

ORGANOMETALLIC π -COMPLEXES XIV*. VINYLMETALLOCENES**

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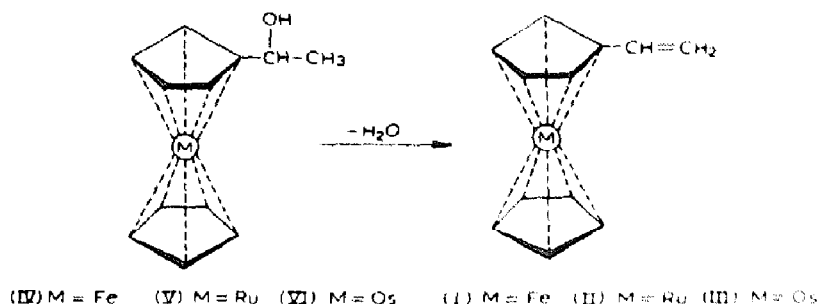
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INTRODUCTION

In conjunction with our program on metallocenylacetylenes¹, we had need for various vinylmetallocenes as intermediates. In the present paper, we wish to report a facile, high-yield route to five mono- and 1,1'-divinylmetallocenes, and to comment on their proton NMR spectra.

Vinylferrocene (I)²⁻⁶, vinylruthenocene (II)⁵ and vinylosmocene (III)⁵ have been previously reported in the literature; they are formed in variable yields by the dehydration of the corresponding carbinols (IV)–(VI), respectively. Early attempts^{3,7,8}



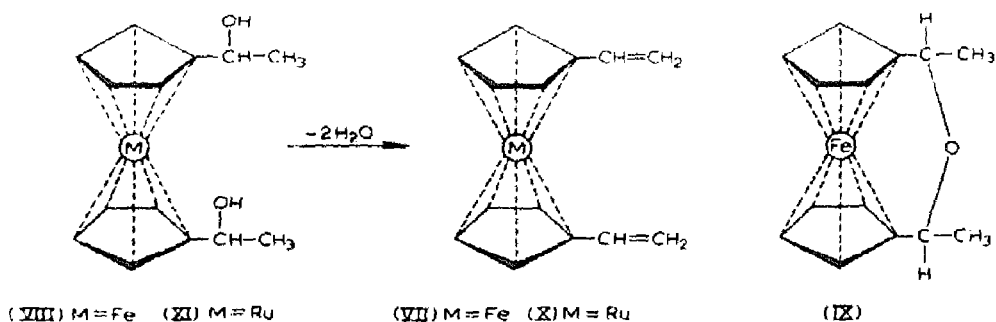
to obtain 1,1'-divinylferrocene (VII) by the dehydration of 1,1'-bis(1-hydroxyethyl)ferrocene (VIII) were largely unsuccessful, however, and the major product isolated was the cyclic ether, 1,1'-diethyl- α,α' -epoxyferrocene (IX). More recently, Michnick⁹ has been able to prepare (VII) in 43% yield by the dehydration of (VIII) under very carefully controlled conditions; (VIII) was dispersed on basic alumina and heated from 60 to 90 seconds at 200°.

RESULTS AND DISCUSSION

The facile route to vinylmetallocenes described herein represents a modification of the pyrolysis procedure of Arimoto and Haven² and of Fitzgerald⁶. The

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starting materials, 1-hydroxyethyl- or 1,1'-bis(1-hydroxyethyl)metallocenes, can be obtained in high yield by either lithium aluminum hydride or sodium borohydride reduction of the corresponding acetyl- or 1,1'-diacetylmetallocenes. The latter are readily obtained by Friedel-Crafts acetylation of the respective metallocene¹⁰. The dehydration is carried out in a vacuum sublimator containing a mixture of the appropriate carbinol and activated alumina by partial immersion in an oil bath at 135–180° (10–35 mm). Under these conditions, the vinylmetallocene sublimes readily onto the cold finger of the sublimator while the carbinol does not sublime. The sublimate obtained in this manner is of high purity and can be used directly in further reactions without the need for additional chromatography, resublimation or recrystallization of the product.

