 184-185 °C (evacuated tube), and soluble in benzene. It is moderately soluble in acetone, ligroin, and ether. These authors also prepared bis-indenyl cobalt by reaction of indenyl magnesium bromide, diluted with toluene, and cobalt(III)acetylacetonate.

A different type of compound was formed by Fischer and Jira (10) by reaction of MnCl_2 and cyclopentadienyl magnesium bromide. They state that the initial product was a light orange mixture of $(\text{C}_5\text{H}_5)_2\text{Mn}$ and $(\text{C}_5\text{H}_5)_2\text{Mg}$. Strong heating sublimed $(\text{C}_5\text{H}_5)_2\text{Mn}$. Above 160 °C, under CO pressure, $(\text{CO})_3(\text{C}_5\text{H}_5)_2\text{Mn}$ was formed, m.p. 77 °C. It is stable in air and soluble in benzene, ether, and alcohol.

Another new class of compounds was synthesized by Wilkinson and collaborators (36) when they began preparing bis-cyclopentadienyl metal dihalides. For instance, reaction of VCl_4 with cyclopentadienyl magnesium bromide formed dark green, unstable, ligroin soluble $(\text{C}_5\text{H}_5)_2\text{VBr}_2$, and pale green, stable, ligroin insoluble $(\text{C}_5\text{H}_5)_2\text{VCl}_2$. The dichloride is soluble in chloroform, ethyl acetate, and ethanol. It decomposes above 250 °C and forms a green, unstable water solution.

These authors also formed bis-cyclopentadienyl nickel from cyclopentadienyl magnesium bromide and $\text{Ni(II)acetylacetonate}$, stating that the dark green crystals from ligroin decomposed slowly, even in the dark. Decomposition occurred below the melting point.

Bis-cyclopentadienyl titanium dibromide was also prepared by these authors upon reaction of TiCl_4 and excess cyclopentadienyl magnesium bromide in toluene. The compound forms dark red crystals, m.p. 240 - 243°C,

and is unstable in water, giving a yellow solution. An analogous reaction, using ZrCl_4 and excess Grignard reagent gave colorless bis-cyclopentadienyl zirconium dibromide which melted with decomposition at 260°C .

Bis-cyclopentadienyl titanium dichloride has been prepared by reaction of cyclopentadienyl lithium and TiCl_4 in xylene by Summers and Uloth (29). The dark red crystalline precipitate was prepared in 74 percent yield. It was recrystallized from chloroform or xylene, sublimed at $190^\circ\text{C}/2\text{ mm Hg}$, and decomposed above 210°C . These authors also prepared, by reaction of phenyl lithium with $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$, a compound which was orange-yellow, soluble in ethanol, ether, and methylene chloride, and melting at $130\text{--}137^\circ\text{C}$. Cryoscopic measurement of the molecular weight led them to believe it to be diphenyl, bis-cyclopentadienyl titanium. Similar compounds, using p- or m-tolyl lithium were prepared, giving 75 percent yields.

Fischer and Hafner (8) have prepared volatile, violet bis-cyclopentadienyl vanadium by reacting VCl_4 and cyclopentadienyl magnesium bromide. The reaction mixture was dried under nitrogen and the residue immediately sublimed in a vacuum. An isomorphous mixture containing $\text{Mg}(\text{C}_5\text{H}_5)_2$ and $\text{V}(\text{C}_5\text{H}_5)_2$ was obtained as product. The mixture was dissolved in ether and dry CO_2 was introduced. The magnesium compound formed an insoluble precipitate. Drying of the liquor, followed by sublimation of the residue, gave a 50-60 percent yield of $\text{V}(\text{C}_5\text{H}_5)_2$, which had a m.p. of $167\text{--}168^\circ\text{C}$ under nitrogen and was very soluble in oxygen free benzene, ether, and petroleum ether. Formation of $(\text{C}_5\text{H}_5)_2\text{V}(\text{CO})_4$ was also noted.

Rare earths provide a still different type of cyclopentadienyl

compound, as was reported by Wilkinson and Birmingham (35). They prepared compounds of the type $(C_5H_5)_3M$, where M is a rare earth metal. A general method of preparation is given, which utilizes reaction of the anhydrous metal chlorides with cyclopentadienyl sodium in tetrahydrofuran solvent. The solvent is removed and the dry residue sublimed at 200 - 250 °C and 10^{-4} mm Hg. The substances are all crystalline, colored solids (except for one), thermally stable to 400 °C, and are generally insoluble in hydrocarbon solvents but are soluble in tetrahydrofuran and glycol dimethyl ether. A list of the compounds prepared is as follows: (only the metal present is listed). Sc, straw color, m.p. 240 °C; Y, pale yellow, m.p. 295 °C; La, colorless, m.p. 395 °C; Ce, orange, m.p. 435 °C; Pr, pale green, m.p. 420 °C; Nd, pale blue, m.p. 380 °C; Sm, orange, m.p. 365 °C, Gd, pale yellow, m.p. 350 °C. These are all ionic compounds, and all react instantly with $FeCl_3$ in tetrahydrofuran to form ferrocene. A brief mention is also made of a brown dicyclopentadienyl chloro-compound of uranium.

The above discussion of various types of cyclopentadienyl metals is a rather complete survey of the field at the time this work was done. With the exception of articles which may have occurred in the Journal of Nuclear Inorganic Chemistry, it is believed that the survey is complete.

The next section of this study will be restricted to reactions of the iron compounds, since the comprehensive study of their reactions deserves to be treated as a special category.

Reactions of bis-cyclopentadienyl iron compounds:

The many reactions which have been performed with iron compounds are

probably typical of bis-cyclopentadienyl metals as a class. No published reports have been seen regarding other than substituted iron compounds, but a private communication from G. Wilkinson of Harvard University indicates that he will soon publish work on a series of substituted neutral compounds of vanadium.

In order to shorten nomenclature, bis-cyclopentadienyl iron will be referred to as "ferrocene" in the remainder of this thesis. The name was first applied by Woodward, Rosenblum, and Whiting (37), who published a notable study of its reactions. These authors reacted ferrocene with maleic anhydride in boiling benzene with no Diels-Alder adduct formation. Hydrogenation in the presence of platinum oxide gave no reaction. Ferrocene and acetyl chloride in CS_2 and in the presence of anhydrous AlCl_3 gave red bis-acetylcyclopentadienyl iron, m.p. 130-131 °C, which was then treated with hypiodite to yield a dicarboxylic acid. This was then characterized by its dimethyl ester, m.p. 114-115 °C. The structure of these compounds was not proven rigorously. Similarly, ferrocene and α -chloropropionyl chloride reacted with AlCl_3 in CS_2 to form the expected bis α -chloropropionyl ferrocene and bis-acryloyl ferrocene. Reaction of ferrocene with aqueous Br_2 or HNO_3 gave only the red ferricinium ion, $\text{Fe}(\text{C}_5\text{H}_5)_2^+$. Friedel-Crafts reaction of ferrocene with phthalic anhydride gave the expected bis o-carboxybenzoyl ferrocene, m.p. 144 °C.

By this series of reactions, these authors sought to prove their postulate that ferrocene reacts as an aromatic substance. Since their work is a major contribution to the study of this type of compound, some of their comments are included here. Their initial postulate assumes

that the structure of ferrocene is that given below:



They then conclude that the equivalent bonds connecting the ring carbons must be of greater order than a single bond, but obviously less than a double bond, which is analogous to the situation found in benzene.

