Journal of Organometallic Chemistry, 445 (1993) 137-141

JOM 23113

The preparation, polymerization and copolymerization of (η^5-vinylcyclopentadienyl)dicarbonylmethyliron monomer

Anjan K. Saha and M. Mahmun Hossain

Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, WI 53201 (USA)

(Received April 14, 1992; in revised form July 6, 1992)

Abstract

The first report on the synthesis, polymerization and copolymerization of the organometallic monomer, (η^5-vinylcyclopentadienyl)dicarbonylmethyl iron is presented. The monomer was prepared in high yield by the coupling reaction of (η^5-iodocyclopentadienyl)dicarbonylmethyliron and vinyltributyltin in the presence of 5 mol% $(CH_3CN)_2PdCl_2$. (η^5-Iodocyclopentadienyl)dicarbonylmethyliron was prepared by lithiation of the cyclopentadienyl ligand in (η^5-cyclopentadienyl)-dicarbonylmethyliron with butyllithium at −78°C and subsequent reaction with iodine. (η^5-Cyclopentadienyl)dicarbonylmethyliron was prepared by the reaction between potassium benzophenone ketyl and cyclopentadienyldicarbonyliron dimer followed by addition of iodomethane. The vinyl complex underwent homopolymerization under radical initiation in benzene. Copolymerization of the vinyl complex with styrene or with methylmethacrylate was also successful under radical initiation in benzene.

1. Introduction

Interest in organometallic polymers has increased in recent years due to their potential applications as catalysts, semiconductors, UV absorbers and antifouling agents [1-3]. In particular, mixed valence state polymers of vinylferrocene (with both ferrocene and ferricinium units present) were shown to be charge-hopping-type semiconductors [4]. Despite their potential importance, only a few organometallic polymers containing a vinyl group have been investigated [5-11]. Recently, Pittman reported the synthesis and polymerization of the first organometallic monomer containing tungsten, (η^5-vinylcyclopentadienyl) tricarbonylmethyltungsten [5,11] and this is the only organometallic monomer which contains a metal-alkyl linkage. Here, we report the first synthesis of the (η^5-vinylcyclopentadienyl)dicarbonylmethyliron monomer and preliminary studies concerning the homopolymerization and copolymerization of the monomer under radical initiation conditions.

2. Results and discussion

2.1. Monomer syntheses

The chemistry of vinylferrocene and related vinylmonomers has been widely investigated in the field of organometallic polymers. In order to determine the potential utility of organoiron polymers, synthesis of polymers containing a variety of different vinylmonomers is required. One such approach would be to synthesize a polymer containing a (η^5-cyclopentadienyl)dicarbonylmethyliron (**2**) linkage. Compound **2** was first synthesized in 1956 [12]. Due to the lack of a synthetic route to the vinyl compound **5**, polymerization of monomers containing **2** as a moiety has not been studied. Recently, lithiation of the cyclopentadienyl ligand in the cyclopentadienyliron complexes (η^5-C_5H_5)$Fe(CO)_2R$ (where R is an alkyl or aryl group) has been reported [13]. We have utilized this functionalization reaction to synthesize the vinylcyclopentadienyliron complex **5** from the parent compound **2**. Using sec-BuLi at −78°C in THF, the methyl complex **2** was converted to the corresponding intermediate lithium cyclopentadienyliron complex **3** (Scheme 1). A colour change from yellow to deep pink suggested the formation of an intermediate which was air and temperature

---

Correspondence to: Dr. M.M. Hossain.

0022-328X/93/$6.00

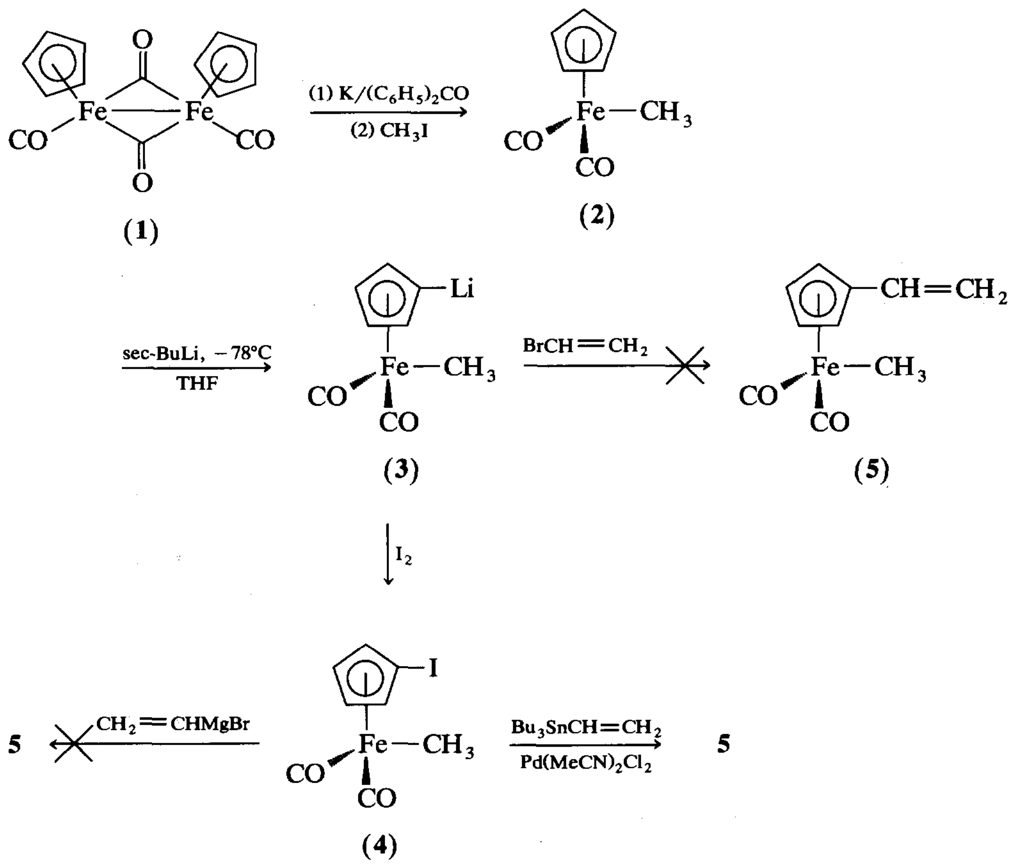
sensitive. The intermediate was treated with vinyl bromide in an attempt to obtain the vinyl complex **5**, but the synthesis was unsuccessful (Scheme 1). No vinyl complex was isolated from the reaction. Alternately, the lithium complex was treated with I_2 at -78°C to prepare the iodo complex **4** (Scheme 1). This reaction was first reported by Stille [14]. An attempted coupling reaction between the iodo complex **4** and vinylmagnesium bromide to prepare the vinyl complex **5** was unsuccessful: only the starting iodo complex was recovered.

A satisfactory synthetic route to the vinyl complex **5** was through the reaction between the iodo complex **4** and vinylstannane in the presence of 5 mol% of $Pd(CH_3CN)_2Cl_2$. This reaction proceeded smoothly at room temperature in DMF and was completed in 2 h giving the vinyl compound in 91% yield [15*]. The vinyl compound was purified by column chromatography on silica gel with pentane and characterized by spectroscopic methods. This is the first example of a vinyliron complex containing an iron–alkyl σ bond along with a carbonyl group attached to iron.

