Journal of Organometallic Chemistry, 474 (1994) 183–189

Hydroxy-group directing hydroiminoacylation of α,ω-dien-3-ol with aldimine by Wilkinson's Complex

Chul-Ho Jun

Department of Chemistry, Yonsei University, Seoul 120-749 (South Korea)

Jong-Soo Han, Jung-Bu Kang

Agency for Defense Development, Yuseong P.O. Box 35, Taejon 305-600 (South Korea)

Sun-Il Kim

Department of Chemical Engineering, Chosun University, Kwangju 501-759 (South Korea)

(Received August 18, 1993; in revised form October 27, 1993)

Abstract

Ferrocenecarboxaldimine (**1**) reacted with 1,4-pentadien-3-ol (**2**) under Wilkinson's catalyst (**3**) to give the hydroacylated product **6** after hydrolysis of the resulting ketimine **4**. Prolonged reaction time induced the isomerization of **6** to **7**. When 1,5-hexadien-3-ol (**11**) was used, the hydroiminoacylation of the allyl alcohol group gave predominantly **12**, which showed a remarkable hydroxy-group directing effect.

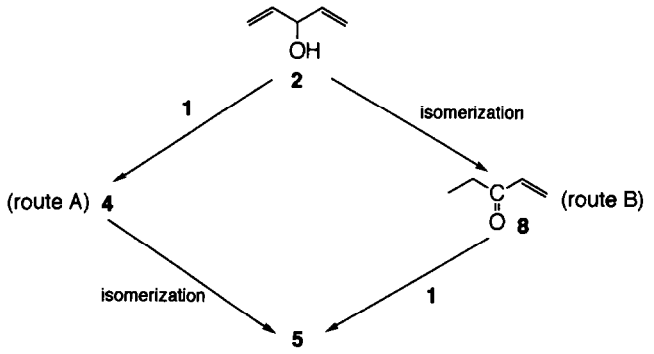
Key words: Rhodium; Iron; Hydroiminoacylation; Ferrocene; C–H activation; Aldimine

1. Introduction

Activation of the C–H bond by transition metal complexes has received much interest [1], and so has the cleavage of the aldehydic C–H bond because of its relevance to organic synthesis through conversion of aldehyde into ketone [2]. Although decarbonylation in the acylmetal intermediate formed by cleavage of the C–H bond of the aldehyde by metal, can be utilized in organic synthesis [3], it also represents a serious problem for the synthesis of ketone from aldehyde. There are ways of evading this problem of decarbonylation such as cyclometallation [4] or stabilizing the metal complex by pressurizing with CO gas under vigorous conditions [2]. For example, hydroacylation with 8-quinolinecarboxaldehyde proceeded catalytically [5] and stoichiometrically [6] through cyclometallation. Aldimine prepared by condensation of aldehyde with 2-amino-3-picoline, is also used for this purpose [7]. Carboxaldimines can be converted by cyclometallation into carboxketimines by cleavage of the C–H bond of aldimine, followed by insertion of olefin into the Rh–H bond, and reductive elimination of the iminoacyl-alkyl group. Organometallic compounds such as ferrocenecarboxaldimine can also be used for this hydroiminoacylation [8]. As an olefin substrate, the phenyl terminated polybutadiene (polymer) with a mixture of internal and terminal olefins could be used as well as the vinyl organic derivatives [9]. Another interesting substrate is an olefin with a hydroxy group. Simple ω-olefinic alcohols like allyl alcohol have been used for this hydroiminoacylation [10]. The hydroxy-group directing effect has been observed in homogeneous hydrogenation with several transition metal complexes [11]. It is quite interesting to apply an α,ω-diene with a hydroxy group for the hydroiminoacylation because the unreacted olefinic alcohol group in the resulting ketimine can be converted into the ketones through isomerization by transition metal catalysts. The hydroxy-group directing effect can be tested by using an asymmetrical hydroxy-α,ω-diene such as 1,5-hexadien-3-ol. This report explains the hydroxy-group directing hydroiminoacylation of α,ω-dien-3-ol and its derivatives, and the mechanism of isomerization of the olefinic alcohol to ketone.

Correspondence to: Dr. C.-H. Jun

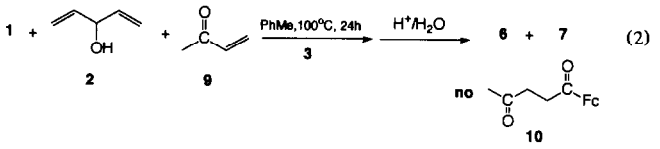
0022-328X/94/$7.00
SSDI 0022-328X(93)24267-9



Scheme 1. Mechanism of formation of **5** by hydroiminoacylation of **2** with **1** under Wilkinson's catalyst (**3**).