Table I summarizes a number of dehydration experiments carried out with

TABLE I

VINYLFERROCENE FROM SUBLIMATION PYROLYSIS OF 1-FERROCENYLETHANOL ON ALUMINA
Three g of alumina is used for each g of carbinol (IV).

Run	(II) (a)	Temperature (°C)	Press. (mm)	Time (hr)	(I) (g) and yield (%)
1	10.4	147	24	5	8.1 (85)
2	10.4	135	10	7	8.2 (86)
3	15.2	160	13	7	12.0 (86)
4	13.6	153	35	8	10.2 (81)
5	20.2	153	20	7	16.0 (86)
6	15.5	158	11	8	12.7 (89)

1-ferrocenylethanol (IV). The excellent yields of vinylferrocene (I) produced under a variety of specified temperature and pressure conditions illustrate the reliability of the method. Depending on the size of the sublimator available, the dehydration seems readily adaptable to large-scale preparations of (I); we have routinely made runs starting with 15–20 g of carbinol (IV). The optimum dehydration conditions for the synthesis of the other vinylmetallocenes (II), (III), (VII), (X) were not studied in detail, although the yields for the first three metallocenes were all appreciably higher than yields previously reported in the literature. 1,1'-Divinylruthenocene (X) has not previously been described, and its synthesis again demonstrates the utility of the method.

Some general comments regarding the oxidative stabilities of vinylmetallocenes may also be useful. High-purity vinylferrocene (I) and vinylruthenocene (II)

appear to be reasonably stable in the crystalline state in air. We have kept a sample of (I) in a closed bottle in air for a period of two years and have observed no change in either the melting point or the infrared spectrum of the sample. Deuteriochloroform solutions of (I) and (II), however, do undergo slight decomposition over a period of several hours. Vinylzirconocene (III), which was obtained as white crystals during the sublimation pyrolysis procedure, darkened considerably on standing in air for several days. A solution of (III) in deuteriochloroform solution also decomposed more rapidly than did similar solutions of (I) and (II). 1,1'-Divinylruthenocene (X) appears to be stable in the crystalline state in air, and only slightly unstable in deuteriochloroform solution. 1,1'-Divinylferrocene (VII), however, is the most air-sensitive vinylmetallocene we have yet studied, since it decomposes fairly rapidly in air in the crystalline state, and its solutions are exceedingly air-sensitive. Because of its limited stability, (VII) is best stored under nitrogen or *in vacuo*.

The proton NMR spectra of all five vinylmetallocenes synthesized in the present program have been recorded, and the results are summarized in Table 2.

TABLE 2

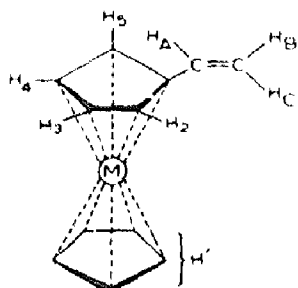
PROTON NMR SPECTRA OF SOME VINYLMETALLOCENES

Metalloocene ^a		Chemical shifts and multiplicity ^{a,b}					
		C ₅ H ₅ ring	H _{2,5}	H _{3,4}	H _A	H _B	H _C
Vinylferrocene	(I)	5.92(s)	5.66(t)	5.82(t)	3.51(q)	4.99(q)	4.69(q)
Vinylruthenocene	(II)	5.52(s)	5.26(t)	5.48(t)	3.66(q)	5.14(q)	4.76(q)
Vinylzirconocene	(III)	5.31(s)	5.08(t)	5.26(t)	3.69(q)	5.09(q)	4.80(q)
1,1'-Divinyl-ferrocene	(VII)		5.75(t)	5.85(t)	3.59(q)	4.93(q)	4.71(q)
1,1'-Divinyl-ruthenocene	(X)		5.30(t)	5.47(t)	3.83(q)	5.05(q)	4.84(q)

^a Determined in dilute solutions in CDCl₃, and τ given in ppm units (estimated accuracy ± 0.02 ppm).

