

Novel intramolecular transformations of amino(diferrocenyl)-vinylcarbenes

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Experimental

1,2-Diferrocenylbenzene 3. Yield 0.09 g (11% from **1a**) and 0.085 g (10% from **1b**), orange powder, mp 102–103 °C. ¹H NMR (CDCl₃, 300 MHz) δ: 4.08 (s, 10H, 2C₅H₅), 4.21 (m, 4H, C₅H₄), 4.34 (m, 4H, C₅H₄), 7.16 (t, 2H, C₆H₄, *J* 7.8 Hz), 7.65 (d, 2H, *J* 7.8 Hz, C₆H₄) (*cf.* ref. 10). ¹³C NMR (CDCl₃, 75 MHz) δ: 69.26, 69.45 (2C₅H₅), 67.15, 67.23, 69.84, 69.98 (2C₅H₄), 87.90 (2C_{ipso}Fc), 131.14, 131.78 (C₆H₄), 134.91, 134.99 (2C_{ipso}). MS, *m/z*: 446 [M]⁺. Found (%): C, 70.13; H, 4.98; Fe, 25.15. Calc. for C₂₆H₂₂Fe₂ (%): C, 70.00; H, 4.97; Fe, 25.03.

3-Allylidene-1,2-diferrocenylcyclopropene 4. Yield 0.054 g (6% from **1a**) and 0.07 g (8% from **1b**), orange oil. ¹H NMR (CDCl₃, 300 MHz) δ: 4.05 (s, 5H, C₅H₅), 4.11 (s, 5H, C₅H₅), 4.02 (m, 1H, C₅H₄), 4.08 (m, 1H, C₅H₄), 4.12 (m, 1H, C₅H₄), 4.17 (m, 2H, C₅H₄), 4.21 (m, 1H, C₅H₄), 4.28 (m, 2H, C₅H₄), 5.21 (dd, 1H, CH₂=, *J* 1.5, 10.5 Hz), 5.30 (dd, 1H, CH₂=, *J* 1.5, 16.8 Hz), 6.78 (d, 1H, CH=, *J* 15.3 Hz), 7.08 (m, 1H, CH=). ¹³C NMR (CDCl₃, 75 MHz) δ: 60.19 (C), 69.76, 69.98 (2C₅H₅), 68.83, 69.57, 70.11, 70.39 (2C₅H₄), 86.32, 86.64 (2C_{ipso}Fc), 118.02 (CH₂=), 126.42, 128.97 (2CH=), 129.68, 130.02 (2C). MS, *m/z*: 446 [M]⁺. Found (%): C, 69.87; H, 5.06; Fe, 25.20. Calc. for C₂₆H₂₂Fe₂ (%): C, 70.00; H, 4.97; Fe, 25.03.

1,3-Diferrocenyl-2-morpholinohexa-1,3,5-triene 5a. Yield 0.44 g (40%), orange crystals, mp 173–174 °C. ¹H NMR (CDCl₃, 300 MHz) δ: 2.94–3.05 (m, 4H, 2CH₂), 3.76 (m, 4H, 2CH₂), 3.96 (s, 5H, C₅H₅), 4.04 (s, 5H, C₅H₅), 4.01 (m, 2H, C₅H₄), 4.17 (m, 1H,

C₅H₄), 4.20 (m, 1H, C₅H₄), 4.24 (m, 2H, C₅H₄), 4.39 (m, 1H, C₅H₄), 4.50 (m, 1H, C₅H₄), 5.14 (dd, 1H, CH₂=, *J* 1.5, 9.3 Hz), 5.29 (dd, 1H, CH₂=, *J* 1.5, 15.9 Hz), 6.63 (m, 1H, CH=), 6.64 (s, 1H, CH=), 6.67 (d, 1H, CH=, *J* 11.1 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ : 47.98 (2CH₂), 67.03 (2CH₂), 68.87, 69.29 (2C₅H₅), 67.27, 67.65, 67.73, 67.89, 68.11, 69.17, 70.79, 71.38 (2C₅H₄), 84.77, 93.69 (2C_{ipso}Fc), 113.82 (CH₂=), 131.47, 132.12, 132.78 (3CH=), 136.96, 147.78 (2C). MS, *m/z*: 533 [M]⁺. Found (%): C, 67.66; H, 5.94; Fe, 20.95; N, 2.57. Calc. for C₃₀H₃₁Fe₂NO (%): C, 67.57; H, 5.86; Fe, 20.95; N, 2.63.

1,3-Diferrocenyl-2-piperidinohexa-1,3,5-triene 5b. Yield 0.45 g (42%), orange crystals, mp 165–167 °C. ¹H NMR (CDCl₃, 300 MHz) δ : 1.57 (m, 2H, CH₂), 2.74 (m, 4H, 2CH₂), 3.11 (m, 4H, 2CH₂), 3.98 (s, 5H, C₅H₅), 4.10 (s, 5H, C₅H₅), 4.02 (m, 1H, C₅H₄), 4.08 (m, 2H, C₅H₄), 4.14 (m, 2H, C₅H₄), 4.18 (m, 1H, C₅H₄), 4.31 (m, 2H, C₅H₄), 5.06 (dd, 1H, CH₂=, *J* 1.5, 9.9 Hz), 5.32 (dd, 1H, CH₂=, *J* 1.5, 16.5 Hz), 6.58 (m, 1H, CH=), 6.73 (s, 1H, CH=), 6.89 (d, 1H, CH=, *J* 9.3 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ : 32.14 (CH₂), 40.71 (2CH₂), 61.01 (2CH₂), 68.76, 69.18 (2C₅H₅), 67.26, 67.59, 67.73, 67.84, 68.01, 69.10, 70.53, 70.29 (2C₅H₄), 84.52, 91.74 (2C_{ipso}Fc), 112.83 (CH₂=), 130.22, 130.97, 131.79 (3CH=), 134.81, 147.56 (2C). MS, *m/z*: 531 [M]⁺. Found (%): C, 70.21; H, 6.18; Fe, 21.09; N, 2.73. Calc. for C₃₁H₃₃Fe₂N (%): C, 70.08; H, 6.26; Fe, 21.02; N, 2.64.

2,3-Diferrocenyl-1-morpholinobicyclo[3.1.0]hex-2-ene 6a. Yield 0.32 g (30%), orange crystals, mp 191–192 °C. ¹H NMR (CDCl₃, 300 MHz) δ : 0.58 (dd, 1H, CH₂, *J* 4.8, 9.6 Hz), 1.58 (dd, 1H, CH₂, *J* 4.8, 8.7 Hz), 1.78 (m, 1H, CH), 2.53 (m, 4H, 2CH₂), 2.62 (dd, 1H, CH₂, *J* 8.1, 17.1 Hz), 3.00 (dd, 1H, CH₂, *J* 6.6, 17.1 Hz), 3.86 (m, 4H, 2CH₂), 4.04 (s, 5H, C₅H₅), 4.14 (s, 5H, C₅H₅), 4.06 (m, 2H, C₅H₄), 4.10 (m, 1H, C₅H₄), 4.13 (m, 1H, C₅H₄), 4.16 (m, 2H, C₅H₄), 4.28 (m, 1H, C₅H₄), 4.79 (m, 1H, C₅H₄). ¹³C NMR (CDCl₃, 75 MHz) δ : 13.57, 21.38 (2CH₂), 39.91 (CH), 50.25, 67.37 (4CH₂), 64.75 (C), 68.52, 68.88 (2C₅H₅), 66.24, 67.48, 67.63, 67.95, 68.54, 68.94, 69.79, 69.88 (2C₅H₄), 82.87, 83.11 (2C_{ipso}Fc), 134.49, 135.43 (2C). MS, *m/z*: 533 [M]⁺. Found (%): C, 67.49; H, 5.77; Fe, 21.11; N, 2.68. Calc. for C₃₀H₃₁Fe₂NO (%): C, 67.57; H, 5.86; Fe, 20.95; N, 2.63.

2,3-Diferrocenyl-1-piperidinobicyclo[3.1.0]hex-2-ene **6b**. Yield 0.30 g (28%), orange crystals, mp 180–181 °C. ¹H NMR (CDCl₃, 300 MHz) δ: 0.56 (dd, 1H, CH₂, *J* 4.2, 9.0 Hz), 1.48 (m, 2H, CH₂), 1.54 (dd, 1H, CH₂, *J* 4.2, 8.7 Hz), 1.67 (m, 4H, 2CH₂), 1.75 (m, 1H, CH), 2.54 (dd, 1H, CH₂, *J* 7.5, 16.8 Hz), 2.69 (m, 4H, 2CH₂), 2.87 (dd, 1H, CH₂, *J* 6.6, 16.8 Hz), 3.97 (s, 5H, C₅H₅), 4.09 (s, 5H, C₅H₅), 4.01 (m, 2H, C₅H₄), 4.04 (m, 1H, C₅H₄), 4.12 (m, 1H, C₅H₄), 4.14 (m, 2H, C₅H₄), 4.21 (m, 1H, C₅H₄), 4.63 (m, 1H, C₅H₄). ¹³C NMR (CDCl₃, 75 MHz) δ: 13.44, 21.22, 28.41 (3CH₂), 36.14 (2CH₂), 44.18 (2CH₂), 39.87 (CH), 63.84 (C), 68.34, 68.65 (2C₅H₅), 66.18, 66.89, 67.23, 67.35, 67.84, 68.04, 68.49, 68.87 (2C₅H₄), 82.35, 82.38 (2C_{ipso}Fc), 134.53, 134.89 (2C). MS, *m/z*: 531 [M]⁺. Found (%): C, 70.12; H, 6.34; Fe, 21.11; N, 2.56. Calc. for C₃₁H₃₃Fe₂N (%): C, 70.08; H, 6.26; Fe, 21.02; N, 2.64.