2. Results and discussion

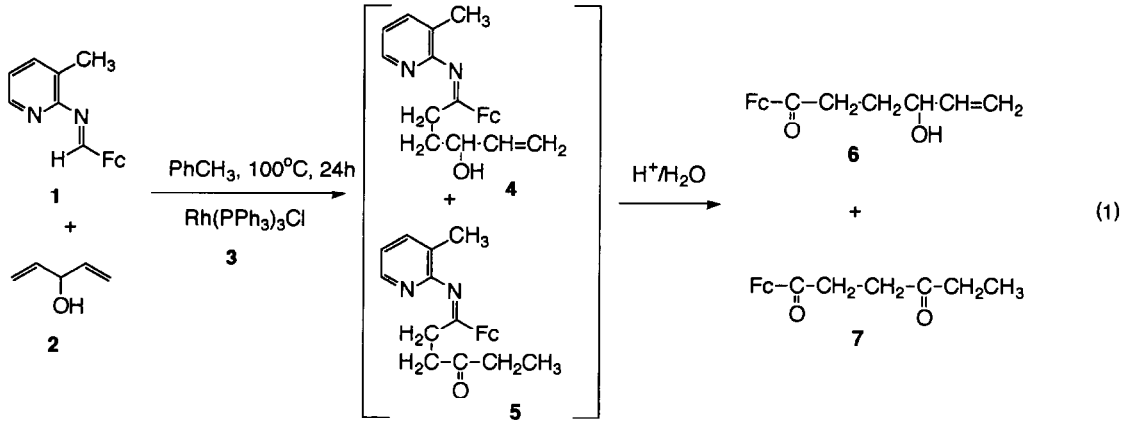
Ferrocenecarboxaldimine **1** reacted with 1,4-pentadien-3-ol (**2**) in toluene at 100°C for 24 h under 10 mol% of Wilkinson's complex (**3**) as a catalyst based upon **1**. Without isolation of the resulting ketimines, their hydrolysis with 1 N HCl aq. solution for 10 min gave 4-hydroxy-hex-5-enoylferrocene (**6**) and 4-ketohexanoylferrocene (**7**) in a 30:70 ratio in 40% yield after isolation by silica-gel choromatography. From the hydrolysis products of **6** and **7**, the prehydrolyzed ketimines, **4** and **5**, were easily inferred. The mechanism of formation of **4** can be explained by direct hydroiminoacylation of **2**, while that of **5** can be explained by two possible routes (Scheme 1). The first is the hydroiminoacylation of **2** to form **4**, followed by isomerization of the allyl alcohol group in **4** to give **5** (route A). The other is the hydroiminoacylation of ethyl vinyl ketone (**8**), formed by isomerization of **2**, with **1** to give **5** (route B). There have been many reports of isomerization of allyl alcohol to ketone by transition metals [12]. Without **1**, compound **2** was completely transformed into **8** under Wilkinson's complex **3** (0.5 mol% based on **2**) at 100°C within 6 h. To test the feasibility of hydroiminoacylation of vinyl ketone with **1** (**8** to **5** in Scheme 1), a mixture of methyl vinyl ketone (**9**) and **2** was allowed to react with **1** under reaction conditions identical to eqn. (1). Only a mixture of **6** and **7** was obtained after hydrolysis of the resulting reaction mixtures, leaving **9** unchanged. The hydroacylated product **10** was not obtained at all.



(2)

The finding that with **1** no hydroiminoacylation of **9** takes place eliminates the possibility of route B. The mechanism of route A is also confirmed by the time-dependent distribution of products. Hydroiminoacylation of **2** with **1** is complete within 3 h to give **6** exclusively after hydrolysis without leaving the starting aldimine **1** or its hydrolyzed form, the aldehyde. The isomerization of the allyl alcohol **6** into the ketone **7** starts just after completion of hydroiminoacylation of **2**, and isomerization of **6** into **7** is 70% complete within 24 h (Fig. 1). Unfortunately, entire isomerization of **6** to **7** has not been achieved, maybe due to decomposition of the catalyst.

The hydroxy group is known to direct very strongly compared with olefinic groups. However, since there is no alternative olefin in the symmetrical α,ω-dien-3-ol, in whose presence the hydroiminoacylation of **2** generates only **4**, the directing effect of the hydroxy group cannot be determined. Therefore this effect should be tested with an asymmetrical hydroxy-α,ω-diene having an allyl alcohol group and a homoallyl alcohol group, such as 1,5-hexadien-3-ol (**11**). Compound **11** was al-



(1)

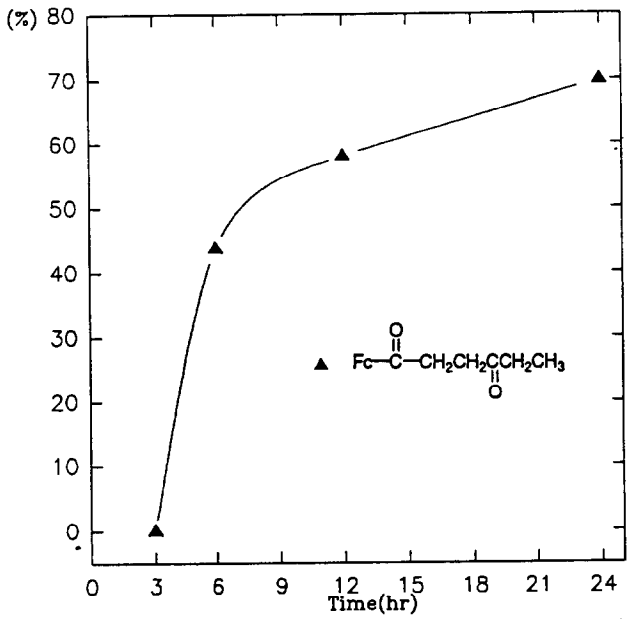
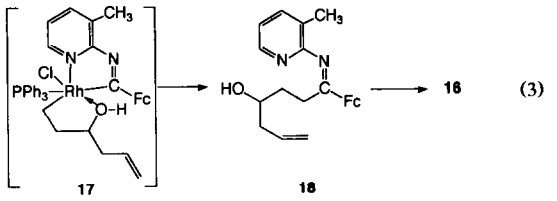


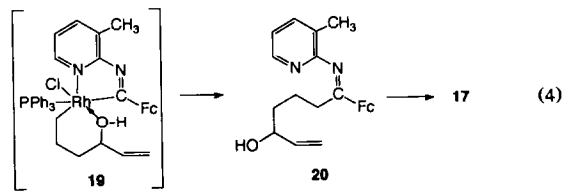
Fig. 1. Catalytic isomerization of **4** into **5** in toluene at 100°C after completion of hydroiminoacylation of **2** with **1** within 3 h under catalyst **3**. The conversion rate of **7** based on **6**, hydrolysis products of the resulting ketimine **4** and **5**, was determined by GC-MSD.

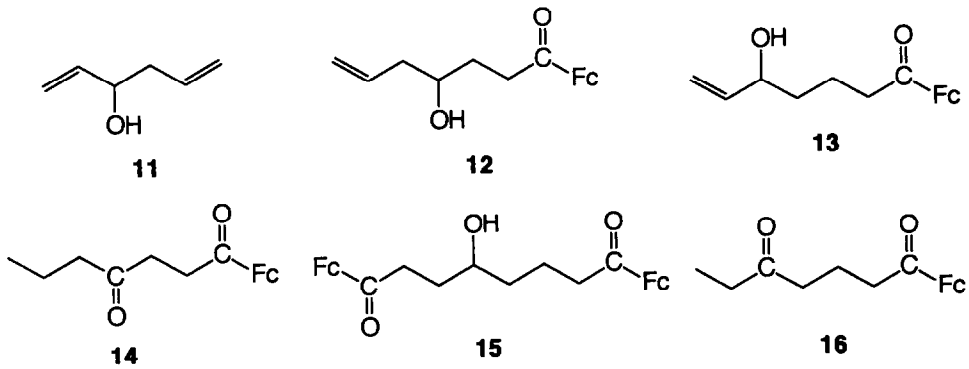
lowed to react with **1** at 110°C for 3 h under 10 mol% of Wilkinson's catalyst based upon **1**, followed by hydrolysis to give a mixture of 4-hydroxy-hept-6-enoylferrocene (**12**) and 5-hydroxy-hept-6-enoylferrocene (**13**) in a 94:6 ratio in 69% yield after chromatographic isolation. Under reaction conditions which were identical except for a reaction time of 48 h, the reaction of **11** with **1** produced a mixture of **12**, **13**, **14** and **15** in a 50:7:36:7 ratio in 69% yield after hydrolysis [13*]. This means that prolonged reaction time promotes the isomerization of **12** into **14**. The result that the major product was **12** rather than **13** suggests that the most plausible intermediate would be a stable 5-membered



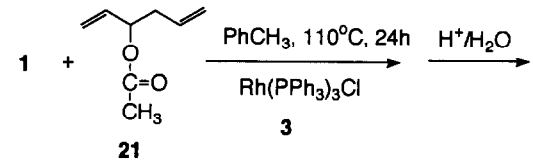
metallacycle intermediate **17**. The minor product distribution of **13** can be explained as follows. Compound **13** must be formed from an intermediate **19** with a 6-membered metallacyclic system which is less stable than a 5-membered one such as **17**. From the ratio of **12** to **13** of 94:6, a strong hydroxy-group directing effect can be measured, which favours **17** over **19**. If there is no such effect, a 1:1 ratio of **12** to **13** should be observed in the product distribution. The above result explains why the hydroiminoacylation takes place at the allyl alcohol group rather than at the homoallyl alcohol group in 1,5-hexadien-3-ol.

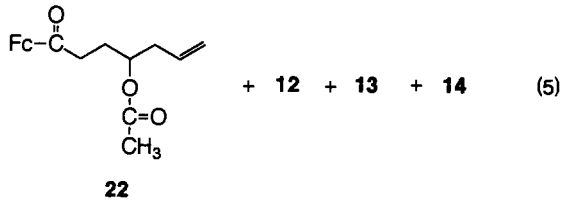
Although the hydroxy group is protected by the acetyl group, a strong directing effect was still observed. Hydroiminoacylation of 3-acetoxy-1,5-hexadiene (**21**) under the catalyst **3** at 110°C for 24 h in toluene, and the hydrolysis of the resulting ketimines in 1 N HCl aq. solution gave **22**, **12**, **14** and **13** in a 43:39:14:4 ratio in 61% yield after chromatographic isolation. Since **12** and **14** might be derived from **22**,





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





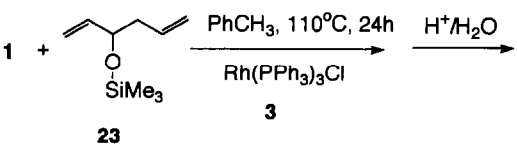
+ 12 + 13 + 14 (5)

the allyl alcohol group directing effect for the hydroiminoacylation can be deduced as 96% for **22**.

Hydroiminoacylation of 3-timethylsilyloxy-1,5-hexadiene (**23**), and the subsequent hydrolysis of the resulting ketimines produced **12**, **13** and **15** in a 78:8:14 ratio in 64% yield. The silicone–oxygen bond was easily hydrolyzed under acidic conditions [14]. Since **14**, the isomer of **12**, was not detected in the final products at all, it could be easily inferred that the silyl group lost its protection during the hydrolysis after hydroiminoacylation. In the case of **23**, the directing effect of the allylether group was determined as 91% which is a little lower than in **11** (93%) and **21** (96%). The reason must be a steric hindrance of the bulky trimethylsilyl group compared with the OH group in **11** or the acetoxy group in **21**.

3. Conclusion

Hydroiminoacylation of α,ω-dien-3-ol with **1** has been successfully achieved by means of Wilkinson's catalyst. In the initial stages of the reaction, only the directly hydroiminoacylated product with an olefinic alcohol group has been observed, and prolonged reaction time induces the isomerization of the olefinic alcohol group to the ketone group. In the case of an asymmetrical α,ω-dien-3-ol such as 1,5-hexadien-3-ol,



12 + 13 + 15 (6)

the hydroxy-group directing effect, which favours the hydroiminoacylation of the allyl alcohol group over that of the homoallyl alcohol group, has been observed to as great an extent as 94%. Even though this hydroxy group is protected by the acetyl group or the trimethylsilyl group, similar directing effects were observed to the extent of 96% and 91%, respectively. From the above results, it is possible to synthesize the 4-hydroxy ω-alkanoylferrocene selectively from ferrocenecarboxaldehyde since hydroiminoacylation takes place in the allyl alcohol group site.

Further directing effects as they occur in hydroiminoacylation are under study.

4. Experimental section

Compound **1** was prepared by the published procedure [7]. Wilkinson's complex (**3**), 1,4-pentadien-3-ol (**2**), 1,5-hexadien-3-ol (**11**), 2-amino-3-picoline, ferrocenecarboxaldehyde and methyl vinyl ketone (**8**) were purchased (Aldrich) and used without further purification. All solvents were distilled and stored over molecular sieves (4 Å). NMR spectra were recorded with a Bruker AC-200 (200 MHz) spectrometer. The chemical shift values (δ) of the ^{1}H NMR and ^{13}C NMR resonances were expressed in ppm relative to internal Me_4Si. Infrared spectra were recorded with Nicolet MX-S FT-IR and Bruker IFS 88 FT-IR spectrophotometers. Mass spectra were obtained with a Hewlett-Packard HP 5971A mass spectrometer equipped with a HP 5890 series II Gas Chromatograph. Column chromatography was performed on Merck Silica Gel 60.

4.1. Hydroiminoacylation of 1,4-pentadien-3-ol (2) with 1 and hydrolysis of the resulting ketimine

A screw-capped pressure vial was charged with 0.031 g (0.0329 mmol) of Wilkinson's complex (**3**) dissolved in 3 ml of toluene, the solution flushed with nitrogen, and 0.1 g (0.329 mmol) of **1** was added. To the mixture was added 0.055 g (0.658 mmol) of **2** followed by heating at 100°C for 24 h. The reaction mixture was hydrolyzed with 10 ml of 1 N HCl aq. solution for 10 min. The products were extracted with 20 ml of ether and purified by column-chromatography to give 0.0392 g (40% yield) of 4-hydroxy-hex-5-enoylferrocene (**6**) and 4-keto-hexanoylferrocene (**7**) in a 30:70 ratio. **6**: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm), 5.9 (m, 1H, –CH=), 5.27 (ABX system, 2H, $=CH_2$), 4.8 (t, $J = 2.01$ Hz, 2H, H-2 and H-5 in substituted Cp ring), 4.51 (t, $J = 2.02$ Hz, 2H, H-3 and H-4 in substituted Cp ring), 4.21 (s, 5H, unsubstituted Cp ring), 4.24 (m, 1H, CH–O), 2.91 (t, $J = 7.0$ Hz, α-CH_2 to CO), 2.62 (br, 1H, OH), 1.92 (m, 2H, β-CH_2 to CO); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 205.2 (*C*=O), 140.8

(-*C*H=), 114.7 (=*C*H_2), 78.7 (C-1 in substituted Cp ring), 72.4 (*C*-OH), 72.1 (C-3 and C-4 in substituted Cp ring), 69.9 (Cs of unsubstituted Cp ring), 69.4 (C-2 and C-5 in substituted Cp ring), 35.4 (α-*C*H_2 to CO), 30.3 (β-*C*H_2 to CO); IR (neat) 3420 (br, OH), 3100, 2920, 1660 (s, C=O), 1455, 1380, 1260, 1110, 1055, 1000, 925, 825 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 281 ($M+1-H_2O$, 22.1), 280 (M^+-H_2O, 100), 213 ($FcCO^+$, 12.5), 186 (FcH, 33.7), 185 (Fc^+, 24), 121 (FcH-C_6H_5, 26.9); Anal. Calcd. for $C_{16}H_{18}O_2Fe$: C, 64.45; H, 6.08. Found: C, 63.6; H, 6.10%. **7**: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 4.81 (t, $J = 1.90$ Hz, 2H, H-3 and H-4 in substituted Cp ring), 4.50 (t, $J = 1.91$ Hz, 2H, H-2 and H-5 in substituted Cp ring), 4.3 (s, 5H, unsubstituted Cp ring), 3.07 (t, $J = 5.8$ Hz, 2H, α-CH_2 to CpCO), 2.8 (t, $J = 5.7$ Hz, 2H, β-CH_2 to CpCO), 2.6 (q, $J = 7.3$ Hz, 2H, CH_2 in ethyl group), 1.1 (t, $J = 7.3$ Hz, 3H, CH_3); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 210.4 (Cp-C=O), 202.7 ($(CH_2)_2$-C=O), 77.6 (C-1 in substituted Cp ring), 72.1 (C-3 and C-4 in substituted Cp ring), 69.9 (Cs of unsubstituted Cp ring), 69.2 (C-2 and C-5 in substituted Cp ring), 36.2 (α-CH_2 to CpCO), 35.3 (β-*C*H_2 to CpCO), 33.4 (*C*H_2CH$_3$), 7.9 (*C*H_3); IR (neat) 3100, 2980, 2940, 1715 (s, $(-CH_2)_2$**C=O**), 1670 (s, Cp*C=O*), 1450, 1410, 1380, 1250, 1110, 1060, 825 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 299 ($M^+ + 1$, 20), 298 (M^+, 100), 241 (11), 213 ($FcCO^+$, 17), 186 (FcH, 83), 185 (Fc^+, 17), 121 (FcH-C_6H_5, 35); Anal. Calcd. for $C_{16}H_{18}O_2Fe$: C, 64.45; H, 6.08. Found: C, 63.17; H, 6.02%.

4.2. Competitive hydroiminoacylation of 1,4-pentadien-3-ol (2) and methyl vinyl ketone (9) with 1 and hydrolysis of the resulting ketimine

A screw-capped pressure vial was charged with 0.032 g (0.0329 mmol) of Wilkinson's complex (**3**) dissolved in 3 ml of toluene and the solution flushed with nitrogen, and 0.1 g (0.329 mmol) of **1** was added. To the solution was added 0.0274 g (0.329 mmol) of **2** and 0.023 g (0.329 mmol) of **9**. The resulting mixtures were heated at 100°C for 3 h and then hydrolyzed with 10 ml of 1 N HCl aq. solution for 10 min. The resulting mixture was extracted with 20 ml of ether, and dried *in vacuo* to give a dark brown residue. The residue was analyzed by GC-MSD, and only **6** was determined.

4.3. Hydroiminoacylation of 1,4-pentadien-3-ol (2) with 1 for 3 h and hydrolysis of the resulting ketimine

(A). A screw-capped pressure vial was charged with 0.031 g (0.0329 mmol) of Wilkinson's complex (**3**) dissolved in 3 ml of toluene and the solution flushed with nitrogen, and 0.1 g (0.329 mmol) of **1** was added. To the mixture was added 0.056 g (0.669 mmol) of **2**. The reaction mixture was heated at 100°C for 3 h. The reaction mixture was hydrolyzed with 10 ml of 1 N HCl aq. solution for 10 min. The products were extracted with 20 ml of ether, and purified by column-chromatography to give 0.0554 g (56% yield) of **6**.

(B). Under identical reaction conditions as those for (A), the reaction proceeded for 24 h. Samples were taken at 3 h, 6 h, 12 h and 24 h, hydrolyzed by 1 N HCl solution and extracted with ether. The extracted ether solutions were analyzed by GC-MSD, and the ratio of **6** and **7** was calculated as 100:0 (3 h), 56:44 (6 h), 42:58 (12 h), 30:70 (24 h), as shown in Fig. 1.

4.4. Hydroiminoacylation of 1,5-hexadien-3-ol (11) with 1 at 100°C for 3 h and hydrolysis of the resulting ketimine

A screw-capped pressure vial was charged with 0.031 g (0.0329 mmol) of Wilkinson's complex (**3**) dissolved in 3 ml of toluene and flushed with nitrogen, then 0.1 g (0.329 mmol) of **1** was added. To the mixture was added 0.0645 g (0.658 mmol) of **11** followed by heating at 110°C for 3 h. The reaction mixture was hydrolyzed with 10 ml of 1 N HCl aq. solution for 10 min. The products were extracted with 20 ml of ether, and purified by column-chromatography to give 66.4 mg (64.7% yield) of 4-hydroxy-hep-6-enoylferrocene (**12**) and 4.5 mg (4.2% yield) of 5-hydroxy-hep-6-enoylferrocene (**13**) in a 94:6 ratio in 69% overall yield. **12**: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm), 5.85 (m, 1H, -CH=), 5.16 (ABX system, 2H, =CH_2), 4.8 (t, $J = 1.7$ Hz, 2H, H-2 and H-5 in substituted Cp ring), 4.51 (t, $J = 1.9$ Hz, 2H, H-3 and H-4 in substituted Cp ring), 4.21 (s, 5H, unsubstituted Cp ring), 3.74 (br, 1H, CH-O), 2.92 (t, $J = 7.0$ Hz, α-CH_2 to CO), 2.65 (brd, 1H, OH), 2.28 (m, 2H, -C*H*$_2$-C=) 1.95 (m, 2H, β-CH_2 to CO); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 205.1 (*C*=O), 134.7 (-*C*H=), 117.9 (=*C*H_2), 78.7 (C-1 in substituted Cp ring), 72.3 (*C*-OH), 70.3 (C-3 and C-4 in substituted Cp ring), 69.8 (Cs of unsubstituted Cp ring), 69.3 (C-2 and C-5 in substituted Cp ring), 42.3 (-*C*H_2-CH=), 35.9 (α-*C*H_2 to CO), 30.7 (β-*C*H_2 to CO); IR (neat) 3420 (br, OH), 3080, 2920, 1650 (s, C=O), 1450, 1410, 1380, 1250, 1100, 1050, 1020, 1000, 912, 890, 820 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 294 ($M^+ - H_2O$, 100), 277 (10), 252 (40), 228 ($FcC(=CH_2)OH^+$), 213 ($FcCO^+$, 10), 186 (FcH, 28), 185 (Fc^+, 18), 121 (FcH-C_6H_5, 56); Anal. Calcd. for $C_{17}H_{20}O_2Fe$: C, 65.37; H, 6.46. Found: C, 64.10; H, 6.54%. **13**: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm), 5.90 (m, 1H, -CH=), 5.19 (ABX system, 2H, =CH_2), 4.79 (t, $J = 1.91$ Hz, 2H, H-2 and H-5 in substituted Cp ring), 4.50 (t, $J = 1.9$ Hz, 2H, H-3 and H-4 in substituted Cp

ring), 4.19 (s, 5H, unsubstituted Cp ring), 4.18 (m, 1H, C*H*–O), 2.77 (t, $J = 7.1$ Hz, α-CH_2 to CO), 1.9–1.4 (m, 4H, β and γ-CH_2 to CO); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 141.0 (–*C*H=), 114.7 (=*C*H_2), 72.8 (*C*–OH), 72.1 (C-3 and C-4 in substituted Cp ring), 69.8 (Cs of unsubstituted Cp ring), 69.3 (C-2 and C-5 in substituted Cp ring), 39.3 (γ-*C*H_2–), 36.7 (α-*C*H_2 to CO), 29.7 (β-CH_2 to CO); IR (neat) 3440 (br, OH), 3100, 2925, 2860, 1660 (s, C=O), 1460, 1383, 1250, 1108, 1045, 1030, 1000, 920, 890, 825 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 294 ($M^+ - H_2O$, 100), 240 (30.5), 213 ($FcCO^+$, 41), 185 (Fc^+, 34), 121 (FcH–C_6H_5, 62); Anal. Calcd. for $C_{17}H_{20}O_2Fe$: C, 65.37; H, 6.46. Found: C, 63.26; H, 6.43%.

4.5. Hydroiminoacylation of 1,5-hexadien-3-ol (11) with 1 at 100°C for 48 h and hydrolysis of the resulting ketimine

Under reaction conditions identical with those of 4.4, the reaction proceeded for 48 h and the reaction mixture was hydrolyzed with 10 ml of 1 N HCl aq. solution for 10 min. After ether extraction, column-chromatography purification gave a mixture of 35.7 mg (34.8% yield) of **12**, 5 mg (4.9% yield) of **13**, 25.2 mg (24.5% yield) of 4-ketoheptanoylferrocene (**14**) and 8.2 mg (5.0% yield) of 3-hydroxy-1,6-hexadiyl acylferrocene (**15**) in a 50:7:36:7 ratio in 69% overall yield [13]. **14**: ^1H NMR (200 MHz, $CDCl_3$) δ (ppm), 4.8 (t, $J = 1.9$ Hz, 2H, H-2 and H-5 in substituted Cp ring), 4.49 (t, $J = 1.9$ Hz, 2H, H-3 and H-4 in substituted Cp ring), 4.26 (s, 5H, unsubstituted Cp ring), 3.06 (t, $J = 6.2$ Hz, α-CH_2 to FcCO), 2.76 (t, $J = 6.2$ Hz, 2H, β-CH_2 to FcCO), 2.53 (t, $J = 7.3$ Hz, 2H, COC*H*$_2$CH$_2$CH$_3$), 1.65 (m, 2H, COCH$_2$C*H*$_2$CH$_3$), 0.92 (t, $J = 7.3$ Hz, 3H, CH_3); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 209.9 (Fc*C*=O), 202.7 (–CH$_2$*CO*CH$_2$–), 72.1 (C-3 and C-4 in substituted Cp ring), 69.9 (Cs of unsubstituted Cp ring), 69.2 (C-2 and C-5 in substituted Cp ring), 45.0 (FcCO*C*H$_2$–), 35.7 (β-*C*H_2 to FcCO), 33.3 (CO*C*H$_2$-CH$_2$CH$_3$), 17.4 (COCH$_2$*C*H$_2$CH$_3$), 13.8 (*C*H_3); IR (neat) 3100, 2975, 2960, 2880, 1720 (s, CH$_2$*CO*CH$_2$), 1673 (s, C=O), 1460, 1400, 1383, 1263, 1240, 1128, 1110, 1065, 1030, 1000, 880, 825 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 313 ($M^+ + 1$, 21), 312 (M^+, 100), 269 ($M^+ - C_3H_7$, 4), 247 ($M^+ - C_5H_5$, 3), 241 ($M^+ - C_3H_7CO$, 15), 213 ($FcCO^+$, 18), 186 (FcH, 99), 185 (Fc^+, 21), 121 (FcH-C_6H_5, 42). **15**: ^1H NMR (200 MHz, $CDCl_3$) δ (ppm), 4.8 (t, $J = 2.0$ Hz, 4H, H-2 and H-5 in substituted Cp ring in 1- and 6-acylferrocenyl groups), 4.50 (t, $J = 2.0$ Hz, 4H, H-3 and H-4 in substituted Cp ring in 1- and 6-acylferrocenyl groups), 4.21 and 4.20(s, 10H, unsubstituted Cp ring in 1- and 6-acylferrocenyl groups), 3.74 (br, 1H, CH–O), 2.93 (t, 2H, –COC*H*$_2$CH$_2$CH(OH)), 2.77 (t, 2H, –COC*H*$_2$-CH$_2$CH$_2$CH(OH)), 2.01–1.5 (m, 6H, –C*H*$_2$C*H*$_2$CH-(OH)C*H*$_2$–); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 72.3 and 72.2 (C-3 and C-4 in substituted Cp ring on 1- and 6-acylferrocenyl groups), 71.0 (*C*HOH), 69.9–69.3 (Cs of unsubstituted Cp ring, C-2 and C-5 in substituted Cp ring in 1- and 6-acylferrocenyl groups), 39.3 (C-1 in 3-hydroxy-1,6-hexadiyl acylferrocene), 37.5 (C-6 in 3-hydroxy-1,6-hexadiyl acylferrocene), 36.1 (C-2 in 3-hydroxy-1,6-hexadiyl acylferrocene), 31.3 (C-4 in 3-hydroxy-1,6-hexadiyl acylferrocene), 20.2 (C-5 in 3-hydroxy-1,6-hexadiyl acylferrocene); IR (neat) 3440 (br, OH), 3080, 2920, 1660 (s, C=O), 1450, 1400, 1370, 1250, 1100, 1045, 1020, 995, 890, 835 cm^{-1}.

4.6. Hydroiminoacylation of 3-acetoxy-1,5-hexadien (21) with 1 at 100°C for 24 h and hydrolysis of the resulting ketimine

A screw-capped pressure vial is charged with 0.031 g (0.0329 mmol) of Wilkinson's complex (**3**) dissolved in 3 ml of toluene and the solution was flushed with nitrogen, and then 0.1 g (0.329 mmol) of **1** was added. To the mixture was added 0.068 g (0.486 mmol) of **21** followed by heating at 110°C for 24 h. The reaction mixture was hydrolyzed with 10 ml of 1 N HCl aq. solution for 10 min. The products were extracted with 20 ml of ether, and purified by column-chromatography to give a mixture of 30.1 mg (26% yield) of 3-acetoyl-hept-6-enoylferrocene (**22**), 24.5 mg (23.9% yield) of **12**, 8.4 mg (8.2% yield) of **14** and 2.6 mg (2.53% yield) of **13** in a 43:39:14:4 ratio in 61% overall yield. **22**: ^1H NMR (200 MHz, $CDCl_3$) δ (ppm), 5.77 (m, 1H, –CH=), 5.12 (ABX system, 2H, =CH_2), 4.77 (t, $J = 1.8$ Hz, 2H, H-2 and H-5 in substituted Cp ring), 4.49 (t, $J = 1.7$ Hz, 2H, H-3 and H-4 in substituted Cp ring), 4.19 (s, 5H, unsubstituted Cp ring), 2.74 (t, $J = 7.6$ Hz, α-CH_2 to FcCO), 2.38 (t, $J = 6.8$ Hz, 2H, *C*H_2–CH=), 2.05 (s, 3H, –COCH_3), 2.14–1.83 (m, 2H, β-CH_2 to CO); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 203.3 (Fc*C* = O), 133.3 (–*C*H=), 118.0 (=*C*H_2), 72.2 (C-3 and C-4 in substituted Cp ring), 69.8 (Cs of unsubstituted Cp ring), 69.3 (C-2 and C-5 in substituted Cp ring), 38.8 (FcCO*C*H$_2$-), 35.4 (β-*C*H_2 to FcCO), 28.2 (*C*H$_2$–C=), 21.2 (*C*H$_3$CO); IR (neat) 3082, 2927, 1734 (s, CH$_3$*CO*), 1668 (s, Fc*CO*), 1412, 1376, 1243, 1107, 920, 824, 721, 696 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 355 ($M^+ + 1$, 20), 354 (M^+, 100), 294 ($M^+ - CH_3COOH$, 8), 271 (FcCOCH$_2$CH$_2$CHO + 1, 6), 228 (FcC(OH)=CH$_2^+$ + 1, 8), 213 ($FcCO^+$, 19), 186 (FcH^+, 16), 185 (Fc^+, 14); Anal. Calcd. for $C_{19}H_{22}O_3Fe$: C, 64.42; H, 6.26. Found: C, 64.50; H, 6.29%.

4.7. Hydroiminoacylation of 3-trimethylsilyl-1,5-hexadien (23) with 1 at 100°C for 24 h and hydrolysis of the resulting ketimine

A screw-capped pressure vial is charged with 0.031 g (0.0329 mmol) of Wilkinson's complex (**3**) dissolved in 3 ml of toluene and the solution was flushed with nitrogen, and then 0.1 g (0.329 mmol) of **1** was added. To the mixture was added 0.105 g (0.618 mmol) of **23** followed by heat at 110°C for 24 h. The reaction mixture was hydrolyzed with 10 ml of 1 N HCl aq. solution for 10 min. The products were extracted with 20 ml of ether, and purified by column-chromatography to give a mixture of 50.8 mg (50% yield) of **12**, 5.5 mg (5.4% yield) of **13** and 15.8 mg (8.7% yield) of **15** in a 78:8:14 ratio in 64% overall yield.

References and notes

1 (a) M.L.H. Green, *Pure Appl. Chem., 57* (1985) 1897; (b) R.H. Crabtree, *Chem. Rev., 85* (1985) 245.

2 T. Kondo, M. Akazome, Y. Tsuji and Y. Watanabe, *J. Org. Chem., 55* (1990) 1286.

3 (a) F.J. McQuillin, D.G. Parker and G.R. Stephenson, *Transition metal organometallics for organic synthesis*, Cambridge University Press, Cambridge, 1991, p. 306; (b) J. Tsuji and K. Ohno, *Tetrahedron Lett.*, (1965) 3669.

4 (a) D.P. Fairlie and B. Bosnich, *Organometallics, 7* (1988) 936; (b) *Organometallics, 7* (1988) 946.

5 C.-H. Jun and J.-B. Kang, *Bull Korean Chem. Soc., 14* (1993) 153.

6 (a) J.W. Suggs, *J. Am. Chem. Soc., 100* (1978) 640; (b) C.-H. Jun and J.-B. Kang, *Bull. Korean Chem. Soc., 10* (1989) 114; (c) C.-H. Jun, *Bull Korean Chem. Soc., 10* (1989) 404; (d) C.-H. Jun and Y.-G. Lim, *Bull Korean Chem. Soc., 10* (1989) 468; (e) C.-H. Jun, *J. Organomet. Chem., 390* (1990) 361.

7 (a) J.W. Suggs, *J. Am. Chem. Soc., 101* (1979) 489; (b) A. Albinati, C. Arz and P.S. Pregosin, *J. Organomet. Chem., 335* (1987) 379; (c) C.-H. Jun, *Bull Korean Chem. Soc., 11* (1990) 187; (d) C.-H. Jun and J.-B. Kang, *Bull Korean Chem. Soc., 14* (1993) 287.

8 C.-H. Jun, J.-B. Kang and J.-Y. Kim, *Bull. Korean Chem. Soc., 12* (1991) 259.

9 C.-H. Jun, J.-B. Kang and J.-Y. Kim, *J. Organomet. Chem., 458* (1993) 193.

10 C.-H. Jun, J.-B. Kang and J.-Y. Kim, *Tetrahedron Lett., 34* (1993) 6431.

11 (a) R.H. Crabtree and M.W. Davies, *J. Org. Chem., 51* (1986) 2655; (b) J.M. Brown and S.A. Hall, *J. Organomet. Chem., 285* (1985) 333; (c) D.A. Evans and M.M. Morrissey, *J. Am. Chem. Soc., 106* (1984) 3866; (d) G. Stork and D.E. Kahne, *J. Am. Chem. Soc., 105* (1983) 1072; (e) J.M. Brown and R.G. Naik, *J. Chem. Soc., Chem. Commun.*, (1982) 348.

12 (a) H. Alper and K. Hachem, *J. Org. Chem., 45* (1980) 2269; (b) R. Damico and T.J. Logan, *J. Org. Chem., 32* (1967) 2356; (c) C.S. Chin, J. Park, C. Kim, S.Y. Lee, J.H. Shin and J.B. Kim, *Catalysis Lett., 1* (1988) 203; (e) ref. (3a), p. 34.

13 A trace amount of 5-keto-heptanoylferrocene (**16**) was determined by GC-MSD in the reaction products. Since **16** was difficult to isolate owing to the small quantity, **13** was transformed into **16** by Wilkinson's complex for characterization. **16**: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm), 4.8 (t, 2H, H-2 and H-5 in substituted Cp ring), 4.50 (t, 2H, H-3 and H-4 in substituted Cp ring), 4.20 (s, 5H, unsubstituted Cp ring), 2.75 (t, J = 7.1 Hz, α-CH_2 to FcCO), 2.55 (t, J = 6.6 Hz, 2H, β-CH_2 to FcCO), 2.45 (q, J = 7.3 Hz, 2H, $COCH_2CH_3$), 2.02 (m, 2H, $FcCH_2CH_2CH_2CO$), 1.07 (t, J = 7.3 Hz, 3H, CH_3); IR (neat) 2930, 2850, 1710 (s, CH_2COCH_2), 1665 (s, Fc*C*=*O*), 1455, 1410, 1375, 1250, 1110, 1060, 1030, 1000, 895, 825 cm^{-1}; mass spectrum, m/e (assignment, relative intensity) 313 (M^+ + 1, 24), 312 (M^+, 100), 241 ($FcCOCH_2CH_2^+$, 19), 229 ($FcC(OH)CH_2^+$ + 1, 33), 213 ($FcCO^+$, 12), 186 (FcH, 20), 185 (Fc^+, 18), 121 ($FcH-C_6H_5$, 50).

14 E.W. Colvin, *Silicon Reagents in Organic Synthesis*, Academic Press, London, 1988, p. 94.