As stated earlier in this report, the unique σ-base and π-acid character of 9S3 might be attributed to the stability of [M(CO)$_3$(9S3)] toward oxidative decarbonylation reaction.[19] A relative measure of π-acidity of L in a series of isoelectronic complexes LM(CO)$_3$, estimated by the comparison of ν_{co} in Table 2, suggests the π-acidity decreases in the order C_6H_6, 12P3, 9S3, $C_2B_9H_{11}^{2-}$, $C_5H_5^-$, $HBPz_3^-$, and 9N3. With this trend in mind, it is worth noting that in case of $L = C_2B_9H_{11}^{2-}$[24] and $C_5H_5^-$,[26] oxidative decarbonylation reactions have been observed. Further studies on the reactivities of three 9S3 complexes and the development of heteroleptic crown thioether chemistry are under investigation.

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New Synthesis of Acylferrocene from Ferrocenecarboxaldehyde by Rh(I) Catalyst

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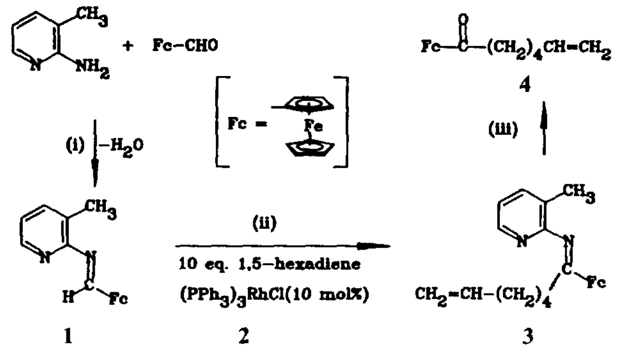
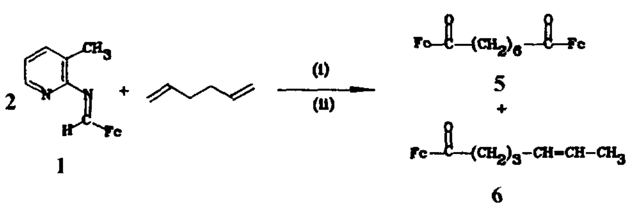
The C-H bond activation by transition metal complexes has been one of the recent interests in organometallic chemistry.[1] It has ben reported that C-H bond activation of the aldimine by Rh(I) generated iminoacylrhodium(III) hydride complex which inserted mono-olefin and conjugate dienes to form iminoacylrhodium(III) alkyl[2] and alkyl-substituted η^3-allyl complexes,[3] respectively. They were readily reductive-eliminated to give corresponding ketimines, potential precursors for ketone since hydrolysis of them produce ketones. Consequently aldehyde can be easily converted to ketone



Scheme 1. (i) *p*-toulenesulfonic acid, benzene at reflux. (ii) toluene, 110℃, 6 hrs (iii) 0.1 N $HCl/CHCl_3$.

through the aldimine C-H bond activation. Acylferrocenes are among the most useful intermediates in the preparation of other ferrocene derivatives. However there are some limitationes to make acylferrocens depending on the reaction conditions.[4] This report describes new type of synthetic methods of acylferrocenes from ferrocenecarboxaldehyde and 1,5-hexadiene using 2-amino-3-methylpyridine as a cyclometallation tool.