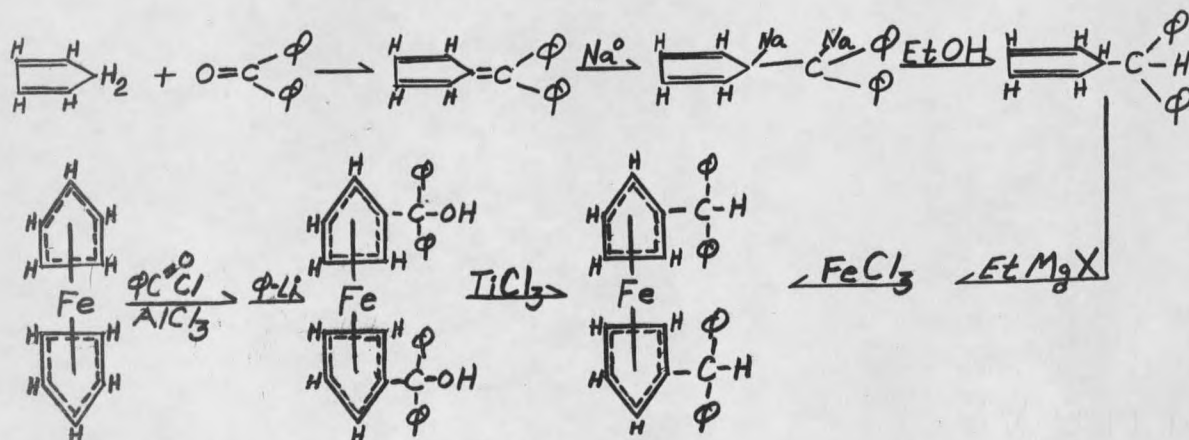
Acidity constants in 2:1 EtOH/H₂O for the ferrocene dicarboxylic acid they prepared were $pK_1 = 3.1 \times 10^{-7}$ and $pK_2 = 2.7 \times 10^{-8}$. These are comparable to the acidity constant of benzoic acid, $pK = 2.4 \times 10^{-7}$.

They stated that the very small difference between the acidity constants of the dicarboxylic ferrocene meant that there was very little interaction between the two groups, showing that they must be far apart and therefore on separate rings. The near identity of the first constant with that of benzoic acid indicates that the ring carbon atoms, and thence also the iron atom, must be essentially electrically neutral. This is proven by showing that ferrocene enters into Friedel-Crafts reactions as a typical aromatic substance, but will not react with dienophiles such as maleic anhydride, showing that it is not olefinic.

Pauson (26) advanced the study by direct synthesis of substituted ferrocenes. He attempted reaction of ferrocene with benzoyl peroxide, but found it unreactive. He prepared several phenyl substituted cyclopentadienes, and found that steric hindrance prevented formation of ferro-

cenes from 1, 2, 3, 4 tetraphenyl cyclopenta-1-3-diene, 1, 2, 3, 4, 5 penta-phenyl cyclopenta-1-3-diene, and 1,2,3 triphenyl cyclopenta-1-3-diene. He notes that all of these have three or more adjacent phenyl groups. Reaction in all cases was with ethyl magnesium bromide, followed by FeCl_3 addition to the ethereal solution. The following substituted cyclopentadienes formed ferrocenes: a) 1-4-diphenyl cyclopenta-1-3-diene, b) 1,2,4-triphenyl cyclopenta-1-3-diene, and c) 1-phenyl cyclopenta-1-4-diene. Pauson also reacted a mixture of cyclopentadiene and 1-phenyl cyclopenta-1-4-diene to produce a mixed ferrocene; cyclopentadienyl, phenyl-cyclopentadienyl iron.

The article also reported preparation of alkyl substituted ferrocenes by either of the two reaction sequences shown below:



Benkeser, Goggin, and Schroll (1) reacted ferrocene with n-butyl lithium followed by addition of the mixture to Dry Ice, thus forming both mono- and di-carboxyl ferrocenes. These acids were also esterified. Tri-phenylsilyl ferrocene and bis-triphenylsilyl ferrocene were also prepared.

THEORETICAL DISCUSSION

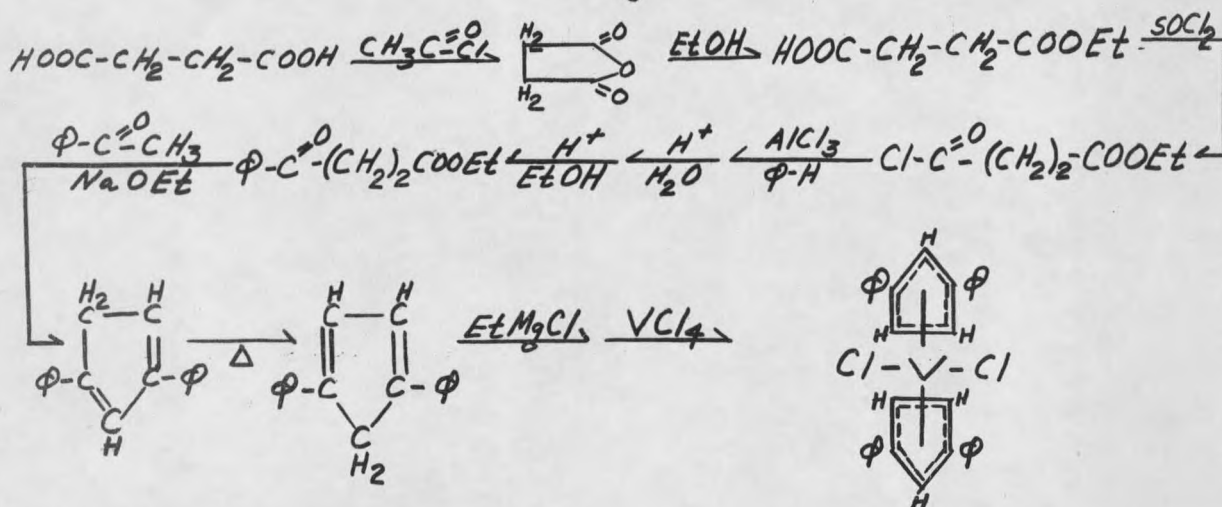
A. VOCl_3 - Grignard adducts:

If an excess of Grignard reagent is available, VOCl_3 would be expected to form a compound, R_4VOMgX . Hydrolysis of this compound would not be expected to yield any recognizable product other than H_3VO_4 , since most, if not all, metal alkyls or metal aryls react in this manner with water. The Grignard adduct would further be expected to be appreciably ionic in character, and therefore insoluble in organic solvents. It must also be mentioned that VOCl_3 reacts with aromatic or aliphatic compounds to form dense precipitates, in the same general manner as VCl_4 does. This would be expected to interfere with preparation of organo-vanadium compounds by confusing and complicating the nature of such products.

Since the only pentavalent vanadium halides known are VOCl_3 and VF_5 , it is even doubtful whether R_4VOMgX can form. It may well be that the steric requirements of such a compound would prevent its existence. In any event, a search for such a compound was not likely to be fruitful, since experimental difficulties in isolation are enormous.

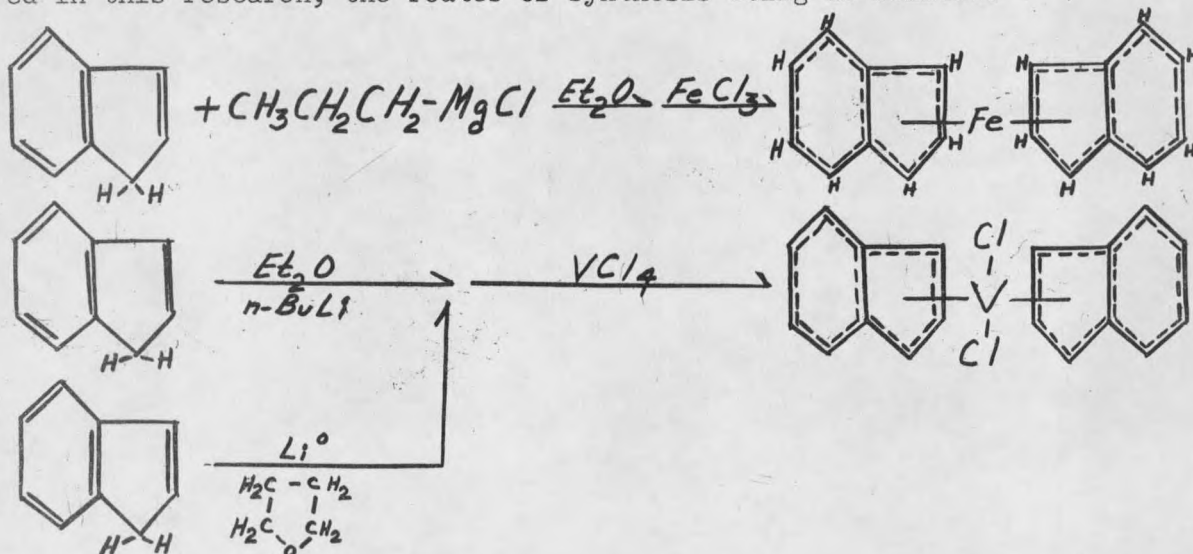
B. Substituted bis-cyclopentadienyl vanadium dichlorides:

Many substituted ferrocenes have now been prepared by other workers, and it was thought that preparation of a substituted "vanadocene" would not be impossible. The simplest substituted cyclopentadiene to prepare is apparently 1,4-diphenyl-1,3-cyclopentadiene. Since this compound has previously been prepared and reacted with FeCl_3 to form a substituted ferrocene, (26) it seemed likely that it should also lead to a substituted "vanadocene". The reaction sequence would be as follows:



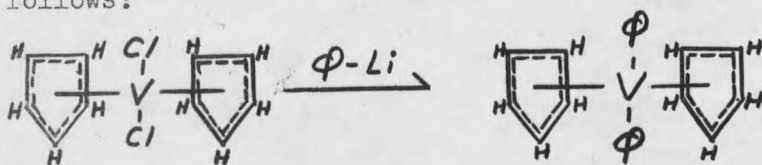
C. Bis-fluorenyl iron and bis-fluorenyl vanadium dichloride:

Since compounds have been formed between indene and transition metals (11, 12, 27), the possibility exists that fluorene may also enter into reaction with transition metals, even though its hydrogen atoms are less acidic than those of indene or cyclopentadiene. Preparations of both bis-fluorenyl iron and bis-fluorenyl vanadium dichloride were attempted in this research, the routes of synthesis being as follows:



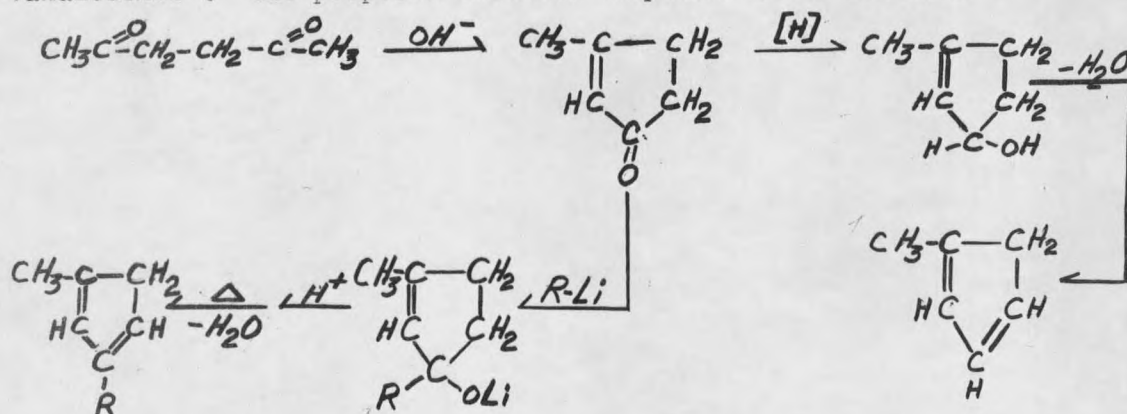
D. Substitution of chlorine moiety of bis-cyclopentadienyl vanadium dichloride:

It should be possible to substitute alkyl or aryl radicals for the chlorine atoms in this compound. A similar reaction has been applied to bis-cyclopentadienyl titanium dichloride by Summers and Uloth (29), who obtained stable compounds when the chlorine atoms were replaced by phenyl groups or substituted aromatic groups. The proposed reaction is as follows:



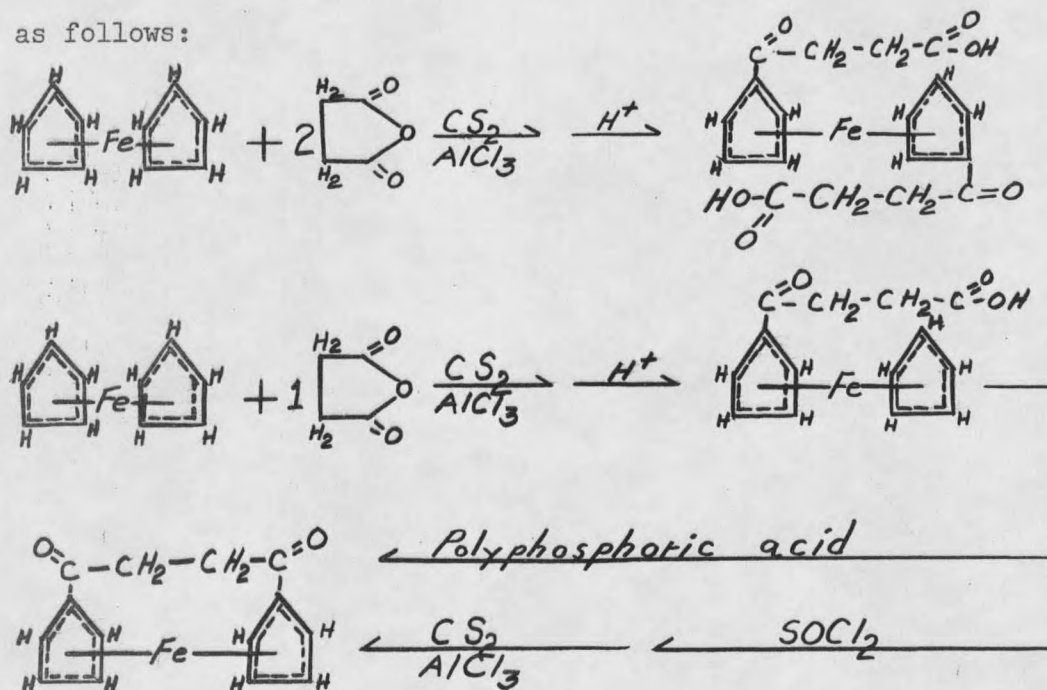
E. Synthesis of alkyl substituted cyclopentadienes:

The work of Hunsdiecker (19) regarding preparation of alkyl cyclopenteneones would afford a valuable route toward preparation of substituted methyl cyclopentadienes if intramolecular cyclization of acetonyl-acetone could be made to occur. These substituted cyclopentadienes would have been intermediates in the synthesis of substituted ferrocenes and "vanadocenes". The proposed reaction sequence is as follows:



F. Synthesis of a bridged-ring ferrocene:

It was known that ferrocene undergoes typical Friedel-Crafts reactions. If one end of a dibasic acid is attached to one of the rings by a Friedel-Crafts reaction, the other end may later be joined to the other ring by dehydration or dehydrohalogenation. The proposed reaction sequences are as follows:



This compound, if synthesized, could have led to such unique compounds as the following (by destructive hydrogenation of the bridged-ring ferrocenes):



EXPERIMENTAL

A. INORGANIC REAGENTS

1. Preparation of VOCl_3 :

The general method consisted of hydrogenation of V_2O_5 to form V_2O_3 and then treating the lower oxide with chlorine gas to form VOCl_3 .

To prepare V_2O_3 , commercial tank hydrogen was passed through a conc. H_2SO_4 bubbler, then through a tube of glass wool, and into a 30 cm x 25 mm Vycor tube containing a mixture of V_2O_5 and about 20 weight percent kieselguhr as a filler material. Waste hydrogen and water of reaction were passed into an inverted gallon jug of water, so that the effluent gasses displaced the water in the jug.

The reaction tube was filled loosely with the kieselguhr- V_2O_5 mixture and placed in an electrical resistance heater. Sufficient hydrogen was passed through the cold tube to purge it of oxygen and heating was then begun. A red heat (600-700 °C) was maintained and hydrogen passed through the tube until a sharp increase in the rate of waste hydrogen flow indicated cessation of the reaction. The tube was allowed to cool partially and was purged with dry nitrogen to remove water and hydrogen.

By means of glass tubing and a minimum of rubber connections, the tube was then connected to a chlorination apparatus, in which tank Cl_2 was passed through a conc. H_2SO_4 bubbler and then into the reaction tube, which was still in its electric heater. The exit end of the reaction tube was connected to the top of two large condensers in upright tandem. The lower condenser was inserted into a one liter distillation flask by a rubber stopper joint, and the side arm of the flask was connected by

rubber tubing to a pair of trap bottles containing 10 percent NaOH.

Chlorination took place at a red heat. Yellowish-green VOCl_3 vapor evolved from the exit end of the reaction tube and was collected in the condensing system.

On completion of the chlorination, the tube was allowed to cool and the residue remaining in the reaction tube was poked out with a stout wire. The residue from each run was saved and later reduced and chlorinated again.

After 40 to 50 such runs, the collected VOCl_3 was distilled at 629 mm Hg and 118-119 °C to give a total of 490 ml of light yellow VOCl_3 . A dark black liquid residue (25 ml) was left over at the end of the distillation. The VOCl_3 was stored in a rubber-stoppered Erlenmeyer flask in a refrigerator and did not decompose noticeably after more than a year of storage. A slight red color developed in the flask each time it was opened, probably due to hydrolysis of the liquid by moist air.

2. Preparation of VCl_4 (34):

Crushed ferrovanadium, ranging in size from dust particles to pieces the size of a lima bean, was placed in a 30 cm x 25 mm Vycor tube connected to a one liter distilling flask by a rubber stopper at the tube's exit. This flask was connected through its side-arm to rubber tubing leading to a 10 percent NaOH solution. The outside of the flask was cooled by a stream of cold water during operation.

In operation, dry chlorine was bubbled through a conc. H_2SO_4 bubbler and then into the reaction tube, which was mounted in an electrical resistance heater. When the air had been displaced by chlorine, heat was applied

until the reaction tube temperature was 300-400 °C. Chlorine was then passed into the tube rapidly, whereupon vapors of VCl_4 and FeCl_3 flowed from the exit end and into the receiving flask. To prevent troublesome plugging of the tubing by solid FeCl_3 , a flame was played upon the tubing where necessary to revaporize the sublimate.

After several such runs, enough product was obtained to fractionate and was diluted with an equal volume of dry CCl_4 , which caused FeCl_3 to precipitate. After allowing the solution to stand several hours, the supernatant liquor was decanted through a glass wool plug into a distilling flask. The distillation was carried out under water aspirator vacuum, through a 20 inch column filled with coarse carborundum chips. CCl_4 and SiCl_4 were removed in the fore-run, and the VCl_4 was then collected in a separate receiver and refrigerated. Very little decomposition to VCl_3 and Cl_2 occurred if the VCl_4 was not refluxed overly long during the distillation. Complete decomposition occurred after a month or two of refrigeration, however, and it was necessary to prepare the reagent several times during the course of this research.

The normal boiling point of the liquid was not recorded, nor was its vacuum boiling point, but it boiled at about 140 °C at 640 mm. A total of 300 to 400 g of the liquid could be prepared in three or four long working days.

3. Preparation of Anhydrous FeCl_3 :

A special piece of glassware was devised for this preparation, consisting of a 250 ml Florence flask, to the bottom of which was sealed an 8 inch test tube. After the bottom of the test tube was cut off, the

apparatus had the appearance of a length of tubing, open at both ends, and with a large bubble in its middle.

Granulated iron was placed between glass wool plugs in one of the tubes, and a cold-finger in the other. Cl_2 was passed through a conc. H_2SO_4 bubbler and over the iron particles while heating with a flame. Purplish-black FeCl_3 evolved and sublimed into the large condensing bulb. Upon completion of the reaction the sublimate was shaken into a tared bottle and weighed.

B. ORGANIC REAGENTS AND COMPOUNDS

1. Cyclopentadiene:

This was prepared in small amounts as needed and was not stored for more than a day. As prepared in this research, commercial 80-90 percent dicyclopentadiene was distilled slowly through a 6 inch column containing coarse carborundum chips. The temperature of the vapor at the top of the column was kept below 50°C . The vapor was condensed over CaCl_2 chips which served to remove a cloudy impurity sometimes observed.

2. Grignard reagents:

The standard method of Gilman and co-workers (16) was used. These metalations were carried out in 500 or 1000 ml 3-necked flasks, equipped with dropping funnel, condenser and CaCl_2 drying tube, and mercury-sealed motor-driven stirrer. The apparatus was dried in an oven, assembled while warm, and flushed with dry nitrogen. Upon cooling, the apparatus was ready for use. Since this apparatus will be much used in describing subsequent preparations, it will in the future be referred to as the "standard Grignard apparatus". This term will be intended to include the man-

ner of assembly and flushing with nitrogen.

3. Attempted preparation of cyclopentadienyl sodium:

A stoichiometric amount of freshly drawn sodium wire was placed in a standard Grignard apparatus containing cyclopentadiene in benzene solution. No reaction was observed after stirring with reflux for several hours and the method was abandoned.

4. Cyclopentadienyl potassium:

The method of Thiele (31) was followed, with slight modification. In a standard Grignard apparatus was placed 200 or more ml of dry benzene. A calculated amount of potassium metal was wiped dry, weighed, and dropped into the benzene as large chunks. Application of steam heat soon melted the metal, and rapid stirring broke it into small globules. The flask was then chilled to about 40-50 °C and about 20 ml fresh cyclopentadiene was added. After addition of the first few drops, the mixture began to reflux, and soon became a thick slurry. Additional benzene was added as needed to provide a stirrable slurry. The remainder of the cyclopentadiene was added in 5 to 10 ml portions and the reaction permitted to go to completion while stirring. More than the calculated amount of cyclopentadiene was usually added to use up unreacted metal. When the mixture began to cool, steam heat was applied for an additional hour. By this time the color of the thick suspension had changed in color to white, brown, pink, or yellow shades. The reaction mixture could be left overnight to use up as much of the potassium as would react, but this was not done unless necessary, since some oxidation invariably occurs over such a length of time. Since cyclopentadienyl potassium is very pyrophoric, it

was never isolated, but was used in the form of its benzene suspension.

5. Ferrocene (Grignard method): (20)

C_5H_5MgCl was prepared by adding cyclopentadiene to an ether solution of either n-propyl- or n-butyl-magnesium chloride. A calculated amount of anhydrous $FeCl_3$, dissolved in ether or in ether-benzene was added, with stirring, after the flask had been chilled to room temperature or to the temperature of an ice bath. The addition was usually completed within 30 minutes. Time of addition did not seem to affect the yield. If the solution was reacted at room temperature, mild warming was observed and the mixture became brown or orange in color. If the reaction occurred below room temperature, little heat was evolved and the initial color change was to a bluish-green, probably caused by the presence of ferrous iron.

The crude reaction mixture was stirred an additional hour and then cooled to room temperature. After standing for periods ranging from 4 to 36 hours, the mixture was filtered. The longer standing time was preferred. The residue was washed with benzene twice and the washings were added to the original ether extract. The combined extracts were evaporated to dryness, and the crude solid was recrystallized from aqueous methanol, giving about 34 percent yields of an orange crystalline solid (ferrocene) melting at 173-174 °C. As has been observed by other authors, the substance is insoluble in conc. HCl , 10 percent $NaOH$, and water. It is soluble in benzene, CS_2 , tetrahydrofuran, ether, acetone, alcohols, nitrobenzene, conc. H_2SO_4 , and conc. HNO_3 , producing deep red solutions with violet fluorescence in the latter two reagents, due to the formation of a colored ferricinium ion, $(C_5H_5)_2Fe^+$.

6. Ferrocene (Cyclopentadienyl potassium method):

A solution of FeCl_3 in ether or ether-benzene was added dropwise with stirring over one to two hours to a cold slurry of cyclopentadienyl potassium, prepared as previously described. The slurry was either at room temperature or chilled by an ice-salt bath. The mixture was allowed to stand overnight and filtered, yielding an orange, clear benzene filtrate and a dark, massive residue. This residue was extracted twice with additional benzene, the extracts being added to the original filtrate. The residue was destroyed by throwing it on the ground outdoors, where it ignited, probably from hydrolysis of the unreacted cyclopentadienyl potassium or oxidation of finely divided potassium, which would ignite the nearby benzene.

Evaporation of the benzene solution was accomplished by vacuum distillation. Ferrocene is very volatile with benzene, and some was lost by this procedure. Fractionation proved to be more efficient. The dry residue after evaporation was either recrystallized from methanol and water or was steam distilled in situ. Steam distillation at first gave low yields of product, since a water insoluble cake formed which trapped much of the ferrocene. It was later found that the yield could be improved by leaching this cake with benzene and continuing with the steam distillation. The ferrocene was recovered by poking it from the condenser, whereupon it was filtered and dried in air. Toward the end of the steam distillation a small amount of unknown yellowish substance was produced. This same impurity was found in aqueous methanol recrystallizations, and is presumably some unknown iron-containing compound or possibly the rare fulvalene.

7. Bis-cyclopentadienyl vanadium dichloride:

After it had been demonstrated that ferrocene could be made by use of cyclopentadienyl potassium, and after isolation of a small amount of bis-cyclopentadienyl vanadium dichloride from a Grignard reaction had been successful, two large batches of the vanadium compound were prepared by the cyclopentadienyl potassium method.

To an ice-cold slurry of cyclopentadienyl potassium, prepared in a standard Grignard apparatus from 7.1 g (0.181 mol) potassium and 15.6 g cyclopentadiene in 350 ml anhydrous benzene was added dropwise and with rapid stirring a solution of 17.5 g (0.091 mol) VCl_4 in 50 ml dry benzene. Much heat was evolved and the mixture was rapidly colored black. Thinning of the slurry was observed. The addition of VCl_4 was made over a two hour period. Plugging of the dropping funnel with a solid benzene- VCl_4 adduct necessitated frequent rodding of the funnel stem with a thin, stiff wire. At the end of the addition, more benzene was added to wash precipitates in the dropping funnel into the flask. The mixture was let stand overnight at room temperature. Filtration produced a black benzene liquor, which was discarded, and a light green filter cake. The filter cake was dried in a vacuum desiccator and extracted with chloroform in a Soxhlet extractor. About half of the product charred to a black, leafy cake while drying in a leaky desiccator overnight. It has since been found that this can be prevented by adding methanol to the mixture before filtration. This decomposes unreacted pyrophoric materials and does not harm the product appreciably.

Soxhlet extraction of the cake gave a black to brownish extract at

first, due to impurities. After most of these impurities had been extracted, the color of the eluted solution was a very pale green. Operation of the extractor was continued until this color disappeared in the eluent. This required approximately 48 hours of operation. The still pot was occasionally removed and its contents filtered, since a heavy, green precipitate of bis-cyclopentadienyl vanadium dichloride in the still pot had a tendency to char and decompose. 8.2 g of crude product was recovered, representing 36 percent yield. A second batch showed 29 percent yield.

The crude product from these two preparations was combined and extracted again. This process removed some, but not all, of the dark impurities. Further purification was made by precipitation from a chloroform-ether solvent. The purified substance was light green and burned with a sooty flame. It decomposed on a hot plate at temperatures greater than 230 °C. At temperatures greater than 250 °C the substance spontaneously ignited. A sample in an evacuated capillary turned light brown, but did not melt or ignite below 300 °C.

Conclusive identification was attempted by chloride analyses, but the technique used (warm nitric acid digestion of a water solution of the compound in presence of silver nitrate) gave low analyses because of incomplete hydrolysis. Two analyses showed that the substance contained 21.1 and 25.2 percent chlorine by weight, whereas the theoretical figure was 28.1 percent by weight. Identity was established by solubility of the substance in tetrahydrofuran, ethyl acetate, ethanol, and chloroform, and insolubility in ligroin and benzene, together with subsequent react-

ion of the substance in an expected manner with phenyl lithium.

8. Attempted metalation of fluorene (potassium method):

In a standard Grignard apparatus were placed 3.3 g potassium, 100 ml dry benzene, and 14.0 g fluorene. The mixture was refluxed with stirring for 12 hours, but produced no fluorenyl potassium. No precipitate had formed, and no reaction occurred upon addition of water to the solution.

9. Attempted preparation of bis-fluorenyl iron (Grignard method):

In a standard Grignard apparatus, 15.8 g fluorene was added to a solution of n-propyl magnesium chloride prepared from 7.5 g (0.0951 mol) n-propyl chloride, 2.3 g (0.0951 mol) Mg, and 50 ml ether. Addition of the fluorene produced a small amount of heat. The mixture was allowed to stand 20 hours. At the end of this time an ethereal solution of FeCl_3 containing 0.03 mol FeCl_3 was added dropwise and with stirring. Heat was evolved and boiling of the ether occurred. The mixture was let stand overnight and then filtered. The residue was extracted in a Soxhlet extractor with benzene, but produced only black, dirty solutions from which nothing could be isolated. Considerable unreacted fluorene remained at the end of the experiment.

10. Attempted preparation of bis-fluorenyl vanadium dichloride:

In the usual nitrogen filled apparatus a solution of n-butyl lithium was made in this manner: To 100 ml dry ether was added 2.9 g (0.418 mol) Li which had been quickly weighed, hammered flat in air, and cut into strips with heavy shears. n-Butyl chloride (19.4 g, 0.209 mol) was added dropwise with stirring. After two hours some metal remained unreacted,

and 5 g more n-butyl chloride was added. The solution was let stand overnight, at the end of which time some Li still remained. Solid fluorene was added (34.8 g, 0.209 mol) through the condenser and flushed into the flask with 50 ml ether. A vigorous reaction took place, in which the solution refluxed well and turned canary yellow. The solution was refluxed for 6 hours over a steam bath. A distilling arm was attached to the condenser socket and the ether removed and replaced with benzene (50 ml). The slurry was now a deep brownish orange color. The flask was chilled in an ice bath and 15.1 g (0.0784 mol) VCl_4 in 35 ml benzene was added over 30 minutes. The solution was allowed to warm, let stand overnight, and filtered. The filter residue was extracted with benzene in a Soxhlet extractor for 24 hours. The first eluents were the customary black or brown, followed by lighter shades until a clear solution was finally obtained. Upon standing for another day, the filter cup developed a light green color.

The reaction flask itself contained a dry residue which was a bright purple. Not much of this was observed and attempted isolation failed.

11. Reaction of fluorenyl lithium with VCl_4 in tetrahydrofuran:

After a preliminary experiment indicated that fluorene would react easily with lithium in boiling tetrahydrofuran solution, it was decided to attempt a new preparation of bis-fluorenyl vanadium dichloride.

The standard nitrogen filled apparatus was used. Lithium metal (1.5 g, 0.209 mol) was cut into small pieces and placed in 100 ml tetrahydrofuran containing 34.8 g (0.209 mol) fluorene. No reaction occurred in the cold. On heating over a steam bath, the lithium became coated with a soluble

green coating. The solution became brown and foamed strongly. When the initial vigorous reaction had ceased, the solution had turned deep red. Refluxing was continued for 3 hours with intermittent stirring.

To this solution, chilled with an ice bath, was added 0.1045 mol (11 ml) VOCl_4 . This halide was not diluted with tetrahydrofuran, since a precipitate forms. Each drop landed explosively, causing formation of a dense red smoke. The addition was carried out over one hour, with stirring. During addition the solution became dark and eventually black. The mixture was let stand at room temperature overnight and allowed to complete its reaction. Filtration in the morning produced a black liquor and a black precipitate. The liquor was evaporated under vacuum, leaving a black, gummy residue. This residue was extracted with ether, giving a black residue and a yellowish ether solution. Addition of methanol to the ether solution precipitated a yellowish-pink solid. This was reprecipitated twice more from ether-methanol and the purified material was found to melt at 246-247 °C. It was thus identified as di-fluorenyl, which has a literature melting point of 246 °C. No other compound was isolated from the reaction.

12. Reaction of VOCl_3 with phenyl magnesium bromide:

This reaction was observed by Vernon (32) and was duplicated in the course of this work to gain familiarity with experimental methods. The substance obtained was identical in properties with that described by Vernon.

In a standard Grignard apparatus a solution of phenyl magnesium bromide was prepared from 9.8 g (0.0623 mol) bromobenzene, 1.5 g (0.0623

mol) Mg, and 50 ml dry ether. The ethereal solution was filtered through a glass wool plug and 0.031 mol VOCl_3 was added to the filtrate. Each drop landed explosively, forming a black precipitate immediately. Upon hydrolysis with cold water, a small amount of grayish-green precipitate settled. This precipitate was insoluble in all solvents and darkened rapidly on exposure to air or when heated under nitrogen. A small amount of biphenyl was isolated and characterized by its melting point and odor.