2.2. Polymerization studies

The vinyl compound homopolymerized sluggishly under radical initiation conditions (Scheme 2). For example, homopolymerization of **5** in benzene using AIBN as the initiator gave only a 12% yield of homopolymer **6** [16*]. The polymer was purified by recrystallization several times from a benzene and pentane mixture. The IR spectra showed absorptions at 2000 and 1943 cm^{-1} in THF which are characteristic of an iron alkyl linkage in the polymer. The ^1H NMR spectrum of the homopolymer was recorded in $C_6D_5NO_2$ and exhibited a singlet at 0.31 ppm for the Fe–CH_3 group and a broad multiplet centred at 4.73 ppm for the cyclopentadienyl protons. These peaks showed an area ratio of 3 : 4. The backbone hydrogens were found at 0.80–2.90 ppm. The vinyl protons of monomer **5** were absent in the spectrum of homopolymer. The homopolymer exhibited a molecular weight ($\overline{M}_n$) of 2800, according to GPC studies versus polystyrene standards.

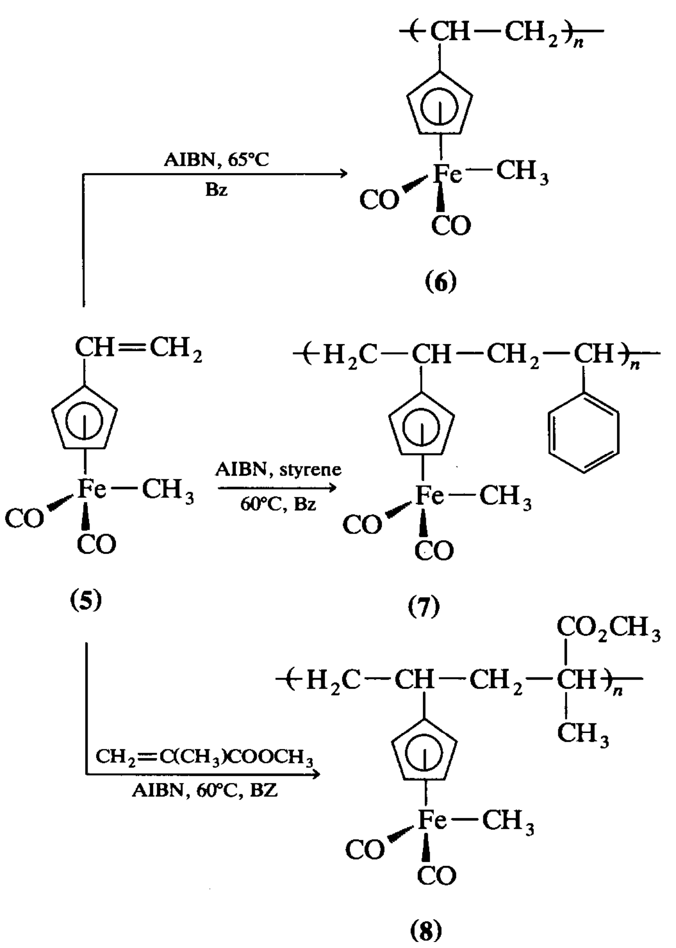
Copolymerization of **5** (M_1) with styrene (M_2), in an



Scheme 1.

---

* Reference number with asterisk indicates a note in the list of references.



Scheme 2.

initial M_1/M_2 molar ratio of 1/1.5 was carried out at 60°C in benzene for 162 h. Several recrystallizations from THF/pentane gave a 26% yield of polymer [16*]. The IR absorptions at 2000 and 1942 cm^{-1} in benzene indicated the presence of an iron alkyl moiety in the copolymer. A ^1H NMR spectrum of polymer in THF-d_8 was recorded. The copolymer **7** exhibited a multiplet centred at 4.57 ppm for the cyclopentadienyl group and another multiplet at 6.85 ppm for the phenyl protons. These peaks showed an area ratio of 25.8/139.5 indicating an m_1/m_2 ratio of 1/4.3. The copolymer exhibited a molecular weight ($\bar{M}_n$) of 9000, according to GPC studies *versus* polystyrene standards.