^b s, singlet; t, triplet; q, quadruplet. ^c The proton resonances for ferrocene, ruthenocene and zirconocene under similar conditions occur at τ 5.86, 5.45 and 5.30, respectively.^{1,2}

The presence of a vinyl group in a given metallocene molecule is reflected by a deshielding of both the α (H_{2,5}) and the β (H_{3,4}) protons relative to the protons of the parent metallocene [for proton assignments, see structure (XII)]. The lower field



(XII)

triplet in each of the vinylmetallocene spectra is assigned to $H_{2,5}$ while the higher field triplet is assigned to $H_{3,4}$. Such assignments can be made conclusively on the basis of the proton NMR spectrum of 2,5-dideuteriovinylferrocene, which shows an absence of the lower field triplet when compared to the spectra of vinylferrocene itself¹¹. A similar result is observed in the proton NMR spectra of acylmetallocenes¹². In contrast to the latter, however, the singlets representing the five equivalent protons (H') of the unsubstituted cyclopentadienyl ring in the monovinylmetallocenes are slightly shielded compared to the corresponding protons in the parent metallocene. Similar divergent effects (*e.g.*, a deshielding of both $H_{2,5}$ and $H_{3,4}$ and a slight shielding of H') are also observed in the proton NMR spectra of phenylferrocene^{13,14} and bisferrocenyl^{15,16} in deuteriochloroform solution.

As in the acylmetallocene series examined earlier, *all* the corresponding cyclopentadienyl ring protons in the three monovinylmetallocenes exhibit a gradual deshielding proceeding from the ferrocene to the ruthenocene to the osmocene derivative; a similar trend is noted in the spectra of 1,1'-divinylferrocene and 1,1'-divinylruthenocene. There is a larger difference in chemical shift between the proton resonances of vinylferrocene and vinylruthenocene than between the latter and vinyl-osmocene, and this trend is also in excellent accord with earlier studies in similar series¹². These trends are conveniently illustrated by Figs. 1 and 2, in which the proton frequencies are given for vinylmetallocenes containing either iron, ruthenium or osmium central atoms.

The vinyl group in vinylmetallocenes possesses three magnetically non-equivalent nuclei and can be analyzed on the basis of an ABX type of grouping, in analogy

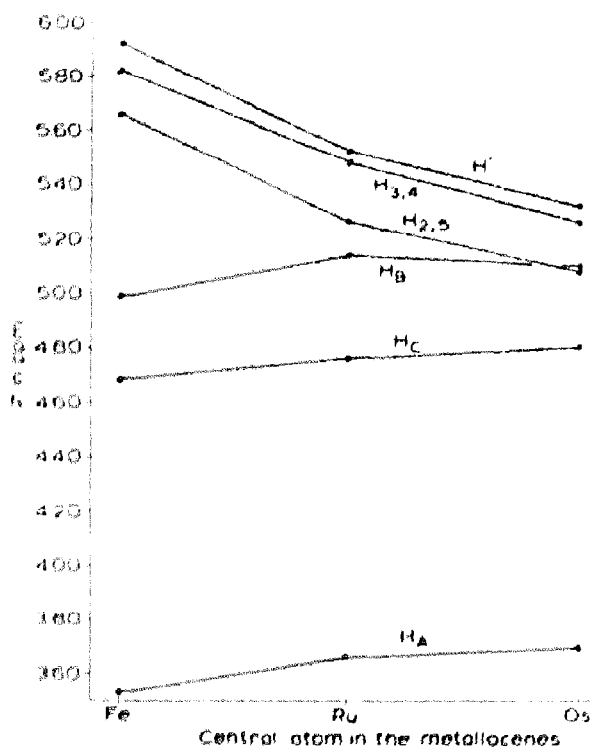


Fig. 1. Variation of the proton frequencies in the NMR spectra of monovinylmetallocenes.

