



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
© Copyright by Norman J Birkholz (1957)

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.

197

BIS - CYCLOPENTADIENYL COMPOUNDS
OF
IRON AND VANADIUM

by

NORMAN J. BIRKHOLO

A THESIS

Submitted to the Graduate Committee

in

partial fulfillment of the requirements

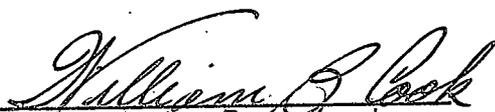
for the degree of

Master of Science in Chemistry

at

Montana State College

Approved:


Head of Major Department


Chairman of Examining Committee


Dean of the Graduate Division

Bozeman, Montana
October, 1957

N378
B 535 b
cop. 2

1198^c

- 2 -

T A B L E O F C O N T E N T S

ABSTRACT	4
OBJECTIVES	5
INTRODUCTION	6
LITERATURE SURVEY	7
THEORETICAL DISCUSSION	15
EXPERIMENTAL	19
A. INORGANIC REAGENTS	19
1. Preparation of VOCl_3	19
2. Preparation of VCl_4	20
3. Preparation of anhydrous FeCl_3	21
B. ORGANIC REAGENTS AND COMPOUNDS	22
1. Cyclopentadiene	22
2. Grignard reagents	22
3. Attempted preparation of cyclopentadienyl sodium	23
4. Cyclopentadienyl potassium	23
5. Ferrocene (Grignard method)	24
6. Ferrocene (cyclopentadienyl potassium method)	25
7. Bis-cyclopentadienyl vanadium dichloride	26
8. Attempted metalation of fluorene (potassium method)	28
9. Attempted preparation of bis-fluorenyl iron	28
10. Attempted preparation of bis-fluorenyl vanadium dichloride	28
11. Reaction of fluorenyl lithium with VCl_4	29
12. Reaction of VOCl_3 with phenyl magnesium bromide	30
13. Reaction of VOCl_3 with n-butyl magnesium bromide	31

124879

14. Di-ethyl succinate	31
15. Attempted preparation of ethyl hydrogen succinate by trans-esterification	32
16. Succinic anhydride	32
17. Ethyl hydrogen succinate	33
18. Succinic acid - ethyl ester - chloride	33
19. Ethyl β -benzoyl propionate	33
20. 1-4 diphenyl-1-3-cyclopentadiene	34
21. Attempted preparation of bis-1,3-diphenyl-cyclopentadienyl vanadium dichloride	35
22. Attempted cyclization of acetylacetone	36
23. Cyclopentadienyl, β -carboxypropionylcyclopentadienyl iron	36
24. Bis- β -carboxypropionylcyclopentadienyl iron	38
25. Attempted cross-ring acylation of cyclopentadienyl, β -carboxypropionylcyclopentadienyl iron	38
26. Attempted dehydration of cyclopentadienyl, β -carboxypropionylcyclopentadienyl iron with polyphosphoric acid	39
27. Reaction of phenyl lithium with bis-cyclopentadienyl vanadium dichloride	40
28. Attempted reaction of ferrocene and succinic anhydride in nitrobenzene	41
DISCUSSION OF EXPERIMENTAL RESULTS AND CONCLUSIONS	42
SUMMARY	45
LITERATURE CITED	46
ACKNOWLEDGEMENTS	49

A B S T R A C T

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. 187.5-188.5 °C, were prepared by reaction of AlCl_3 , ferrocene, and succinic anhydride.

Attempted cyclization of cyclopentadienyl, β -carboxypropionyl-cyclopentadienyl 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.

O B J E C T I V E S

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.

I N T R O D U C T I O N

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.

