# Organometallic Reactions and Syntheses

## Volume 6

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# Organometallic Reactions and Syntheses

## Volume 6

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# Preface

The primary literature on organometallic chemistry has undergone phenomenal growth. The number of papers published from 1951 to 1976 is about equal to all prior literature. Together with this intense activity there has developed a complexity in the literature. Thus, specialized texts and teaching texts, a review journal, an advanced series, and a research journal have all appeared during this period. The present series also reflects this growth and recognizes that many categories of organometallic compounds now have numerous representatives in the literature.

The purpose of *Organometallic Reactions and Syntheses* is to provide complete chapters on selected categories of organometallic compounds, describing the methods by which they have been synthesized and the reactions they undergo. The emphasis is on the experimental aspects, although structures of compounds and mechanisms of reactions are discussed briefly and referenced. Tables of all of the compounds prepared in the category under consideration and detailed directions for specific types make these chapters particularly helpful to the preparative chemist. While the specific directions have not been referenced in the same way as are those in *Organic Syntheses* and *Inorganic Syntheses*, the personal experiences of the authors often lend special merit to the procedures and enable the reader to avoid many of the pitfalls frequently encountered in selecting an experimental procedure from the literature.

We acknowledge a debt of gratitude to the contributing authors whose dedication and skill in preparing the manuscripts cannot adequately be rewarded. It has been gratifying to note that virtually all invitations to contribute have been accepted at once. We also owe thanks to the publisher for encouragement and even the "gentle prod" when necessary to see these volumes to their completion.

Ernest I. Becker
Minoru Tsutsui

# Contents

*Chapter 1*

## Vinyl Polymerization of Organic Monomers Containing Transition Metals

CHARLES U. PITTMAN, JR.

## *Chapter 2*

## Reactions of Metallocarboranes

RUSSELL N. GRIMES

*Chapter 3*

## Homogeneous Catalysis by Arene Group-VIB Tricarbonyls

MICHAEL F. FARONA

## Chapter 1

# Vinyl Polymerization of Organic Monomers Containing Transition Metals

Charles U. Pittman, Jr.

## I. INTRODUCTION AND SCOPE

In this chapter the reactivity toward vinyl homopolymerization and copolymerization of organic monomers containing transition metals is discussed. Vinylferrocene (**1**) is an excellent example and the most thoroughly studied member of this unique class of monomers. Other model examples include vinylcyclopentadienylmanganesetricarbonyl (**2**), styrenetricarbonylchromium (**3**), and *trans*-bis(tributylphosphine) (4-styryl)palladium chloride (**4**). Each of these monomers undergoes vinyl addition polymerization, and each contains a transition metal in the monomer which is retained in the polymer. The first vinyl polymerization of an organometallic derivative was the radical-initiated homopolymerization of vinylferrocene by Arimoto and Haven[1,2] in 1955. They also showed that vinylferrocene could be copolymerized with methyl acrylate, styrene, and chloroprene. Despite this success, organometallic vinyl monomers were virtually neglected for the next decade in comparison with the vast attention given to the preparation of condensation polymers[3,4] and coordination polymers[5] of transition-metal derivatives.

Recently, studies of vinyl derivatives of transition-metal compounds have appeared which allow a more quantitative description of their reactivity

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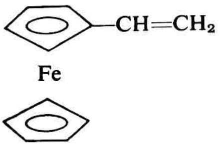

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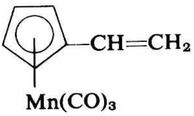

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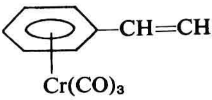

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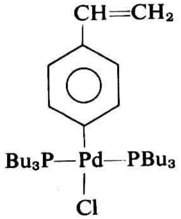


(4)

in homo- and copolymerization. It is of fundamental interest to understand how organometal functions affect vinyl polymerization behavior. In particular, it is of interest to see how monomers such as **(1–4)** behave in terms of the quantitative copolymerization scheme pioneered by Mayo, Lewis and Walling[6–8] and the *Q–e* scheme of Price.[8,9] This knowledge will help to predict the copolymerization behavior of organometallic monomers with classic organic vinyl monomers, and it also will provide a qualitative picture of the electronic effects that organometallic functions impart. Thus, in addition to reviewing the literature, the correlation of existing reactivity data is tentatively interpreted in this chapter to provide a framework in which to view organometallic monomers.

Transition-metal-containing monomers offer the polymer chemist many unique options. Since transition metals often exist in more than one stable oxidation state, mixed-oxidation polymers can be envisioned. Polymers with catalytic properties can be constructed. The thermal or photochemical degradation of organometallic polymers might be designed to free metals or metal oxides within films or crosslinked polymers to produce systems with new properties. With these opportunities coexist many pitfalls. The transition-metal–ligand system may undergo undesirable reactions with radical, anionic, cationic, or Ziegler–Natta catalysts which would preclude polymerization. Many organometallic compounds react with air or moisture or are thermally unstable. The fields of transition metal and polymer chemistry are seldom bridged by the same chemists. These and other problems exist. Even where such polymers have been prepared, detailed property studies still lag behind synthetic efforts.[10,11]

## II. POLYMERIZATION AND COPOLYMERIZATION OF VINYL MONOMERS CONTAINING FERROCENE

### A. Homopolymerization

Vinylferrocene has been homopolymerized using radical, cationic, and Ziegler–Natta initiators. Peroxide initiators are not suitable. Many research groups[1,12–15] have demonstrated that vinylferrocene is oxidized by peroxides to ferricenium ion and that peroxide decomposition is catalyzed in this system. Azo initiators have been used most often both in bulk and in solution systems.[1,2,12–21] Persulfate has been used in emulsion systems but only oils were formed.[1,2] In solution, fairly low-molecular-weight polymers are formed with azobisisobutyronitrile (AIBN)[15–19,22,23] but higher molecular weights are achieved in bulk polymerization.[13,15] Table I summarizes some representative molecular weights which have been obtained.

Using cationic or Ziegler catalyst systems, only very low-molecular-weight polymers have been found.[1,24–25] Despite the high tendency of the cyclopentadienyl rings of ferrocene to undergo electrophilic attack, only vinyl propagation was observed. Simionescu *et al.*[25] reported that $Et_2AlCl/M(acac)_2$ and $Et_3Al/M(acac)_2$—where M = Ni, Cu, and V(O)—gave polymers which were partially methanol soluble.

Baldwin and Johnson[14] reported that the homopolymerization of vinylferrocene [VF] and styrene were quite similar, and they claimed the rate of polymerization followed the normal bimolecular termination mechanism found with most vinyl monomers, i.e., $r_p = k[\mathrm{VF}]^{1}[\mathrm{In}]^{1/2}$ for AIBN initiation at 70° in benzene solution. Kinetics were followed by dilatometry and nmr. However, Pittman *et al.*[16,22] showed that solution polymerizations in benzene gave low yields unless multiple initiator additions were employed. In addition, the molecular weights resulting from solution polymerizations were low $\overline{M}_n = 4000\text{–}6000$ and the distribution was narrow ($\overline{M}_w/\overline{M}_n = 1.2\text{–}1.5$ using 1 g VF per 1 ml benzene).[16,20] Furthermore, the molecular weight was not increased on reducing the initiator concentration, and the degree of polymerization increased with an increase in monomer concentration reaching its highest level in bulk polymerizations.[16] Cassidy *et al.*[13] obtained degrees of polymerization as high as 226 in bulk polymerizations. These relationships are very unusual for vinyl polymerization and unlike the behavior of styrene.

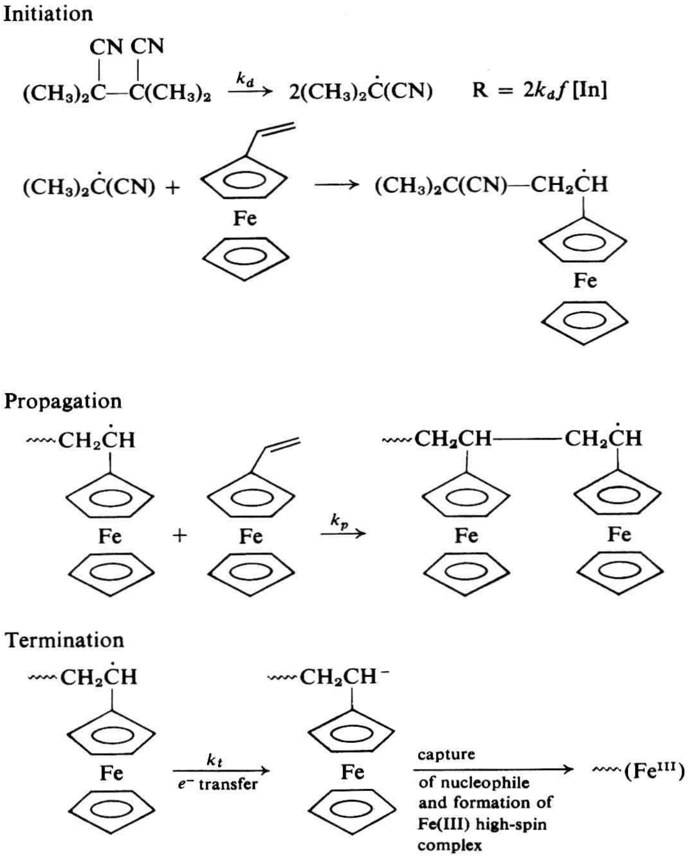
An extensive study of the kinetics of vinylferrocene homopolymerization in benzene has been performed by George and Hayes.[15,19] They conclusively demonstrated that the $r_p = k[\mathrm{VF}]^{1.2}[\mathrm{AIBN}]^{1.1}$ in benzene at 60°, using AIBN as the initiator. This rate law requires a monomolecular termination process. The termination step apparently involved an intramolecular electron transfer from iron to the chain-propagating radical, followed by trapping of the anionic chain end and the formation of a Fe(III) high-spin complex at the chain end.

## TABLE I
Representative Number-Average Molecular Weights Obtained in Polyvinylferrocene Homopolymerizations

| Solvent temperature | Vinylferrocene, mol/liter | Initiator | Initiator, mol/liter | Conversion, % | $M_n$ | Ref. |
|---|---|---|---|---|---|---|
| Benzene, 60° | 1.0 | AIBN | $1.0 \times 10^{-2}$ | 1.1 | 6,100 | 15 |
| Benzene, 60° | 1.0 | AIBN | $1.0 \times 10^{-2}$ | 15.0 | 5,000 | 15 |
| Benzene, 60° | 2.0 | AIBN | $1.0 \times 10^{-2}$ | 10.0 | 8,800 | 15 |
| Benzene, 60° | 3.0 | AIBN | $1.0 \times 10^{-2}$ | 1.9 | 5,800 | 15 |
| Benzene, 60° | 3.0 | AIBN | $1.0 \times 10^{-2}$ | 7.6 | 11,000 | 15 |
| Benzene, 60° | 4.0 | AIBN | $1.0 \times 10^{-2}$ | 2.1 | 8,500 | 15 |
| Benzene, 60° | 4.0 | AIBN | $1.0 \times 10^{-2}$ | 7.0 | 12,800 | 15 |
| Benzene, 60° | 4.0 | AIBN | $1.8 \times 10^{-2}$ | 3.1 | 6,800 | 15 |
| Benzene, 60° | 4.0 | AIBN | $2.0 \times 10^{-2}$ | 3.2 | 7,900 | 15 |
| Benzene, 80° | 5.3 | AIBN | $6.4 \times 10^{-2}$ | 25 | 4,600 | 16 |
| Benzene, 80° | 5.3 | AIBN | $1.2 \times 10^{-1}$ | 69 | 10,000 | 16 |
| Benzene, 70° | 5.3 | AIBN | $1.2 \times 10^{-1}$[a] | 60 | 4,200 | 16 |
| Dioxane, 60° | 1.0 | AIBN | $5.0 \times 10^{-2}$ |  | 5,800 | 18 |
| Dioxane, 60° | 2.5 | AIBN | $4.9 \times 10^{-2}$ |  | 9,500 | 18 |
| Dioxane, 60° | 3.0 | AIBN | $5.0 \times 10^{-2}$ |  | 10,800 | 18 |
| Dioxane, 60° | 2.0 | AIBN | $1.0 \times 10^{-2}$ |  | 11,500 | 18 |
| Dioxane, 60° | 2.0 | AIBN | $2.5 \times 10^{-2}$ |  | 11,100 | 18 |
| None, 80° | bulk | AIBN | 0.74[b] | 21.6 | 7,300 | 16 |
| None, 80° | bulk | AIBN | 1.02[b] |  |  |  |
|  |  |  | 1.00 | 46.8 | 6,300 | 16 |
| None, 70° | bulk | AIBN | 2.00[b] | 70.6 | 23,200 | 16 |
| None, 60° | bulk | AIBN | 2.00[b] | 57.6 | 36,800 | 16 |
| Toluene, 0° | 1.0 | $BF_3 \cdot OEt_2$ | 0.05 | 52 | 2,200 | 24 |
| $CH_2Cl_2$, 0° | 1.0 | $BF_3 \cdot OEt_2$ | 0.05 | 35 | 1,500 | 24 |
| $CH_2Cl_2$, 0° | 1.0 | $TiCl_4$ | 0.05 | 63 | 1,100 | 24 |
| $CH_2Cl_2$, 0° | 1.0 | $Et_2AlCl \cdot t\text{-}BuCl$ | 0.05 | 28 | 3,500 | 24 |

[a] Dual addition of initiator at 3-hr intervals.
[b] Weight percent of AIBN.

This process is shown in Scheme 1. The conversion of ferrocenium groups to a high-spin Fe(III) species is not unexpected since Golding and Orgel showed that organic solutions of ferricenium salts decompose to give Fe(III) compounds.[26] Each termination event produced a high-spin Fe(III) complex.[15,19,27] This was supported by spectral evidence.[15,27] Magnetic susceptibility measurements confirmed that the polymers did not contain ferromagnetic impurities.[15,27] The nmr spectra of polyvinylferrocene exhibited pronounced paramagnetic broadening which could not be removed by treatment with ascorbic acid.[15,27] Since ascorbic acid readily reduces ferrocenium ions to ferrocene, this finding is consistent with a high-spin paramagnetic Fe(III) species.



$Rp = (2k_p k_d f/k_t)\,[\mathrm{M}]\,[\mathrm{In}]$

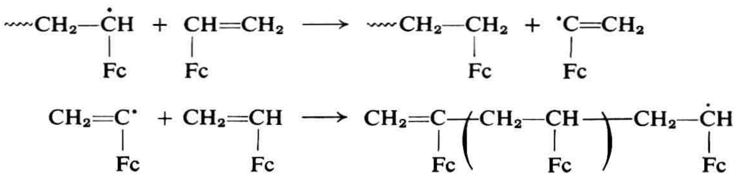
SCHEME 1

The Mössbauer spectra of high-molecular-weight bulk polymerized polyvinylferrocene exhibits a clean doublet ($Q = 2.4$ mm sec$^{-1}$) consistent with unoxidized ferrocene groups.[22] However, the Mössbauer spectra of the lower-molecular-weight polymers, produced in benzene, exhibited a peak at 0.14 mm sec$^{-1}$, which is not consistent with either ferrocene or ferrocenium ion spectra.[15,27] This peak was temperature dependent. The area of this peak varied from 3 to 14% of the total iron content and its intensity was larger for low-molecular-weight polymers.[27] The lower-molecular-weight polymers are the ones with the higher percentage of end groups. The relative intensity of this peak correlated well with the degree of polymerization,[27] which strongly implies that about one such Fe(III) species exists for each polymer chain present. It is just these low-molecular-weight polymers which have a higher mole fraction of chain ends. Finally, a broad line esr spectrum was observed: $g = 2.06$ and 425 gauss band width in benzene and 600 gauss width in the solid.[15,27] The intensity of this band was greatest for the lower-molecular-weight polymers.