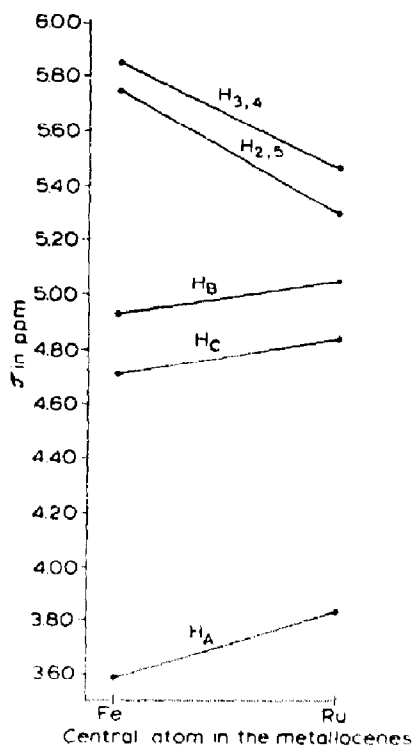


Fig. 2. Variation of the proton frequencies in the NMR spectra of 1,1'-divinylmetalocenes.

to the vinylic protons of styrene^{17,18}. Each of the vinylic protons appear as a quartet (doublet of doublets). The quartet at lowest field in each spectrum is assigned to H_A. H_A appears as a quartet since it is coupled to both of the neighboring protons H_B and H_C. The spacing in this quartet indicates that the coupling constants between H_A and H_B, and between H_A and H_C, are approximately 11 and 18 cps, respectively. H_B and H_C resonate at somewhat higher fields in each vinylmetalocene examined, and both appear as quartets due to coupling of each nuclei with H_A and with each other ($J(BC) = 2$ cps). Since the coupling constant between *trans* protons in vicinally substituted ethylenes is normally larger than between *cis* protons, the quartet at highest field in which $J = 11$ cps is assigned to H_B, while the middle quartet ($J = 18$ cps) represents H_C.

A comparison of the relative chemical shifts of vinylic protons as a function of the central metal atom is also of interest, especially when compared to similar correlations concerning acetyl-, ethyl- and benzylmetalocenes¹⁹. These relationships are likewise conveniently illustrated by Figs. 1 and 2. In agreement with our earlier studies, a *divergence* in the relative shielding of ring protons and side-chain protons is observed. *All* the vinylic protons (H_A, H_B, H_C) in monovinylmetalocenes experience substantially greater shielding in both ruthenium and osmium derivatives relative to the iron analog. In an analogous manner, *all* the vinylic protons in 1,1'-divinylruthenocene resonate at higher fields than do corresponding protons in 1,1'-divinylferrocene. The introduction of a second vinyl group results in a shielding of H_A and H_C as well as a deshielding of H_B. This effect is especially noticeable in the spectra of monovinyl- and 1,1'-divinylruthenocene. It is also of interest that the chemical shifts of all vinylic

protons in vinylmetallocenes fall at higher fields than do the chemical shifts of analogous protons in styrene*.

The striking variations in chemical shifts of both ring and exocyclic protons in a series of metallocenes in which only the central metal atom is changed may be related to a variety of factors. Such factors may include differences in the magnitude of induced ring currents (as the result of variations in the strength of ring-to-metal bonding), metal electronegativity differences, variations in diamagnetic anisotropy affects associated with the metal, etc. Mulay and Withstandley²⁰ have recently concluded on the basis of magnetic susceptibility studies on metallocenes that the ring π -electron density decreases in the series ferrocene, ruthenocene, and osmocene. Decreasing π -electron densities should normally lower the magnitude of any ring current effect on the chemical shifts of the cyclopentadienyl protons. On the basis of this effect alone, trends in the cyclopentadienyl resonances in a given series of iron-group metallocenes might be expected to fall in a reverse order (protons in osmium derivatives would resonate at higher fields, protons in ferrocene derivatives at lower fields). On the other hand, such a variation in the π -electron density of the cyclopentadienyl rings could also conceivably leave the ring with an increasing net partial positive charge proceeding from the iron to the ruthenium to the osmium derivatives**. Positive charge generally leads to a lower shielding of neighboring protons, and any differences in relative charge effects might be expected to have a very important effect on the chemical shifts of such protons. Electrostatic interaction between this charge and the electrons in the C-H bond would then result in a deshielding of the ring protons in the order observed, in analogy to studies on the cyclopentadienyl anion, benzene, and the tropylium cation^{21,22}. Such a factor, together with any variations in metal anisotropic effects, could overcompensate for proton chemical shift changes due to variations in ring currents, and may possibly account for the observed trends.