13. Reaction of VOCl_3 with n-butyl magnesium bromide:

In a standard Grignard apparatus a solution of n-BuMgBr was made from 5.9 g (0.0428 mol) n-BuBr, 1.04 g (0.0428 mol) Mg, and 30 cc dry n-butyl ether. This Grignard reagent was cooled in an ice bath and 1.08 g (0.00622 mol VOCl_3) added dropwise with rapid stirring. A bright green precipitate formed immediately, together with a dark gray or black precipitate. Isolation was attempted, but the compound turned gray upon vacuum removal of the ether in the cold. The compound was insoluble in all solvents tried. It remained stable when refrigerated under ether over a period of a few months. No analyses were attempted, since the compound could not be purified.

14. Di-ethyl succinate:

This ester was prepared by refluxing gently for 12 hours a mixture of 60 g (1.30 mol) ethanol, 2.0 ml conc. H_2SO_4 , and 35.3 g (0.299 mol) succinic acid. A second batch was prepared by refluxing for 5.5 hours a mixture of 41.5 g (0.351 mol) succinic acid, 100 ml ethanol, and 4 ml conc. H_2SO_4 . The two mixtures were then combined and solid Na_2CO_3 was added until bubbling ceased. After cooling and filtering to remove solid

Na_2SO_4 , the filtrate was vacuum distilled until the ethanol and water had been removed. At this point some succinic acid precipitated. The solution was washed in a separatory funnel with dilute NaOH twice, then twice with water. The ester was dried with CaCl_2 chips and vacuum distilled. The clear, colorless product boiled at 130-132 °C/60 mm Hg. A total of 55.9 g was prepared.

15. Attempted preparation of ethyl hydrogen succinate by trans-esterification:

The method used here is from that of Swann, Oehler, and Buswell (30).

A mixture of 20 ml n-butyl ether, 55.9 g (0.320 mol) diethyl succinate, 65.2 g (0.552 mol) succinic acid, and 8 ml conc. HCl was refluxed gently for 2 hours. 95 percent ethanol (11 ml) was added and reflux was continued 5 hours more. Vacuum distillation at 16 mm Hg removed water, ethanol, and n-butyl ether, all below 90 °C. The solution was then chilled and filtered to remove precipitated succinic acid. The di-ethyl ester distilled at 112-135 °C (72.4 g) and a little succinic anhydride came over and solidified in the condenser. None of the desired mono-ester was obtained.

16. Succinic anhydride (6):

To 59.0 g (0.500 mol) succinic acid in a reflux flask fitted with ground glass condenser and CaCl_2 drying tube was added 117.8 g (1.500 mol) acetyl chloride. The material was refluxed very gently for 4 hours, at which time the last of the solid had dissolved. The solution was allowed to cool, whereupon the anhydride precipitated as large white crystals. The precipitate was filtered, washed with ether, dried, and weighed. The

final yield was 47.5 g, or 95 percent of theoretical yield.

17. Ethyl hydrogen succinate (3):

In a 500 ml flask fitted with condenser and CaCl_2 drying tube were placed 46.5 g (0.430 mol) succinic anhydride, and 39.6 g (0.860 mol) absolute ethanol. After 70 minutes the solid had dissolved under reflux. Reflux was continued 10 minutes longer and the mixture distilled under vacuum. After removal of a large fore-run of ethanol, 63.0 g of the mono-ester was collected at 137-144 °C and 11-12 mm Hg. The odorless, colorless liquid had a refractive index of $n_D^{26} = 1.423$. Literature values (40) are $n_D^{20} = 1.433$ and b.p. 138.5-140 °C at 10 mm Hg. A 98 percent yield was obtained.

18. Succinic acid-ethyl ester-chloride (25):

In a 500 ml flask fitted with reflux condenser and CaCl_2 drying tube were placed 63.0 g (0.431 mol) mono-ethyl succinate and 71.8 g (0.604 mol) thionyl chloride in one rapid addition. No reaction occurred in the cold. On heating briefly with a small flame, reaction began with evolution of gasses. After the initial reaction subsided, steam heat was applied for one hour. The solution was then vacuum distilled, whereupon the thionyl chloride gassified and was removed. At 87-91 °C/9-10 mm, 59.6 g of ethyl succinic acid chloride (84 percent of theory) was recovered. The product was clear and colorless. The literature value of b.p. 92 °C/20 mm is believed to be in error (38), since a subsequent reaction using this compound sufficiently identified it (see following preparation).

19. Ethyl β -benzoyl propionate (5, 24, 25):

A Friedel-Crafts reaction was used as the method of synthesis. In

a standard Grignard apparatus, modified to include a solids funnel in place of the dropping funnel, were placed 175 ml dry benzene and 59.6 g (0.363 mol) ethyl succinic acid chloride. A bottle of anhydrous AlCl_3 was connected to the flask by a short length of large diameter rubber tubing, and its contents added gradually and with stirring to the ice-chilled flask. The addition took one hour and was accompanied by heat. The mixture was warmed to room temperature and then refluxed 3 hours with stirring. After standing at room temperature an additional 5 hours, the mixture was poured into 1:1 HCl and snow. A yellowish solid was filtered off and a small amount was recrystallized from water. The recrystallized material had the odor of an aromatic acid or ester, and melted at 114-115 °C. Since this agreed with the literature melting point (116 °C) of the free acid (25), it was evident that hydrolysis had occurred during decomposition of the reaction mixture. The residue was heated under vacuum to remove traces of water. Five ml conc. HCl and 100 ml absolute ethanol were added and the mixture refluxed 11 hours. Vacuum distillation gave a large forerun of HCl, ethanol, and water, and at 162-164 °C and 9-10 mm Hg a total of 46.2 g, or 61.8 percent of theory, of ethyl, β -benzoyl propionate was recovered. This had a red color from dissolved free acid and was impure, but was not further purified for the next reaction.

20. 1-4 diphenyl-1-3-cyclopentadiene (5):

Dry sodium ethoxide was prepared from 10.4 g sodium wire and 27.0 g absolute ethanol in 100 ml dry benzene. The solvents were then removed by vacuum distillation. To the solid ethoxide was added 250 ml dry ben-

zene and 46.2 g (0.224 mol) ethyl, β -benzoyl propionate, and the mixture was shaken until the NaOEt had nearly all dissolved (about 20 minutes). Acetophenone (26.9 g, 0.224 mol) was added and the mixture let stand with occasional shaking at 40 °C for 24 hours. The mixture was cooled and poured into a separatory funnel containing 1500 ml ice water. This was shaken well and the benzene layer allowed to separate. The aqueous layer was removed and heated to 60 °C over a steam bath, at which temperature a heavy white solid precipitated. The flask was let stand until cool and then filtered. A small amount of the yellowish-tan product was recrystallized from benzene-petroleum ether and melted at 156.5-157 °C. A yield of 10.1 g, or 20.7 percent of theoretical, was obtained. The literature m.p. is 158-158.5 °C (18).

21. Attempted preparation of bis-1,3-diphenyl-cyclopentadienyl vanadium dichloride:

In a standard Grignard apparatus a solution of ethyl magnesium chloride was prepared from 1.1 g (0.046 mol) Mg, 6.0 g (0.0916 mol) ethyl chloride, and 30 ml dry ether. 1-4 diphenyl-1,3-cyclopentadiene (10.0 g, 0.046 mol) was added at once. Since it was insoluble in the amount of ether present, 50 ml benzene were added and the mixture refluxed over steam for one hour. A gas was evolved, noted by the inflation of a balloon attached to the condenser. At the end of the refluxing, nearly all the solid had dissolved. The mixture was cooled with an ice bath and 4.4 g (0.0229 mol) VCl_4 in 30 ml benzene added dropwise with stirring over a half hour. The solution became black in color. After allowing the mixture to stand 12 hours, filtration yielded a black filter cake and a very dark

greenish-black liquor. Addition of ligroin to the filtrate yielded only a black precipitate of inorganic compounds.

The filter cake was dried in a vacuum desiccator, followed by chloroform extraction in a Soxhlet extractor. The chloroform became dark brown and foamed. A Soxhlet extraction on another sample with petroleum ether gave a similar solution which deposited a brownish sludge on standing. The expected compound was not isolated.

22. Attempted cyclization of acetonylacetone:

A very dilute solution of 28.5 g acetonylacetone in 2500 ml of water was heated to boiling, and 50 g NaOH pellets added slowly. The solution turned milky and precipitated a white solid almost immediately. Continued boiling caused formation of a deep red color, but did not destroy the white solid. Extraction of the cold solution with ether yielded only high boiling oils (200-300 °C) and none of the desired cyclic compound. (The literature b.p. for 1-methyl cyclopent-1-ene-3-one is 157-158 °C (18).)

This cyclization was attempted in several other manners, using very weak base, cold solutions, acidified reaction mixtures, and longer times of reflux, but the same result occurred in all cases. The nature of the white solid obtained is unknown.

23. Cyclopentadienyl, β -carboxypropionylcyclopentadienyl iron:

A Friedel-Crafts synthesis of this acid was made as follows: A well mixed powder of 13.7 g (0.0737 mol) ferrocene and 7.4 g (0.0737 mol) succinic anhydride was placed in a standard Grignard apparatus. AlCl_3 (21.6 g, 0.1621 mol) was added, and the flask was chilled with ice. CS_2 (100 ml, reagent grade) was added slowly and with stirring. No reaction

took place in the cold. Upon warming the flask to reflux temperature, a dark purplish, gummy precipitate formed almost immediately, stopping the stirrer. The mixture was refluxed 6 hours and the CS₂ solution decanted and saved. Later, 1.2 g ferrocene was steam distilled from this portion after evaporation of the CS₂.

A 1:1 solution of HCl was mixed with snow and added slowly to the flask. Little reaction occurred cold, but gentle heating with steam, combined with slow stirring, produced a vigorous reaction. When the hydrolysis was complete, the mixture was filtered and the filtrate discarded. The residue was returned to the flask and digested with 100 ml of hot 10 percent Na₂CO₃ solution. The mixture was filtered, the filtrate boiled with a little decolorizing carbon and again filtered, and the filtrate acidified with conc. HCl. A small amount of black tar rose to the surface during acidification and was filtered off before the end-point of the acidification. The brownish precipitate was recrystallized three times from hot water (accompanied by much loss of product) and finally produced 2.0 g of light orange acid, m.p. 155 °C.

A sample of this material (0.2838 g) was titrated with 0.03085 N KOH, using phenolphthalein, in 150 ml hot water. The volume of base used was 10.0 ml, compared with 9.24 ml required for the anticipated mono-acid, and 13.7 ml required for the possible dibasic acid.

Because of a poor end-point (the color of the material obscures the phenolphthalein color change) it is likely that the titration was over-shot. It therefore seems reasonable to conclude that this substance was the expected cyclopentadienyl, β -carboxypropionylcyclopentadienyl iron.

A later preparation gave an 18.4 percent yield. Low yields can be attributed to poor mixing of the reactants in CS_2 after the precipitation of the initial gummy mass.

24. Bis- β -carboxypropionylcyclopentadienyl iron:

In the usual apparatus, chilled with an ice bath, were placed 14.7 g (0.079 mol) ferrocene and 16.1 g (0.161 mol) succinic anhydride. AlCl_3 (46.4 g, 0.348 mol) was added, and 60 ml cold CS_2 were added slowly. No reaction occurred in the cold. Warming to reflux temperature precipitated a black gummy cake which stalled the stirrer. Refluxing was continued for 16 hours, after which time the solvent was decanted. The residue was hydrolyzed with 1:1 HCl mixed with snow. The mixture was filtered and the filtrate discarded. The residue was dissolved in 10 percent Na_2CO_3 , boiled, filtered, acidified with conc. HCl, and filtered. Recrystallization from hot water gave a small yield of bright red-orange crystals melting at 187.5-188.5 °C.

The substance was identified by titration of a 0.2468 g sample with 0.03085 N KOH and phenolphthalein in hot water (150 ml). The end-point was poor. 12.0 ml of base were required to neutralize the acid, compared with 12.08 ml calculated for the di-acid and 8.04 ml calculated for the mono-acid. The substance was thus identified as bis- β -carboxypropionylcyclopentadienyl iron. By analogy with a similar reaction reported in the literature (38), it is inferred that the acid groups are on different rings.

25. Attempted cross-ring acylation of cyclopentadienyl, β -carboxypropionylcyclopentadienyl iron:

In a 125 ml flask was placed 1.9 g (0.00664 mol) cyclopentadienyl, β -carboxypropionylcyclopentadienyl iron. A very liberal excess of SOCl_2 , 6 ml, was added dropwise. It dissolved the solid acid easily, turning to a purplish-black solution. Vigorous bubbling ensued for 20 minutes. Excess SOCl_2 was removed under vacuum and the substance heated to ensure dryness. A black amorphous residue remained in the flask, of about the same general bulk as the original mono-acid. Upon cooling, 4.0 g AlCl_3 and 20 ml CS_2 were added and a condenser attached to the flask. No apparent reaction took place and the solvent was replaced with nitrobenzene 2 hours later, which caused a vigorous exothermic reaction. The black solid dissolved. The mixture was decomposed with 1:1 HCl and snow after overnight standing. An insoluble black substance precipitated which was found to be mostly inorganic. A good test for iron was obtained on this residue with acidic KCNS solution. It is believed that the nitrobenzene oxidized the ferrocene during the course of the reaction.

26. Attempted dehydration of cyclopentadienyl, β -carboxypropionylcyclopentadienyl iron with polyphosphoric acid:

Polyphosphoric acid was prepared (17) by dissolving 6.2 g P_2O_5 in 4 ml of 85 percent orthophosphoric acid over 2 hours at 80-90 °C. At the end of this time, undissolved phosphoric anhydride was ignored and cyclopentadienyl, β -carboxypropionylcyclopentadienyl iron (0.2 g) was added in small portions. A purplish-black solution resulted. This was kept at 80-90 °C for two hours and then cooled and poured over cracked ice. When the ice had all melted, the solution was extracted with ether, washed with water, then with Na_2CO_3 solution. The ether extract was dried and evap-

orated, but left only a faint yellow gum. The Na_2CO_3 extract, deep black in color, was acidified, yielding a black solid which was insoluble in organic solvents, acids, and hot water. The material could be dissolved in Na_2CO_3 and re-precipitated with acid, however. It burned in air, giving flashes of flame, but did not melt below 300°C and was not observed to melt before burning on a spatula. The substance was decomposed in hot nitric acid, diluted with water, and tested with KCNS solution. A red color developed, indicating the presence of iron. The nature of the substance is unknown.

27. Reaction of phenyl lithium with bis-cyclopentadienyl vanadium dichloride:

A solution of phenyl lithium was prepared from 0.0540 mol (8.5 g) bromobenzene, 0.75 g Li (0.108 mol), and 60 ml dry ether in a standard Grignard apparatus. The solution was refluxed 1 hour after the initial reaction had ceased, then allowed to cool for two hours. The solution was decanted into a separatory funnel placed in an identical apparatus containing 125 ml dry ether and 6.8 g (0.0270 mol) bis-cyclopentadienyl vanadium dichloride, which dissolved in ether only very slightly. The phenyl lithium solution was added dropwise with stirring over 1 hour. The solution turned from light green to a dark red-black-green color. No heating of the mixture occurred.

After allowing the mixture to stand for 4 hours, the mixture was filtered and the solvent evaporated. A dull red-brown solid coated the interior of the reaction flask when it dried in air. The dry residue after evaporation of solvent was dissolved in absolute ethanol and filt-

ered. Water was added to the ethanol and the solution chilled, whereupon a dark red-brown precipitate formed which decomposed by spontaneous ignition above 139 °C. By analogy with the diphenyl bis-cyclopentadienyl titanium prepared by Summers and Uloth (29), it is believed that this compound is diphenyl, bis-cyclopentadienyl vanadium.

It was later observed that addition of the vanadium compound to the phenyl lithium solution did not produce this compound. An excess of the vanadium compound is apparently necessary during the reaction.