The first-order termination step in vinylferrocene homopolymerizations in benzene requires that the degree of polymerization follow the relation $\overline{\mathrm{DP}} = k_p[M]/k_t$. This explains why the degree of polymerization was found to be approximately proportional to the monomer concentration and independent of initiator concentration.

The low molecular weights found in solution homopolymerizations and the fact that the degree of polymerization (DP) was not strictly linear with monomer concentration suggested that chain transfer to monomer and polymer could not be neglected in vinylferrocene polymerizations. Further, Pittman *et al.*[16] found in viscosity–molecular-weight studies, that as the molecular weights increased in bulk polymerizations, the resulting polymers became increasingly branched. Gel-permeation chromatography (gpc) demonstrated that polymers produced in bulk also gave binodal distributions.[16] Low-molecular-weight fractions ($5000\text{–}23{,}000 = \overline{M}_n$) were readily fractionated and the values of $K$ and $a$ in $|\eta| = K(M)^a$ were $6.64 \times 10^{-4}$ and 0.49 in benzene, and $7.20 \times 10^{-5}$ and 0.72 in THF, respectively.[16] The high-molecular-weight modes could not be fractionated.[16] For example, it proved impossible to fractionate a sample with $\overline{M}_n = 1.5 \times 10^5$ and $\overline{M}_w = 6.3 \times 10^5$.[16] The low viscosities observed for the high-molecular-weight nodes suggest a particularly dense, highly branched polymer.[16] Branching would be expected if chain transfer to polymer was pronounced. This supposition was confirmed by George and Hayes.[15] The value of the chain-transfer constant to monomer, $C_m$, was $8 \times 10^{-3}$ for vinylferrocene versus $0.06 \times 10^{-3}$ for styrene at 60°.[15] As the concentration of polymer in solution increases (this is quite important in high-conversion bulk polymerizations) the polymer increasingly acts as a chain-transfer agent leading to highly branched soluble and perhaps even to crosslinked insoluble polymers. Gel-permeation chromotography studies of lower-molecular-weight fractions are best interpreted by concluding that polyvinylferrocene is even branched at low conversions.[27]

The high chain transfer to monomer suggests that the following process should be important[27]:



$$\sim\!\mathrm{CH_2}\!-\!\underset{\mathrm{Fc}}{\underset{|}{\dot{\mathrm{C}}\mathrm{H}}} + \underset{\mathrm{Fc}}{\underset{|}{\mathrm{CH}}}\!=\!\mathrm{CH_2} \longrightarrow \sim\!\mathrm{CH_2}\!-\!\underset{\mathrm{Fc}}{\underset{|}{\mathrm{CH_2}}} + \underset{\mathrm{Fc}}{\underset{|}{{}^{\bullet}\mathrm{C}}}\!=\!\mathrm{CH_2}$$

$$\mathrm{CH_2}\!=\!\underset{\mathrm{Fc}}{\underset{|}{\mathrm{C}^{\bullet}}} + \mathrm{CH_2}\!=\!\underset{\mathrm{Fc}}{\underset{|}{\mathrm{CH}}} \longrightarrow \mathrm{CH_2}\!=\!\underset{\mathrm{Fc}}{\underset{|}{\mathrm{C}}}\!-\!\left(\mathrm{CH_2}\!-\!\underset{\mathrm{Fc}}{\underset{|}{\mathrm{CH}}}\right)\!-\!\mathrm{CH_2}\!-\!\underset{\mathrm{Fc}}{\underset{|}{\dot{\mathrm{C}}\mathrm{H}}}$$