EXPERIMENTAL SECTION

The alumina used in this investigation was either Merck or CAMAG neutral grade and was activated in an oven at 200° for at least 24 h before using. Infrared spectra were obtained in CCl₄ solution on a Beckmann IR-10 spectrophotometer. Proton NMR spectra were obtained in CCl₃D solution on a Varian A-60 spectrometer. In several comparative spectra in which sample concentrations were varied from 5 to 10%, no effect due to dilution could be detected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Vinylferrocene (I)

1-Ferrocenylethanol² (9.9 g, 0.043 mole) and 30 g of activated alumina were

* We observe the following NMR spectral data for styrene in dilute deuteriochloroform solution: H_A(q), 2.48 τ ; H_B(q), 4.84 τ ; H_C(q), 4.34 τ ; J(AB) = 11 cps; J(AC) = 18 cps; J(BC) = 1 cps.

** Decreasing π -electron densities and concurrent increasing net charge effects on the cyclopentadienyl rings may also be related to the striking decrease in Friedel-Crafts reactivity of the iron-group metallocenes¹⁶, although comparisons should be more accurately made between analogous transition states in such substitution reactions.

intimately mixed and were placed in a large vacuum sublimator equipped with a water-cooled probe. The surface of the mixture was then covered with a small additional amount of alumina. The system was evacuated and partially submerged in an oil bath maintained at 155° (13 mm) for a period of 6 h. The bath was removed and the system was allowed to cool to room temperature. Air was then bled in very slowly in order to keep the product from dislodging from the cooling probe. The orange crystals of vinylferrocene removed from the probe amounted to 7.83 g (85%); m.p. 51–52.5°.

Other experiments involving the formation of (I) are summarized in Table 1.

Vinylruthenocene (II)

By a similar procedure, 100 mg (0.36 mmole) of 1-ruthenocenyloethanol⁵ and 3.0 g of alumina were heated at 180° (16 mm) for 6 h and afforded 83 mg (89%) of yellow crystals of vinylruthenocene, m.p. 53.5–54.5° (lit.⁵ 51–52°).

Vinylsoscene (III)

By a similar procedure, 121 mg (0.33 mmole) of 1-osmocenyloethanol⁵ and 1.5 g of alumina, heated at 175–180° (12 mm) for 8 h afforded 82 mg (72%) of white crystals of vinylsoscene, m.p. 69–70° (lit.⁵ 59–59.5°).

1,1'-Divinylferrocene (VII)

In a manner analogous to that described for vinylferrocene, 6.0 g (0.022 mole) of 1,1'-bis(1-hydroxyethyl)ferrocene (m.p. 69–70°)^{2,3} and 36 g of alumina were heated at 155° (13 mm) for 6 h. Red crystals of 1,1'-divinylferrocene, 3.2 g (61%), were collected; m.p. 40–41° (lit.⁹ 40.5–42°). In four additional runs carried out under similar conditions, the yield of (VII) varied from 60 to 70%.

1,1'-Divinylruthenocene (X)

In a manner analogous to that described for vinylferrocene, 100 mg (0.31 mmole) of 1,1'-bis(1-hydroxyethyl)ruthenocene (prepared in 74% yield by sodium borohydride reduction of 1,1'-diacetyl ruthenocene)¹⁰ and 3.0 g of alumina were heated at 180° (17 mm) for 6 h. There was produced 57 mg (65%) of yellow crystals of 1,1'-divinylruthenocene; m.p. 55–57°. (Found: C, 59.09; H, 4.90. C₁₄H₁₄Ru calcd.: C, 59.34; H, 4.98%.)

ACKNOWLEDGEMENTS

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SUMMARY

A facile, high-yield route to mono- and 1,1'-divinylmetallocenes has been developed, based on the sublimation pyrolysis of respective metallocenylcarbinols in the presence of alumina under controlled conditions. The proton NMR spectra of five vinylmetallocenes containing iron, ruthenium or osmium central atoms have been recorded and analyzed, and the findings are compared to earlier correlations concerning the spectra of acetyl- and alkylmetallocenes.

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