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New synthesis of acylferrocene by hydroiminoacylation of the terminal olefin with ferrocenecarboxaldimine and application to polymer-supported acylferrocene

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Abstract

Acylferrocenes were synthesized by hydroiminoacylation of the ω-olefins 1-pentene (**3a**), vinylferrocene (**3b**) and but-3-enylferrocene (**3c**), with the ferrocenecarboxaldimine **2**, prepared from ferrocenecarboxaldehyde (**1**) and 2-amino-3-picoline, under the action of Wilkinson's catalyst, followed by hydrolysis of the corresponding ketimines (**5a**, **5b** and **5c**). This hydroiminoacylation was used to incorporate the ferrocenyl group into phenyl-terminated poly-butadiene (PTPB, consisting of 27% vinyl and 73% internal olefin group). 74% hydroacylation of the vinyl group in **7** was accomplished in the first catalytic reaction and in **10** the second hydroacylation completed the conversion of the vinyl group into acylferrocene.

1. Introduction

Recently interest has been growing in polymer-supported metal complexes since they have potential for catalysts and for new functionalized materials [1]. Organometallic complexes have been incorporated into polymers by a variety of methods, some of which are as follows: (1) introducing metal complexes onto functionalized supports (polymer) including phosphorus [2], nitrogen [3], or oxygen [4] donors by coordination; (2) metal complexes bound to polymeric supports through metal–carbon bonds [5]; (3) polymerization of functionalized monomers containing organometallic complexes [6]. In most cases a preformed polymer must be functionalized, except in (3), so that a catalytic complex can be attached. This may be done by derivatizing the polymer with a ligand, which is used to bind the metal. However, there are only limited methods for incorporating organometallic complexes into a polymer through a metal–carbon σ-bond without functionalizing a preformed polymer. Already we and others have studied the hydroiminoacylation of the terminal olefin group with aldimine, prepared from aldehyde and amine, by an Rh^I catalyst to give ketimine, the precursor of ketone [7]. Even organometallic complexes such as ferrocenecarboxaldehyde can be converted into diacylferrocene as well as into alkenyl acylferrocene, through hydroiminoacylation of 1,5-hexadiene [8]. Acylferrocenes are particularly important in the synthesis of alkylferrocenes, of α-hydroxyalkylferrocenes, and of alkenylferrocenes from the alcohol [9]. Although acylferrocene cannot be synthesized catalytically by general methods such as the Friedel-Crafts acylation [9], hydroiminoacylation of aldimine makes it possible to prepare acylferrocenes with Rh^I catalyst. Through this catalytic reaction, it is possible to attach the ferrocenyl group to a variety of compounds having the vinyl group. In this paper we report a method for incorporating the ferrocenyl group into the non-functionalized preformed polymer (poly-butadiene) as well as into various vinyl compounds through the metal–carbon σ-bond.

2. Result and discussion

Ferrocenecarboxaldimine (**2**), the starting organometallic compound for hydroiminoacylation, was obtained by condensation of ferrocenecarboxaldehyde (**1**) and 2-amino-3-picoline with continuous removal of water under acid catalyst. Compound **2** was reacted

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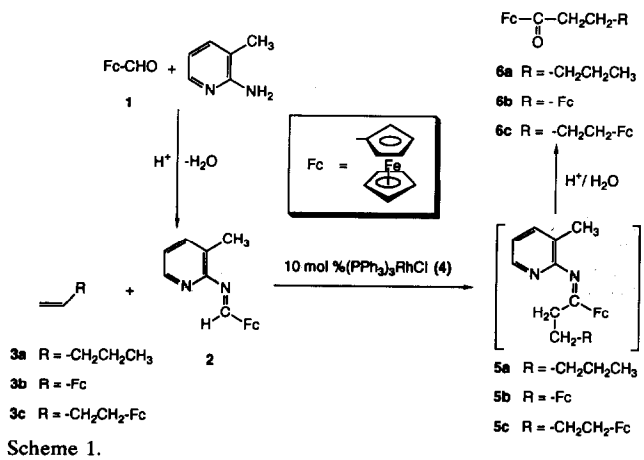
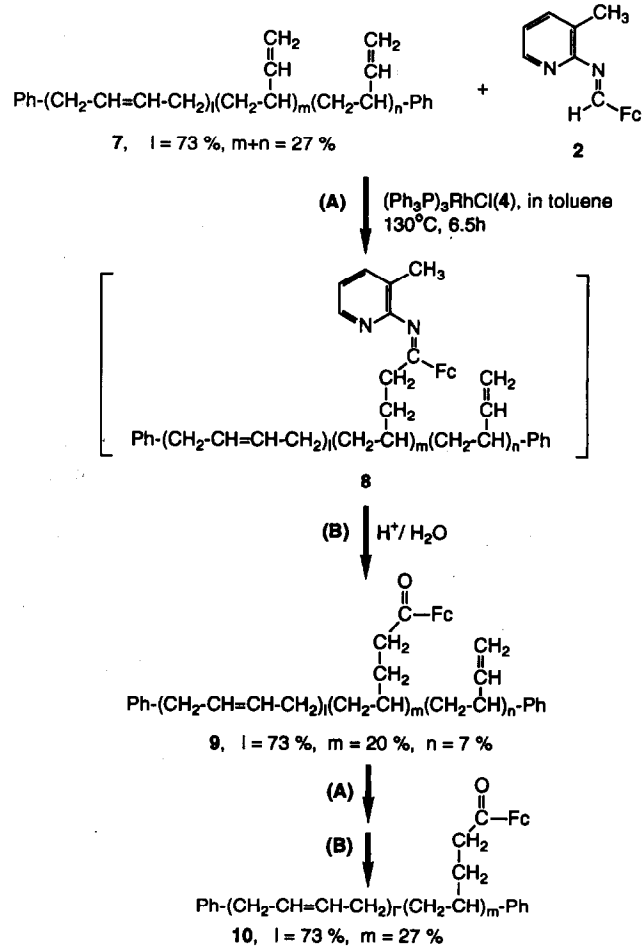


Scheme 1.

with the terminal olefin in **3a** under Wilkinson's complex (**4**) as a catalyst to give ketimine **5a** (Scheme 1). The mechanism proposed was that the C–H bond of aldimine was initially cleaved by the Rh^{I} species to generate the iminoacyl rhodium(III) hydride complex, and the subsequent migration of hydride into the vinyl group in ω-olefins gave the iminoacyl rhodium(III) alkyl complex by Markownikoff's rule, followed by reductive-elimination to give the ketimine [7a]. Without isolation of **5a**, it was hydrolyzed by aqueous acidic solution to give hexanoylferrocene (**6a**) in 79% yield after chromatographic isolation. Consequently through this reaction, it become possible to convert ferrocenecarboxaldehyde (**1**) to alkanoylferrocene. Instead of ω-alkene as a substrate, a simple organometallic complex with a vinyl group, like vinylferrocene (**3b**), was used for this hydroiminoacylation. The reaction of **3b** and **2** in a 1:1 ratio at 130°C for 6 h with **4** as catalyst and hydrolysis of the resulting ketimine **5b** gave 3-ferrocenylpropanoylferrocene (**6b**) in 56% yield after chromatographic isolation. Compound **2** also reacted catalytically with but-3-enyl ferrocene (**3c**), another ferrocene derivative having a longer chain ω-olefin than the vinyl group, to give **5c**, which was also hydrolyzed to give the acylferrocene **6c** in 40% yield. Comparing the yield of **6c** with that of **6b**, there is no observable improvement, indicating that **3b** has no bigger a steric hindrance than **3c** in hydrometallation after catalytic C–H bond cleavage of aldimine by Rh^{I}.

One of the interesting substrates for hydroiminoacylation is polybutadiene because it has both olefins, the internal olefin (consisting of *cis*- and *trans*-olefins) and the terminal olefin (the vinyl group) [10 *]. We chose phenyl-terminated polybutadiene (PTPB) (**7**) containing 27% of the terminal vinylic olefin and 73% of the internal olefin. Chemical methods for binding the organometallic compounds with the polymer through the metal–carbon σ-bond do exist [5]. Under the above reaction conditions, compound **2** reacted catalytically with the polymer **7** to give **8** (Scheme 2). The ketimine-impregnated polymer **8** was hard to isolate in the pure form due to its partial hydrolysis during purification by column chromatography. Complete hydrolysis of **8** with 1 N HCl aqueous solution and purification by column-chromatography gave the ferrocenyl group-impregnated polymer **9** in 67% yield. The polymer **9** was characterized by IR, ^{1}H and ^{13}C NMR spectra. The IR band of the carbonyl peak appeared at 1680 cm^{-1}, indicating that ketimine was completely hydrolyzed to ketone. The characteristic band of the vinyl group at 910 cm^{-1} was diminished dramatically while those of the *trans*-1,4-internal olefin at 964 cm^{-1} and the *cis*-1,4-internal olefin at 725 cm^{-1} still existed [11] (Fig. 1b). The ratio of the vinylic olefin and the internal olefins in polybutadiene compounds can be



Scheme 2.

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

measured by ^{1}H NMR spectra, by measuring the integrations of the vinylic CH_2 peak in the range 4.9–5.0 ppm and the internal olefinic –CH=CH– and the vinylic –CH= in the range 5.3–5.6 ppm; evidently 74% of the vinyl group in **7** was hydroacylated (Fig. 2b). In particular, α-CH_2 to the carbonyl group in **9** appeared at 2.7 ppm as a triplet that was not noted in the starting polymer **7**. The partially ferrocene-impregnated polymer **9** could be rehydroacylated under identical reaction conditions to give the complete vinyl-hydroacylated polymer **10**. ^{1}H NMR spectra show that the vinyl peaks in 4.9–5.0 ppm disappeared completely (Fig. 2c). Further evidence for the complete hydroacylation of the vinyl group in **7** is the disappearance of the IR band at 910 cm^{-1} as shown in Fig. 1c.

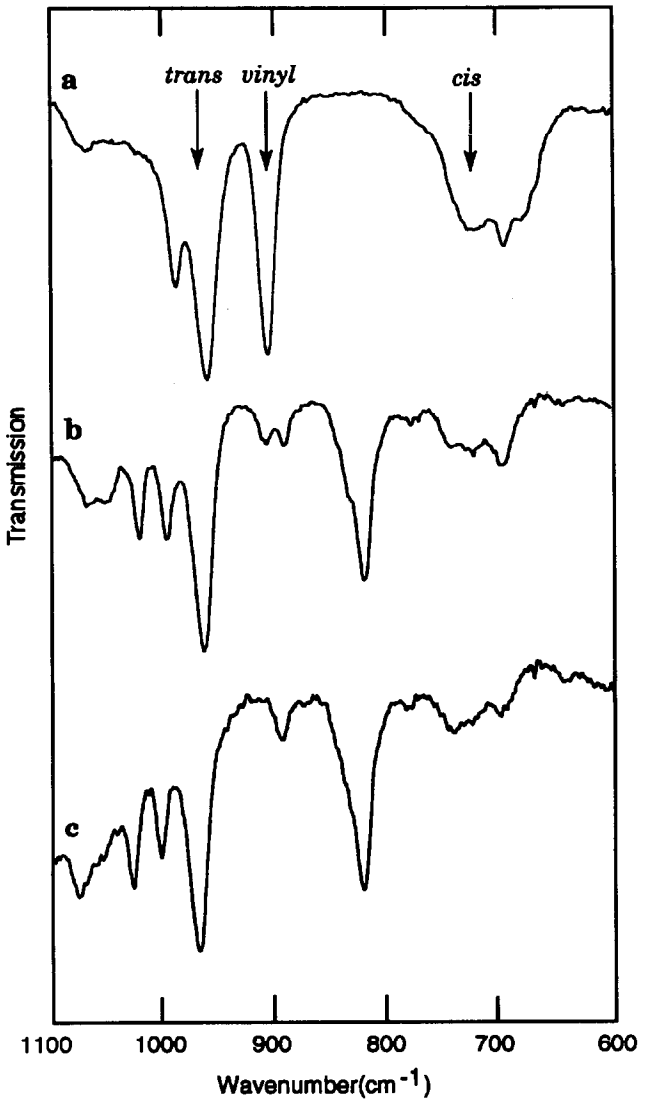


Fig. 1. (a) characteristic IR bands of *trans* (964 cm^{-1}), vinyl (910 cm^{-1}) and *cis* olefins (725 cm^{-1}) in **7**, (b) decreased vinyl IR band in **9**, and (c) complete disappearance of vinyl IR band in **10**

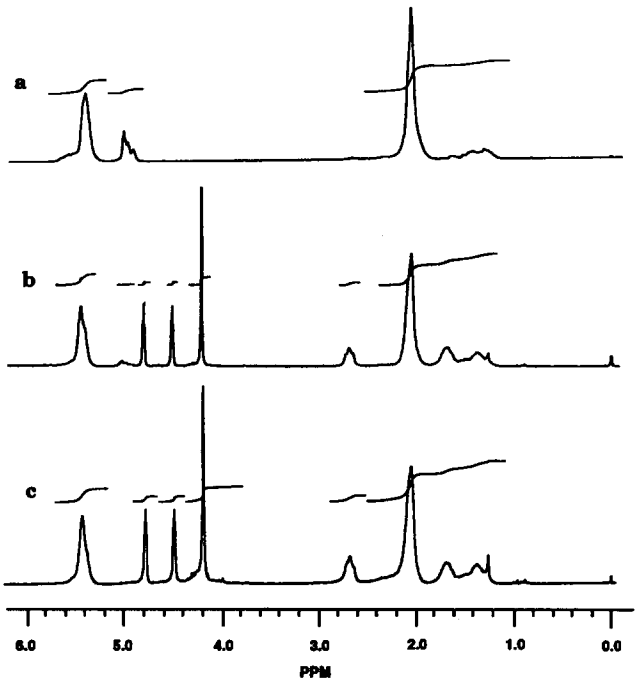


Fig. 2. ^{1}H NMR spectra of (a) PTPB **7**, (b) 74% of vinyl group-hydroacylated PTPB **9**, and (c) vinyl group-hydroacylated PTPB **10**

The ^{13}C NMR spectra also showed the characteristic peaks for **10** (Fig. 3). While the signals of terminal olefinic carbons at 142.4 and 114.2 ppm in **7** have completely disappeared in **10**, new characteristic peaks of the acylferrocenyl group have appeared at 79.0 (C-1 in substituted Cp group), 72.0 (C-2,5 in substituted Cp group), 69.6 (unsubstituted Cp group) and 69.3 ppm (C-3,4 in substituted Cp group) for the ferrocenyl group [12] as well as 204.6 ppm for the carbonyl group. One interesting feature of **10** is the ^{13}C NMR chemical shift of α-CH_2 to the carbonyl group, 36.95 ppm, which is different from that of **6a** and **6c**, 39.6 ppm. This can be explained by a γ-effect which leads to a 2.5 ppm up-field shift because the α-carbon to the carbonyl group in polymer **10** has two γ-carbons while **6a** and **6c** each have only one γ-carbon to the carbonyl group [13]. Complete conversion of **2** and **7** to **10** was not achieved in a single step, maybe due to catalytic poisoning during the reaction. It might be possible to improve catalytic activity by changing the reaction conditions.

The above result indicates that a new method for incorporating organometallic compounds into the polymer has been developed. We are now studying further applications, under modified reaction conditions, of aldimine **2** to the polymer chemistry and the one-step complete conversion of **2** and **7** to **10**.

3. Experimental section

Compound **1** [9] and **3c** [14] were prepared by published procedures. Wilkinson's complex, 1-pentene (**3a**), vinyl ferrocene (**3b**), 2-amino-3-picoline and phenyl-terminated polybutadiene (PTPB, containing 27% terminal vinylic olefin [10]; average M.W. 3400) (**7**) were purchased from Aldrich and used without further purification. All solvents were distilled and stored over molecular sieves (4 Å). NMR spectra were recorded with either a Bruker AC-200 (200 MHz) or a Varian FT-80 A (80 MHz) spectrometer. The chemical shifts (δ) of the ^{1}H NMR and ^{13}C resonances are in ppm relative to internal Me_4Si. Infrared spectra were recorded with a Perkin-Elmer 683 spectrometer. Microanalyses were conducted by ADD Analytical Laboratory. Mass spectra were obtained on Hewlett-Packard HP 5971 A mass spectrometer equipped with an HP 5890 series II Gas Chromatograph. Column chromatography was performed on Merck silica gel 60.

3.1. Synthesis of 3-methyl-2-aminopyridyl ferrocenecarboxaldimine (2)

To a mixture of 10 g (0.047 mol) of ferrocenecarboxaldehyde (**1**) and 11.56 g (0.11 mol) of 3-methyl-2-amino pyridine in 50 ml of benzene was added 0.01 g (0.053 mmol) of p-toluenesulfonic acid as catalyst. The reaction mixture was allowed to heat at 100°C with removal of water by Dean-Stark apparatus. After complete removal of the calculated amount of water, solvent and excess 3-methyl-2-aminopyridine were evaporated and distilled off under high vacuum to give **2**. **2**: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 8.9 (s, 1H, *H*–C(–Fc)=N–), 8.26 (d, $J = 4.55$ Hz, H-6 in picoline group), 7.50 (d, $J = 7.03$ Hz, 1H, H-4 in picoline group), 7.04 (m, 1H, H-5 in picoline group), 4.87 (t, $J = 1.9$ Hz, 2H, Hs-2,5 in substituted Cp ring), 4.51 (t, $J = 1.9$ Hz, 2H, Hs-3,4 in substituted Cp ring), 4.25 (s, 5H, Cp ring), 2.40 (s, 3H, CH_3–); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ(ppm) 163 (*C*=N), 146–120 (carbons of picoline ring), 73.1(C-1 in substituted Cp ring), 71.5 (C-2,5 in substituted Cp ring), 69.6 (C-3,4 in substituted Cp ring), 69.4 (Cp ring), 17.5 (CH_3–); IR (neat) 3060, 2900, 1600s, 1560s, 1440, 1400, 1220, 1090, 1025, 865, 810s, 770 cm^{-1}.; mass spectra (assignment, relative intensity) 305 ($M^+ + 1$, 100), 304 (M^+, 14), 239 (M^+-C_5H_5, 33), 211 (Fc – CN^+, 27), 183 (M^+-C_5H_5Fe, 13), 122 ($C_5H_5Fe^+$, 24); Anal. Calcd. for $C_{17}H_{16}N_2Fe$: C, 67.11; H, 5.26; N, 9.21. Found: C, 65.66; H, 5.68; N, 9.22%.

3.2. Hydroiminoacylation of 1-pentene with 2 and hydrolysis of the resulting ketimine

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A screw-capped pressure vial was charged with 0.031 g (0.0329 mmol) of Wilkinson's complex (**4**) dissolved in 3 ml of THF and the solution was flushed with nitrogen, and 0.1 g (0.329 mmol) of aldimine **2** was added. To the mixture was added 0.028 g (0.395 mmol) of 1-pentene and it was heated at 130°C for 6 h. The

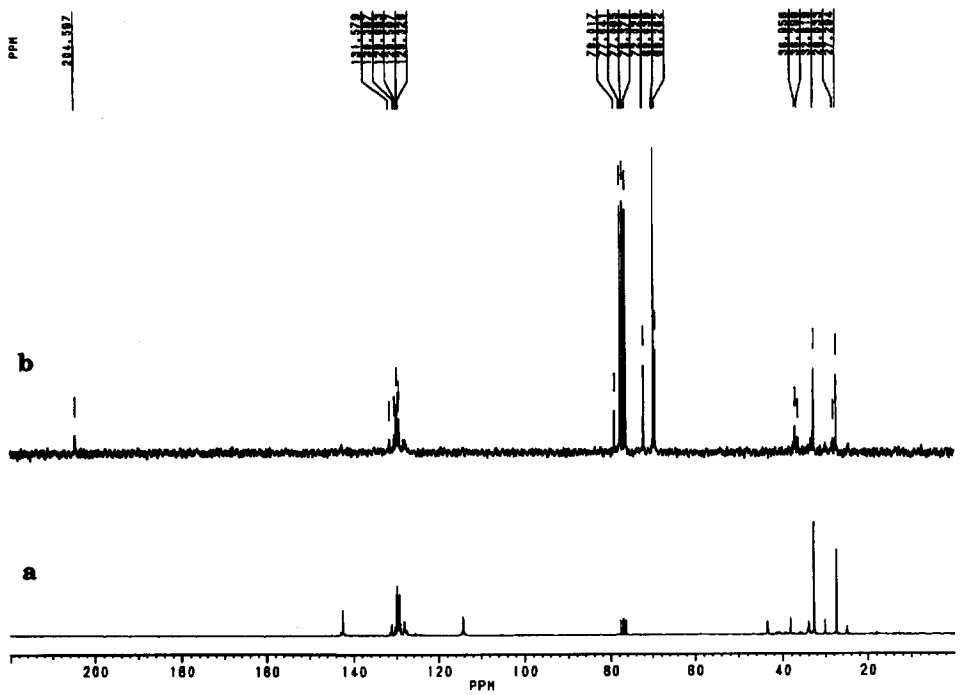

Fig. 3. ^{13}C NMR spectra of (a) PTPB **7**, and (b) vinyl group-hydroacylated PTPB **10**

reaction mixture was hydrolyzed with 10 ml of 1 N HCl aq. solution. The product was extracted with 20 ml of ether and purified by column chromatography to give 0.073 g (79% yield) of pure acylferrocene **6a**. **6a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 4.78 (t, $J = 1.94$ Hz, 2H, Hs-2,5 in substituted Cp ring), 4.48 (t, $J = 1.90$ Hz, 2H, Hs-3,4 in substituted Cp ring), 4.2 (s, 5H, Cp ring), 2.7 (t, $J = 7.2$ Hz, α-CH_2 to CO), 1.7 (m, 2H, β-CH_2), 1.3 (m, 4H, γ,δ-CH_2). 0.95 (t, $J = 6.3$ Hz, 3H, CH_3–); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 79.3 (C-1 in substituted Cp ring), 72 (C-2,5 in substituted Cp ring), 69.7 (Cp ring), 69.3 (C-3,4 in substituted Cp ring), 39.6 (α-CH_2 to CO), 31.7 (γ-CH_2 to CO), 24.3 (β-CH_2 to CO), 22.5 (δ-CH_2 to CO), 13.9 (CH_3–); IR (neat) 3100, 2960, 2930, 2860, 1670vs (C=O), 1450, 1380, 1250, 1110, 1065, 1025, 1000, 820 cm^{-1}.; mass spectra (assignment, relative intensity) 284 (M^+, 100), 228 (Fc – C(OH)=CH_2^+, 45), 213 ($FcCO^+$, 28), 185 (Fc^+, 43), 121 ($Fc^+ - C_5H_5 + 1$, 44); Anal. Calcd. for $C_{16}H_{20}OFe$: C, 67.61; H, 7.04. Found: C, 65.80; H, 7.50%.

3.3. Hydroiminoacylation of vinylferrocene (3b) with 2 and hydrolysis of the resulting ketimine

A screw-capped pressure vial was charged with 0.031 g (0.033 mmol) of Wilkinson's complex dissolved in 3 ml of toluene and the solution was flushed with nitrogen, and 0.1 g (0.33 mmol) of aldimine **2** was added. To the mixture was added 0.070 g (0.33 mmol) of **3b** and it was heated at 130°C for 6 h. The reaction mixture was hydrolyzed with 20 ml of 1 N HCl aqueous solution. The product was extracted with 20 ml of chloroform, and purified by column chromatography to give 0.078 g (56% yield) of pure acylferrocene **6b**. **6b**: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 4.76 (t, $J = 1.85$ Hz, 2H, Hs-2,5 in substituted acyl Fc ring), 4.48 (t, $J = 1.86$ Hz, 2H, Hs-3,4 in substituted acyl Fc ring), 4.14–4.06 (m, 14H, Cp rings in alkyl Fc and unsubstituted Cp ring in acyl Fc), 2.85 (A_2B_2 system, $J = 7.6$ Hz, 2H, α-CH_2 to CO), 2.77 (A_2B_2 system, $J = 7.6$ Hz, 2H, β-CH_2 to CO); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 203.4 (CO), 88.2 (C-1 in substituted alkyl Fc ring), 79.0 (C-1 in substituted acyl Fc ring), 72.1 (C-2,5 in substituted acyl Fc ring), 69.7 (unsubstituted acyl Fc ring), 69.2 (C-3,4 in substituted acyl Fc ring), 68.5 (unsubstituted alkyl Fc ring), 68.3 and 67.4 (C-2,5 and C-3,4 in substituted alkyl Fc ring), 41.5 (α-CH_2 to CO), 24.2 (β-CH_2 to CO); IR (neat) 3090, 2930, 1660vs (C=O), 1465, 1405, 1380, 1262, 1240, 1105, 1080, 1030, 1000, 870, 820 cm^{-1}.; mass spectra (assignment, relative intensity) 426 (M^+, 100), 361 ($M^+ - C_5H_5$, 27), 304 ($FcFc^+ - C_5H_5$ – 1, 12), 241 ($FcCH_2CH_2CO^+$, 31), 213 ($FcCH_2CH_2^+$, 13), 121 ($Fc^+ - C_5H_5$-1, 28); Anal. Calcd. for $C_{23}H_{22}OFe_2$: C, 64.79; H, 5.16. Found: C, 64.50; H, 5.36%.

3.4. Hydroiminoacylation of but-3-enylferrocene (3c) with 2 and hydrolysis of the resulting ketimine

A screw-capped pressure vial was charged with 0.031 g (0.033 mmol) of Wilkinson's complex dissolved in 3 ml of toluene and the solution was flushed with nitrogen, and 0.1 g (0.33 mmol) of aldimine **2** was added. To the mixture was added 0.079 g (0.33 mmol) of **3c** and it was heated at 125°C for 6 h. The reaction mixture was hydrolyzed with 10 ml of 1 N HCl aqueous solution. The product was extracted with 20 ml of chloroform, and purified by column chromatography to give 0.06 g (40% yield) of pure acylferrocene **6c**. **6c**: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 4.78 (t, $J = 1.91$ Hz, 2H, Hs-2,5 in substituted acyl Fc ring), 4.48 (t, $J = 1.90$ Hz, 2H, Hs-3,4 in substituted acyl Fc ring), 4.2 (s, 5H, unsubstituted acyl Fc ring), 4.1 (s, 5H, unsubstituted alkyl Fc ring), 4.09–3.97 (m, 4H, substituted alkyl Fc ring), 2.7 (t, $J = 7.1$ Hz, 2H, α-CH_2 to CO), 2.4 (t, $J = 7.4$ Hz, δ-CH_2 to CO), 1.8–1.5 (m, 4H, β and γ-CH_2 to CO); ^{13}C NMR (50.5 MHz, $CDCl_3$)δ (ppm) 72 (C-2,5 in substituted acyl Fc ring), 69.7 (unsubstituted acyl Fc ring), 69.3 (C-3,4 in substituted acyl Fc ring), 68.5 (unsubstituted alkyl Fc ring), 68.1 and 67.1 (C-2,5 and C-3,4 in substituted alkyl Fc ring), 39.6 (α-CH_2 to CO), 31.0 (δ-CH_2 to CO), 29.6 (β-CH_2 to CO), 24.6 (γ-CH_2 to CO); IR (neat) 3090, 2930, 2860, 1670vs (C=O), 1450, 1410, 1380, 1245, 1105, 1020, 1000, 890, 820 cm^{-1}.; mass spectra (assignment, relative intensity) 454 (M^+, 100), 389 ($M^+ - C_5H_5$, 46), 241 ($FcCH_2CH_2CH_2CH_2^+$, 18), 228 (FcC(OH)=CH_2^+, 12), 199 ($FcCH_2^+$, 10), 185 (Fc^+, 8), 121 ($Fc^+ - C_5H_5$-1, 45); Anal. Calcd. for $C_{25}H_{26}OFe_2$: C, 66.08; H, 5.73. Found: C, 67.90; H, 5.51%.

3.5. Hydroiminoacylation of phenyl terminated polybutadiene (PTPB) (7) with 2 and hydrolysis of the resulting ketimine-impregnated polymer

A screw-capped pressure vial was charged with 0.0372 g (0.0402 mmol) of Wilkinson's complex dissolved in 3 ml of toluene and the solution was flushed with nitrogen, and 0.122g (0.402 mmol) of aldimine **2** was added. To the mixture was added 0.0843 g of PTPB (**7**) and it was heated at 120°C for 6 h. The reaction mixture was hydrolyzed with 10 ml of 1 N HCl aqueous solution. The product was extracted with 20 ml of chloroform, and purified by column chromatography to give 0.099 g (67% yield based upon **7**) of **9**. 0.07 g of polymer **9** was dissolved in 3 ml of toluene and to the resulting solution was added mixtures of 0.029 g (0.032 mmol) of Wilkinson's complex and 0.097 g (0.032 mmol) of aldimine **2**. The reaction mixture was heated at 130°C for 6 h, hydrolyzed by 20 ml of 1 N HCl aqueous solution, and extracted with chloroform. The extracted organic layer was reduced in volume and

purified by column chromatography to give 0.075 g (97% yield based upon **9**) of pure ferrocene-impregnated polymer **10**: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 5.7–5.3 (br m, carbons of –CH= group), 4.77 (t, $J = 1.77$ Hz, Hs-2,5 in substituted Cp ring), 4.48 (t, $J = 1.78$ Hz, Hs-3,4 in substituted Cp ring), 4.19 (s, unsubstituted Cp ring), 2.67 (t, $J = 7.2$ Hz, α-CH_2 to CO), 2.1–1.2 (m, saturated CH_2 and CH); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 204.6 (C=O), 131.6–127.9 (n-CH=CH–), 79.0 (C-1 in substituted Cp ring of Fc), 72.0 (C-2,5 in substituted Cp ring of Fc), 69.6 (unsubstituted Cp ring of Fc), 69.3 (C-3,4 in substituted Cp ring of Fc), 36.95 (α-CH_2 to CO), 36.3–27.3 (saturated CH and CH_2); IR (neat) 3100, 3000, 2920s, 2840, 1670vs (C=O), 1450, 1380, 1250, 1110, 1050, 1000, 970, 820 cm^{-1}; Anal. Calcd. for $C_{431.0}$ $H_{533.0}$ $O_{16.2}$ $Fe_{16.2}$: C, 75.26; H, 7.75. Found: C, 73.92; H, 8.33%.

Acknowledgments

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