The aldimine **1** could be prepared in high yield from 2-amino-3-methyl pyridine and ferrocenecarboxaldehyde in benzene at reflux in the presence of *p*-toluenesulfonic acid with continuous removal of water (Scheme 1).[5] The aldimine **1** reacted with 1,5-hexadiene in toluene at 110℃ for 6 hrs under $(PPh_3)_3RhCl$ catalyst (10 mol%) in a screw-capped vial. The chromatographic isolation of the resulting reaction mixture gave the hex-5′-enyl ketimine **3** in 58% yield (580% yield based on Rh catalyst). **3**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.24 (dd, 1H, H-6 of pyridine group), 7.45 (d, J=7.3 Hz, 1H, H-4 of pyridine group) 6.9 (dd, 1H, H-5 of pyridine group), 5.7 (m, 1H, -CH=) 4.92 (ABX pattern, 2H, $=CH_2$) 4.8 (brs, 2H, 2,5-Hs of substituted ferrocenyl Cp) 4.44 (brs, 2H, 3,4-Hs of substituted Cp) 4.2 (s, 5H, unsubstituted ferrocenyl Cp) 2.4 (t, J=8.2 Hz, 2H, α-CH_2 to CN) 2.13 (s, 3H, $-CH_3$) 1.92 (q, J=7 Hz, 2H, $=C-CH_2$) 1.61 (m, 2H, β-CH_2 to CN) 1.32 (m, 2H, γ-CH_2 to CN); ^{13}C-NMR (50.5 MHz, $CDCl_3$) δ (ppm) 145.9, 118.5 (Cs of pyridine group) 137.5 (C of -CH=) 114.6 (C of $=CH_2$) 70.7 (s, 2,5-Cs of substituted ferrocenyl Cp) 69.4 (s, Cs of unsubstituted ferrocenyl Cp) 68.6 (s, 3,4-Cs of unsubstituted ferrocenyl Cp) 33.0 (C of α-CH_2 to CN) 32.5 (C of δ-CH_2 to CN) 29.0 (C of β-CH_2 to CN) 27.9 (C of γ-CH_2 to CN) 17.6 (C of $-CH_3$); IR (neat) 3070, 2920, 2850, 1625, 1580, 1405, 1245, 1100, 995, 905, 815 cm^{-1}; TLC $R_f=0.38$, hexane: ethylacetate=5:3, SiO_2; MS m/e (relative intensity) 386 (M^+, 100), 331 (20), 320 (59). One of the characterestic MS fragmentation patterns for the ferrocenyl group is the loss of C_5H_5 (cyclopentadienyl) unit from the ferrocene compound like 331 from 386 $(M^+)^6$. The catalytic conversion mechanism of the aldimine to the ketimine has been reported.[2a] The hex-5′-enyl ketimine **3** was easily hydrolyzed by H^+/H_2O, extracted with $CHCl_3$, and purified by column-chromatography to give hex-5′-enyl acylferrocene **4** in 96% yield (based upon **3**). **4**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 5.8 (m, 1H, -CH=) 4.9 (ABX pattern, 2H, $=CH_2$) 4.77 (t, J=1.9 Hz, 2H, 2,5-Hs of substituted ferrocenyl Cp) 4.46 (t, J=1.9 Hz, 3,4-Hs of substituted ferrocenyl Cp) 4.19 (s, 5H, Hs of unsubstituted ferrocenyl Cp) 2.7 (t, J=7.1 Hz, 2H, α-CH_2 to CO) 2.10 (q, 2H, $-CH_2-C=$) 1.73 (m, 2H, β-CH_2 to CO) 1.84 (m, 2H, γ-CH_2 to CO); ^{13}C-NMR (50.5 MHz, $CDCl_3$) δ (ppm) 138.6 (C of -CH=) 114.5 (C of $=CH_2$) 70.5 (s, 3,4-Cs of substituted ferrocenyl Cp) 69.4 (s, Cs of unsubstituted ferrocenyl Cp) 68.7 (s, 2,5-Cs of substituted ferrocenyl Cp) 39.5 (C of α-CH_2 to CO) 33.6 (C of δ-CH_2 to CO) 28.7 (C of β-CH_2 to CO) 24.1 (C of γ-CH_2 to CO); IR (neat) 3080, 2920, 2860, 1975, 1665, 1450, 1250, 1025, 910, 820 cm^{-1}; TLC $R_f=0.71$, hexane: ethylacetate=5:2, SiO_2; MS m/e (relative intensity) 296 (M^+, 100), 228 (34), 213 (23), 185 (23), 138 (3). The IR bands of C=N for the ketimine **3** at 1625 cm^{-1} were shifted to that of C=O for the acylferrocene **4** at 1665 cm^{-1} after complete hydrolysis of **3**. Any olefin migrated isomer (internal olefinic compound) of **3** or **4** has not been detected.



Scheme 2. (i) $(PPh_3)_3RhCl$ (10 mol%), toluene, 110℃, 6 hrs (ii) 0.1 N $HCl/CHCl_3$.

To synthesize the 1,6-hexadiyl acylferrocene **5**, the same type of reaction was applied with a half equivalent of 1,5-hexadiene instead of large excess (10 eq.) of that based on the aldimine **1** (Scheme 2). Without isolation of the intermediated ketimines, hydrolysis, of the resulting reaction mixtures afforded a mixture of 1,6-hexadiyl acylferrocene **5** and hex-4′-enyl acylferrocene **6** in 75% yield in a 3:5 ratio (based upon 1,5-hexadiene) with trace of **4**. **5**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 4.78 (t, J=1.9 Hz, 4H, 2,5-Hs of substituted ferrocenyl Cp) 4.48 (t, J=1.9 Hz, 4H, 3,4-Hs of substituted ferrocenyl Cp) 4.19 (s, 10H, Hs of unsubstituted ferrocenyl Cp) 2.7 (t, J=7.2 Hz, 4H, α-CH_2 to CO) 1.74 (m, 4H, β-CH_2 to CO) 1.45 (m, 4H, γ-CH_2 to CO); ^{13}C-NMR (50.5 MHz, $CDCl_3$) δ (ppm) 72.0 (s, 3,4-Cs of substituted ferrocenyl Cp) 69.7 (s, Cs of unsubstituted ferrocenyl Cp) 69.3 (s, 2,5-Cs of substituted ferrocenyl Cp) 39.6 (s, Cs of α-CH_2 to CO) 29.4 (s, Cs of β-CH_2 to CO) 24.4 (s, Cs of γ-CH_2 to CO); IR (neat) 3080, 2920, 2850, 1970, 1660, 1445, 1245, 1020, 995, 820 cm^{-1}; TLC $R_f=0.56$, hexane: ethylacetate=2:5, SiO_2; MS m/e (relative intensity) 510 (M^+, 100), 445 (55), 379 (22)[6]. **6**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 5.45 (m, 2H, -CH=CH-) 4.77 (t, J=1.9 Hz, 2H, 2,5-Hs of substituted ferrocenyl Cp) 4.48 (t, J=1.9 Hz, 2H, 3,4-Hs of substituted ferrocenyl Cp) 4.18 (s, 5H, Hs of unsubstituted ferocenyl Cp) 2.69 (t, J=7.3 Hz, 2H, α-CH_2, to CO) 2.10 (m, 2H, $=C-CH_2-$) 1.77 (m, 2H, β-CH_2 to CO) 1.67 (d, J=4.3 Hz, 3H, $CH_3-C=$); IR (neat) 3080, 2920, 1660, 1447, 1240, 1020, 960, 817 cm^{-1}; TLC $R_f=0.73$, hexane: ethylacetate=5:2, SiO_2; MS m/e (relative intensity) 296 (M^+, 100), 228 (82), 213 (20), 185 (26), 138 (4). The MS spectra of **5** shows the successive loss of C_5H_5 unit like 445 and 379 from 510 (M^+). The isomerization mechanism of the terminal olefinic group to the internal olefinic group of **6** is not clear. Any hydrometallation evidence of the internal olefin in **6** to generate a secondary alkyl complex as an intermediate has not been observed probably due to the steric hindrance.

From the above results it is possible to synthesize the alkenyl or alkyl acylferrocence from ferrocenecarboxaldehyde and alkene by C-H bond activation with aid of 2-amino-3-methylpyridine as a cyclometallation tool. Further mechanistic investigation of the olefin isomerization is under study.

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