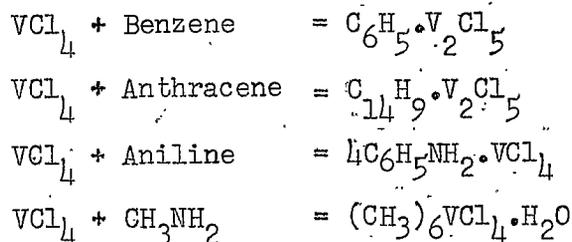
Since no substituted bis-cyclopentadienyl vanadium compounds had been prepared by other investigators, and since no one had yet investigated the possibility of creating bridged-ring ferrocenes, the major part of the work was directed toward their preparation.

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, $(C_5H_5)_2Fe$, 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 $(C_5H_5)_2Mn$ and $(C_5H_5)_2Mg$. Strong heating sublimed $(C_5H_5)_2Mn$. Above 160 °C, under CO pressure, $(CO)_3(C_5H_5)_2Mn$ 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 $(C_5H_5)_2VBr_2$, and pale green, stable, ligroin insoluble $(C_5H_5)_2VCl_2$. 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 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 $260^\circ C$.

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 $190^\circ C/2$ mm Hg, and decomposed above $210^\circ C$. These authors also prepared, by reaction of phenyl lithium with $(C_5H_5)_2TiCl_2$, a compound which was orange-yellow, soluble in ethanol, ether, and methylene chloride, and melting at $130-137^\circ C$. 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 $Mg(C_5H_5)_2$ and $V(C_5H_5)_2$ 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 $V(C_5H_5)_2$, which had a m.p. of $167-168^\circ C$ under nitrogen and was very soluble in oxygen free benzene, ether, and petroleum ether. Formation of $(C_5H_5)_2V(CO)_4$ 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 hypoiodite 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, $Fe(C_5H_5)_2^+$. 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.

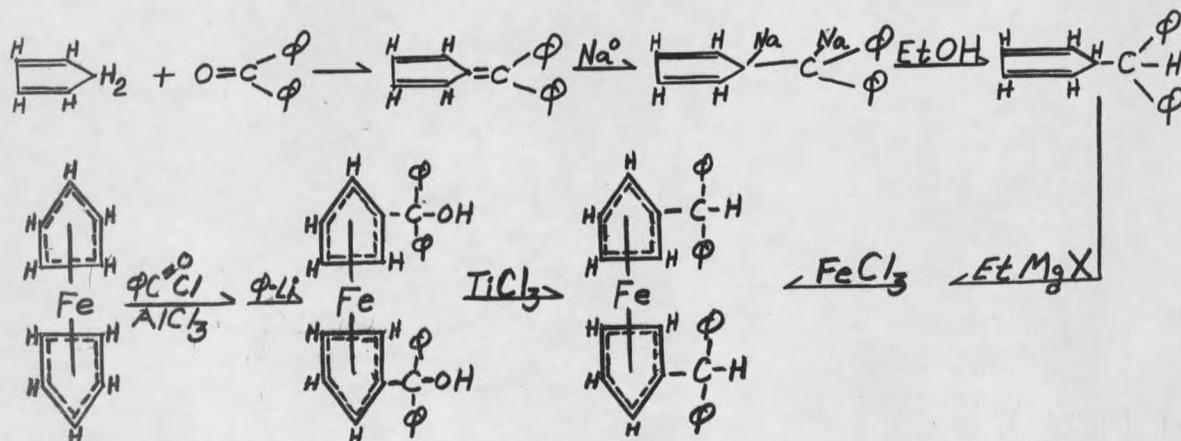
Acidity constants in 2:1 EtOH/H₂O for the ferrocene dicarboxylic acid they prepared were $pK_1 = 3.1 \times 10^{-7}$ and $pK_2 = 2.7 \times 10^{-8}$. These are comparable to the acidity constant of benzoic acid, $pK = 2.4 \times 10^{-7}$.

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-

enes 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. Triphenylsilyl ferrocene and bis-triphenylsilyl ferrocene were also prepared.

T H E O R E T I C A L D I S C U S S I O N

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:

