Communications to the Editor

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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 v_{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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10. (a) Anal. data for **1** (C₉H₁₂O₃S₃Cr). Calcd (found): C, 34.2 (34.2); H, 3.82 (3.83); (b) Anal. data for **3** (C₉H₁₂O₃S₃W). Calcd (found): C, 24.1 (24.1); H, 2.70 (2.66); (c) Analysis of **2** was omitted since its synthesis[1,12] and structure[11] have been previously reported.
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13. Suitable crystals of **3** were grown by diffusing Et₂O into a DMF solution. Crystallographic data for **3**: C₉H₁₂O₃S₃W, monoclinic, space group $P2_1/n$, $a = 9.134(1)$, $b = 11.060(2)$, $c = 12.619(2)$ Å, $β = 92.74$ (1)°, $V = 1273.3(3)$ Å³, $R(R_w) = 0.0310$ (0.0335). A parallelepiped yellow crystal (0.21×0.25 ×0.41 mm) was sealed in a glass capillary and mounted on an Enraf-Nonius CAD4 diffractometer. Diffraction data were collected at ambient temperature using MoKα radiation to a maximum 2θ value of 50° with w-2θ scan mode. Data were corrected for Lorentz, polarization and absorption effects. Intensity data for 1791 reflections with I>3σ(I) were used for Patterson method and SHELX 76.
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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 η³-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
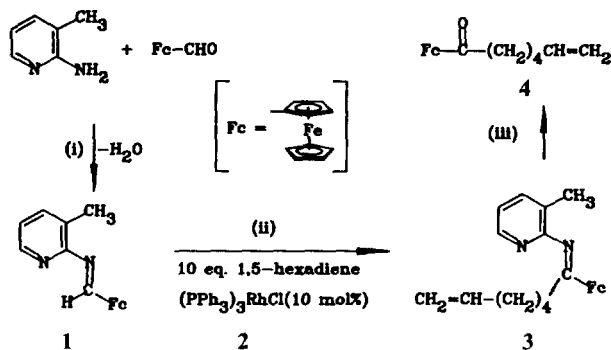
Scheme 1. (i) p-toulenesulfonic acid, benzene at reflux. (ii) toluene, 110℃, 6 hrs (iii) 0.1 N HCl/CHCl₃.

Scheme 2. (i) (PPh₃)₃RhCl (10 mol%), toluene, 110℃, 6 hrs (ii) 0.1 N HCl/CHCl₃.

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 (PPh₃)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: ¹H-NMR (200 MHz, CDCl₃) 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, =CH₂) 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-CH₂ to CN) 2.13 (s, 3H. -CH₃) 1.92 (q, J=7 Hz, 2H, =C-CH₂) 1.61 (m, 2H, β-CH₂ to CN) 1.32 (m, 2H, γ-CH₂ to CN); ¹³C-NMR (50.5 MHz, CDCl₃) δ (ppm) 145.9, 118.5 (Cs of pyridine group) 137.5 (C of -CH=) 114.6 (C of =CH₂) 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-CH₂ to CN) 32.5 (C of δ-CH₂ to CN) 29.0 (C of β-CH₂ to CN) 27.9 (C of γ-CH₂ to CN) 17.6 (C of -CH₃); IR (neat) 3070, 2920, 2850, 1625, 1580, 1405, 1245, 1100, 995, 905, 815 cm⁻¹; TLC R$_f$=0.38, hexane: ethylacetate=5:3, SiO₂; 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 C₅H₅ (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⁺/H₂O, extracted with CHCl₃, and purified by column-chromatography to give hex-5'-enyl acylferrocene 4 in 96% yield (based upon 3). 4: ¹H-NMR (200 MHz, CDCl₃) δ (ppm) 5.8 (m, 1H, -CH=) 4.9 (ABX pattern, 2H, =CH₂) 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)
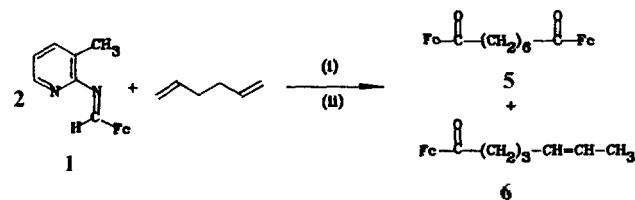
4.19 (s, 5H, Hs of unsubstituted ferrocenyl Cp) 2.7 (t, J=7.1 Hz, 2H, α-CH₂ to CO) 2.10 (q, 2H, -CH₂-C=) 1.73 (m, 2H, β-CH₂ to CO) 1.84 (m, 2H, γ-CH₂ to CO); ¹³C-NMR (50.5 MHz, CDCl₃) δ (ppm) 138.6 (C of -CH=) 114.5 (C of =CH₂) 70.5 (s, 3,4-Cs of substituted ferrocenyl Cp) 69.4 (s, Cs of unsubstituted ferrocenyl Cp) 68.7 (s, 2,5-Cs of substituted ferrocenyl Cp) 39.5 (C of α-CH₂ to CO) 33.6 (C of δ-CH₂ to CO) 28.7 (C of β-CH₂ to CO) 24.1 (C of γ-CH₂ 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, SiO₂; 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.

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: ¹H-NMR (200 MHz, CDCl₃) 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-CH₂ to CO) 1.74 (m, 4H, β-CH₂ to CO) 1.45 (m, 4H, γ-CH₂ to CO); ¹³C-NMR (50.5 MHz, CDCl₃) 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-CH₂ to CO) 29.4 (s, Cs of β-CH₂ to CO) 24.4 (s, Cs of γ-CH₂ 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, SiO₂; MS m/e (relative intensity) 510 (M⁺, 100), 445 (55), 379 (22)[6]. 6: ¹H-NMR (200 MHz, CDCl₃) 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-CH₂, to CO) 2.10 (m, 2H, =C-CH₂-) 1.77 (m, 2H, β-CH₂ to CO) 1.67 (d, J=4.3 Hz, 3H, CH₃-C=); IR (neat) 3080, 2920, 1660, 1447, 1240, 1020, 960, 817 cm⁻¹; TLC R$_f$=0.73, hexane: ethylacetate=5:2, SiO₂; 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 C₅H₅ 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 inter-

mediate 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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