Copolymerization of **5** (M_1) with methylmethacrylate (M_2) in a 1.45 M_2/M_1 molar ratio gave a copolymer in 28% yield [16*]. The IR absorptions at 2001, 1942 and 1734 cm^{-1} indicated the presence of both iron–alkyl and methylmethacrylate moieties in the polymer **8**. A ^1H NMR spectrum of polymer in C_6D_6 was recorded. The peak ratio of the cyclopentadienyl group and the methyl group in CO_2CH_3 was 2.93/10.38 indicating an m_1/m_2 ratio of 1/4.7. The copolymer exhibited a molecular weight ($\bar{M}_n$) of 4200, according to GPC studies *versus* polystyrene standards.

The polymers **6**, **7** and **8** represent the first examples of polymers containing an iron–alkyl linkage in which carbonyl groups are also attached to the iron. Work is underway in the synthesis of high molecular weight homo- and copolymers. In addition, electrochemical studies of the polymers are being pursued.

3. Experimental details

All the operations were performed under a nitrogen atmosphere using Schlenk tube techniques. Reagent grade pentane and benzene were distilled from sodium under nitrogen immediately prior to use. Reagent grade ether and tetrahydrofuran were freshly distilled under a nitrogen atmosphere from sodium benzophenone ketyl. Dichloromethane was distilled under nitrogen from phosphorous pentoxide. *N*,*N*-Dimethylformamide (DMF) was purified by distillation at reduced pressure from magnesium sulphate. AIBN (2,2′-azobis-2-methylpropionitrile, 98%) was recrystallized from methanol and then dried under vacuum for several days. Methylmethacrylate and styrene were purified by washing with 10% NaOH and 10% H_2SO_4 to remove inhibitor, followed by water washes, drying with Na_2SO_4 and distillation from CaH_2 under vacuum. Deuterated chloroform and deuterated nitrobenzene were degassed several times and distilled from phosphorous pentoxide. Deuterated benzene and deuterated tetrahydrofuran were dried over sodium and distilled immediately prior to use. Cyclopentadienyldicarbonyliron dimer, vinyltributyltin, sec-BuLi and $(CH_3CN)_2PdCl_2$ were obtained from Aldrich Co.; iodine was obtained from Fischer Scientific Company; silica gel (40–140 mesh) and potassium fluoride were obtained from J. T. Baker.

Infrared spectra were obtained using a Nicolet MX-1 FT-IR spectrometer. ^1H NMR spectra were recorded using a Bruker 250 MHz NMR spectrometer. Mass spectra were performed on a Hewlett-Packard 5985B (H/P), GC/MS system, operated with the DIP "Direct insertion probe" E1-70 eV. For the CH microanalysis, a Perkin–Elmer 240C Elemental Analyzer was employed. GPC experiments were carried out on a Waters GPC setup consisting of a Model 410 differential refractometer detector and a Waters Data module. Chloroform was used as solvent. A constant flow rate of 1.0 ml min^{-1} was maintained. The instrument was calibrated by using polystyrene standards.

Dicarbonylmethyl iron complex **2** was prepared from the cyclopentadienyldicarbonyliron dimer **1** by the known procedure [12]. The (η^5-iodocyclopentadienyl)-

dicarbonylmethyliron **4** was prepared from methyl complex **2** by the procedure reported by Stille [13].

3.1. Preparation of (η^5-vinylcyclopentadienyl)dicarbonylmethyl-iron (5)

A nitrogen-purged flask was charged with vinyltributyltin (1.32 g, 4.15 mmol), DMF (65 ml) and iodo complex **4** (1.32 g, 4.15 mmol). To the stirred solution, 0.054 g (0.20 mmol) of $(CH_3CN)_2PdCl_2$ dissolved in DMF (7 ml) was added by syringe. Stirring was continued at room temperature for 2 h, and then 85 ml of ether was added to the reaction mixture, followed by addition of 43 ml of a 50% solution of potassium fluoride in water. This reaction mixture was stirred for 1 h. The solution was transferred to a separating funnel and the ether solution was washed three times with 150 ml of water. The organic layers were combined and dried over sodium sulphate. Filtration and removal of the solvent under a vacuum gave an orange oil (0.82 g, 91%) of **5** with the following spectral characteristics: IR (pentane): 2014 and 1961 cm^{-1} (CO), ^1H NMR ($CDCl_3$): δ 6.18 (1 H, dd, $J_1 = 18$ Hz, $J_2 = 11$ Hz); 5.33 (1 H, d, $J_1 = 18$ Hz); 5.24 (1 H, d, $J_2 = 11$ Hz); 4.79 (2 H, t, $J = 2$ Hz); 4.71 (2H, m); 0.27 (3H, s). Mass: *m/e* 218 $[M]^{+\cdot}$, 190$[M - CO]^{+\cdot}$, 162$[M - 2CO]^{+\cdot}$, and 147 $[M - (2CO + CH_3)]^{+\cdot}$. Anal. Found: C, 54.86; H, 4.59. $FeC_{10}H_{10}O_2$ calc.: C, 55.09; H, 4.62%.

3.2. Homopolymerization of 5.

The monomer **5** (0.453 g, 2.08 mmol) and AIBN (15 mg) were dissolved in 2 ml of dried benzene. This solution was placed into a polymerization tube and subjected to four freeze–pump–thaw cycles. The tube was sealed and heated in an oil bath at 65°C for 168 h. When the reaction was completed, the tube was opened and the reaction mixture was poured into pentane (200 ml) to precipitate the polymer, which was then filtered and washed with pentane. Recrystallization three times from benzene/pentane gave 0.054 g (12%) of homopolymer **6** with the following spectral properties: IR (THF): 2000 and 1943 cm^{-1} (CO). ^1H NMR ($C_6D_5NO_2$): δ 4.73 (m, C_5H_4); 0.80–2.90 (m, $>CH-CH_2-$); 0.31 (s, $-CH_3$). The vinyl protons of monomer **5** were absent in the spectrum of the homopolymer. The polymer had a molecular weight ($\overline{M}_n$) of 2800, according to GPC studies *versus* polystyrene standards.

3.3. Copolymerization of 5 with styrene

Monomer **5** (M_1) (0.25 g, 1.15 mmol), 0.18 g (1.73 mmol) of styrene (M_2), 11 mg of AIBN and 3 ml of dry benzene were introduced into a polymerization tube and subjected to four freeze–pump–thaw cycles. The tube was sealed under a vacuum and heated at 60°C for 162 h. When the polymerization was complete, the tube was opened and the reaction mixture was added to pentane (180 ml). The copolymer was filtered and washed with pentane. The purification was accomplished by dissolving the crude material in 3 ml of THF and adding the solution to 180 ml of pentane. The yield of copolymer was 0.11 g (26%). IR (C_6H_6): 2000 and 1942 cm^{-1} (CO). ^1H NMR (THF-d_8): δ 6.85 (m, C_6H_5); 4.57 (m, C_5H_4); 0.8–2.70 (m, $CH-CH_2$); −0.10 (s, CH_3). The copolymer exhibited multiplets centred at 4.57 ppm for cyclopentadienyl protons and at 6.85 ppm for phenyl protons. These peaks showed an area ratio of 25.8/139.5 indicating an m_1/m_2 ratio of 1/4.3. The polymer had a molecular weight ($\overline{M}_n$) of 9000, according to GPC studies *versus* standards.

3.4. Copolymerization of 5 with methylmethacrylate

Monomer **5** (M_1) A (0.24 g, 1.10 mmol), 0.16 g (1.60 mmol) of methylmethacrylate (M_2), 12 mg of AIBN and 3 ml of dry benzene were placed in a polymerization tube and subjected to four freeze–pump–thaw cycles. The tube was sealed under a vacuum and heated in an oil bath at 60°C for 155 h. The tube was opened and the reaction mixture was added to pentane. The polymer appeared as a precipitate. The copolymer was filtered and washed with a pentane/ether mixture. The polymer was recrystallized three times by dissolving in THF and adding the solution into dry pentane. The yield of copolymer was 0.112 g (28%). IR (CH_2Cl_2): 2001, 1942 cm^{-1} (CO) and 1734 cm^{-1} (carbonyl group). ^1H NMR (C_6D_6): δ 4.73 (m, C_5H_4); 3.35 (d, CO_2CH_3); 0.80–2.50 (m, $CH-CH_2$, $CH-CH_3$); 0.36 (s, CH_3). The peak ratio of the cyclopentadienyl group and the methyl group in CO_2CH_3 was found to be 2.93/10.38 indicating an m_1/m_2 ratio of 1/4.7. The copolymer had a molecular weight ($\overline{M}_n$) of 4200, according to GPC studies *versus* polystyrene standards.

Acknowledgment

We are grateful to Mr. A.M. Sarker, Department of Chemistry, University of Massachusetts, Amherst, MA for helping us to determine the molecular weights of the polymers.

References

1 C. E. Carraher, Jr., J. E. Sheats and C. U. Pittman, Jr., *Organometallic Polymers*, Academic Press, New York, 1978.
2 J. E. Sheats, C. E. Carraher and C. U. Pittman, Jr., *Metal-Containing Polymer Systems*, Plenum, New York, 1985.
3 C. U. Pittman, Jr. and J. R. Reynolds, Organometallic polymers, in *Encyclopedia of Polymer Science & Engineering*, Vol. 10, Wiley, New York, 1987, pp. 541–594.
4 D. O. Cowan, J. Park, C. U. Pittman, Jr., Y. Sasaki, T. K. Mukherjee and N. A. Diamond, *J. Am. Chem. Soc., 94* (1972) 5110.

5 D. W. Macomber, M. D. Rausch, T. V. Jayaraman, R. D. Priester and C. U. Pittman, Jr., *J. Organomet. Chem., 205* (1981) 353.

6 C. U. Pittman, Jr., T. D. Rounsefell, E. A. Lewis, J. E. Sheats, B. H. Edwards, M. D. Rausch and E. A. Mintz, *Macromolecules, 11* (1978) 560.

7 F. S. Arimoto and A. C. Haven, Jr., *J. Am. Chem. Soc., 77* (1955) 6295.

8 J. C. Lai, T. D. Rounsefell and C. U. Pittman, Jr., *J. Polym. Sci., A-1, 9* (1971) 651.

9 C. U. Pittman, Jr. and R. D. Priester, Jr., *J. Polym. Sci, Polym Chem. Ed., 19* (1981) 3351.

10 D. W. Macomber, W. P. Hart, M. D. Rausch, R. D. Priester and C. U. Pittman, Jr., *J. Am. Chem. Soc., 104* (1982) 884.

11 C. U. Pittman, T. V. Jayaraman, R. D. Priester, Jr., S. Spencer, M. D. Rausch and D. Macomber, *Macromolecules, 14* (1981) 237.

12 T. S. Piper and G. J. Wilkinson, *J. Inorg. Nucl. Chem., 3* (1956) 10.

13 C. L. Sterzo, M. M. Miller and J. K. Stille, *Organometallics, 8* (1989) 2331.

14 (a) For a general review: J. K. Stille, *Angew. Chem. Int. Ed. Engl., 25* (1986) 508; (b) J. H. Simpson, *Ph. D. Dissertation*, Colorado State University, 1986.

15 Meyers has recently published a paper for the synthesis of (η^5-vinylcyclopentadienyl)tricarbonylmethyltungsten via palladium-catalyzed cross-coupling reaction: E. C. Brehm, J. K. Stille and A. I. Meyers, *Organometallics, 11* (1992) 938.

16 The yields of the polymerization reactions were not optimized.