28. Attempted reaction of ferrocene and succinic anhydride in nitrobenzene:

In a standard apparatus were placed 14.7 g (0.0790 mol) ferrocene and 23.2 g (0.174 mol) dry AlCl_3 . A few drops of nitrobenzene were cautiously added by means of the dropping funnel. This caused an immediate violent reaction which filled the flask with smoke and caused the flask to become quite hot. The flask was then chilled to the temperature of a snow-acetone bath (about -20 °C) and nitrobenzene again cautiously added. When about 20 cc had been added, a near explosion occurred, blowing the dropping funnel from the flask. Examination of the flask later showed that finely divided carbon was profusely distributed inside the flask. The method was abandoned, and is mentioned here only because of its hazardous nature.

DISCUSSION OF EXPERIMENTAL RESULTS AND CONCLUSIONS

Of the numerous experiments which did not yield results, little can be said, except "they should have worked". Attempted preparations of all kinds belong in this class, including Grignard reactions with VOCl_3 , attempts to form bis-fluorenyl compounds, and the long-drawn struggle to synthesize bis-1,3-diphenylcyclopentadienyl vanadium dichloride. It must be stated that these failures do not preclude the existence of, or the possibility of preparing, these compounds; they only mean that methods of isolation failed to find them. From the unique colors formed in some of the reactions, it is believed that the desired substances were formed, but not isolated.

The Friedel-Crafts reactions of ferrocene with succinic anhydride are regarded as being eminently successful, even though they do little toward advancing the knowledge of the substance. They do illustrate, however, that simple variance of the mol ratio of succinic anhydride to ferrocene will produce the required mono- or di-acid. Since these compounds have not yet been reported in the literature, their physical and chemical character as reported here may be regarded as new work.

The new, unidentified substance that has been prepared in the attempted cyclic dehydration of cyclopentadienyl, β -carboxypropionyl-cyclopentadienyl iron did not have the neutral character expected for the desired bridged-ring ferrocene, but was instead acidic. It is likely that the substance is an intermolecular dehydration product, perhaps of the following structure:

is stable to heat and oxygen, while the precipitate found was not.

The remaining successful experiment, that in which phenyl lithium was reacted with bis-cyclopentadienyl vanadium dichloride to form a red compound of unknown composition, was prompted by the work of Summers and Uloth (29), and by the reported formation of a picrate of bis-cyclopentadienyl vanadium dichloride by Wilkinson (36). The compound formed in this research is believed to be diphenyl, bis-cyclopentadienyl vanadium, which is analogous to the diphenyl, bis-cyclopentadienyl titanium prepared by Summers and Uloth. An insufficient amount of the compound was prepared to analyze; therefore, its identity must remain in doubt.

S U M M A R Y

1. A green crystalline substance has been observed in a reaction between n-butyl magnesium bromide and VOCl_3 . The substance was insoluble in all solvents tried and decomposed upon attempted isolation.
2. Friedel-Crafts methods have produced cyclopentadienyl, β -carboxypropionylcyclopentadienyl iron and bis- β -carboxypropionylcyclopentadienyl iron from 1:1 and 2:1 mol ratios of succinic anhydride and ferrocene, respectively. The first acid was light orange and melted at 155°C . The second acid was red-orange and melted at $187.5\text{--}188.5^\circ\text{C}$.
3. Attempted cyclization of cyclopentadienyl, β -carboxypropionylcyclopentadienyl iron with polyphosphoric acid has resulted in the formation of a black, acidic solid which was organic, contained iron, and did not melt below 300°C or before ignition.
4. A dark red-brown compound has been prepared from phenyl lithium and bis-cyclopentadienyl vanadium dichloride. The substance decomposed in air above 139°C . The substance was believed to be di-phenyl bis-cyclopentadienyl vanadium.

L I T E R A T U R E C I T E D

1. R. Benkeser, D. Goggin, and G. Schroll, J. Am. Chem. Soc., 76
4025 (1954).
2. Briscoe and Little, J. C. S., 105, 1310 (1914).
3. Cason, J. Am. Chem. Soc., 64, 1106 (1942).
4. G. Dauben and H. Tilles, J. Org. Chem., 15, 785 (1950).
5. N. Drake and J. Adams, Jr., J. Am. Chem. Soc., 61, 1326 (1939).
6. L. Fieser and E. Martin, Organic Syntheses, Vol. XV, 93, Wiley
and Sons, Inc., New York (1935).
7. E. O. Fischer and W. Hafner, Z. Naturforsch., 8b, 444 (1953).
8. E. O. Fischer and W. Hafner, Z. Naturforsch., 9b, 503 (1954).
9. E. O. Fischer and R. Jira, Z. Naturforsch., 8b, 217 (1953).
10. E. O. Fischer and R. Jira, Z. Naturforsch., 9b, 618 (1954).
11. E. O. Fischer and D. Seus, Z. Naturforsch., 8b, 694 (1953).
12. E. O. Fischer, D. Seus, and R. Jira, Z. Naturforsch., 8b, 692 (1953).
13. L. Friedman, A. Irsa, and G. Wilkinson, J. Am. Chem. Soc., 77, 3689
(1955).
14. Gilman, Beel, Brannen, Bullock, Dunn, and Miller, J. Am. Chem. Soc.,
71, 1499 (1949).
15. H. Gilman, W. Langham, and F. Moore, J. Am. Chem. Soc., 62, 2327 (1940).
16. H. Gilman, E. Zoellner, and J. Dickey, J. Am. Chem. Soc., 51, 1576
(1929).
17. R. Gilmore, Jr., J. Am. Chem. Soc., 73, 5879 (1951).
18. M. Godchot and F. Taboury, Compt. Rend., 156, 1779 (1913).
19. H. Hunsdiecker, Ber., 75, 455 (1942).

20. J. Kealy and P. Paulson, *Nature*, 168, 1039 (1951).
21. J. W. Mellor, Inorganic and Theoretical Chemistry, Vol. IX, 714-836, Longmans, Green, and Co., New York, (1929).
22. E. Mertes, Bachelor's Thesis, Colo. School of Mines, Golden (1912).
23. S. Miller, J. Tebboth, and J. Tremaine, *J. C. S.*, 632 (1952).
24. C. Noller and R. Adams, *J. Am. Chem. Soc.*, 46, 1889 (1924).
25. D. Papa, E. Schwenk, and H. Hankin, *J. Am. Chem. Soc.*, 69, 3018 (1947).
26. Pauson, *J. Am. Chem. Soc.*, 76, 2187 (1954).
27. P. Pauson and G. Wilkinson, *J. Am. Chem. Soc.*, 76, 2024 (1954).
28. C. Shomate, *J. Am. Chem. Soc.*, 69, 220 (1947).
29. L. Summers and R. Uloth, *J. Am. Chem. Soc.*, 77, 3604 (1955).
30. S. Swann, Jr., R. Oehler, and R. Buswell, Organic Syntheses, Vol. XIX, 45, Wiley and Sons, Inc., New York (1939).
31. J. Thiele, *Ber.*, 34, 68 (1901).
32. C. Vernon, *J. Am. Chem. Soc.*, 53, 3831 (1931).
33. E. Wagner and W. Hunt, *J. Chem. Ed.*, 28, 309 (1951).
34. A Whittaker and D. Yost, *J. C. P.*, 17, 188 (1949).
35. G. Wilkinson and J. Birmingham, *J. Am. Chem. Soc.*, 76, 6210 (1954).
36. G. Wilkinson, P. Pauson, J. Birmingham, and F. Cotton, *J. Am. Chem. Soc.*, 75, 1011 (1953).
37. R. Woodward, M. Rosenblum, and M. Whiting, *J. Am. Chem. Soc.*, 74, 3458 (1952).
38. _____, Beilstein's Handbuch der Organischen Chemie, 4th Ed., Vol. II, 613, Julius Springer, Berlin (1920).

39. _____, Beilstein's Handbuch der Organischen Chemie, 4th Ed.,
Vol. V, 748, Julius Springer, Berlin (1922).
40. _____, Beilstein's Handbuch der Organischen Chemie, 4th Ed.,
1st Supplement, Vol. II, 263, Julius Springer, Berlin (1929).

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