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SYNTHESIS OF [2,2] FERROCENOPHANE-1,13-DIENE

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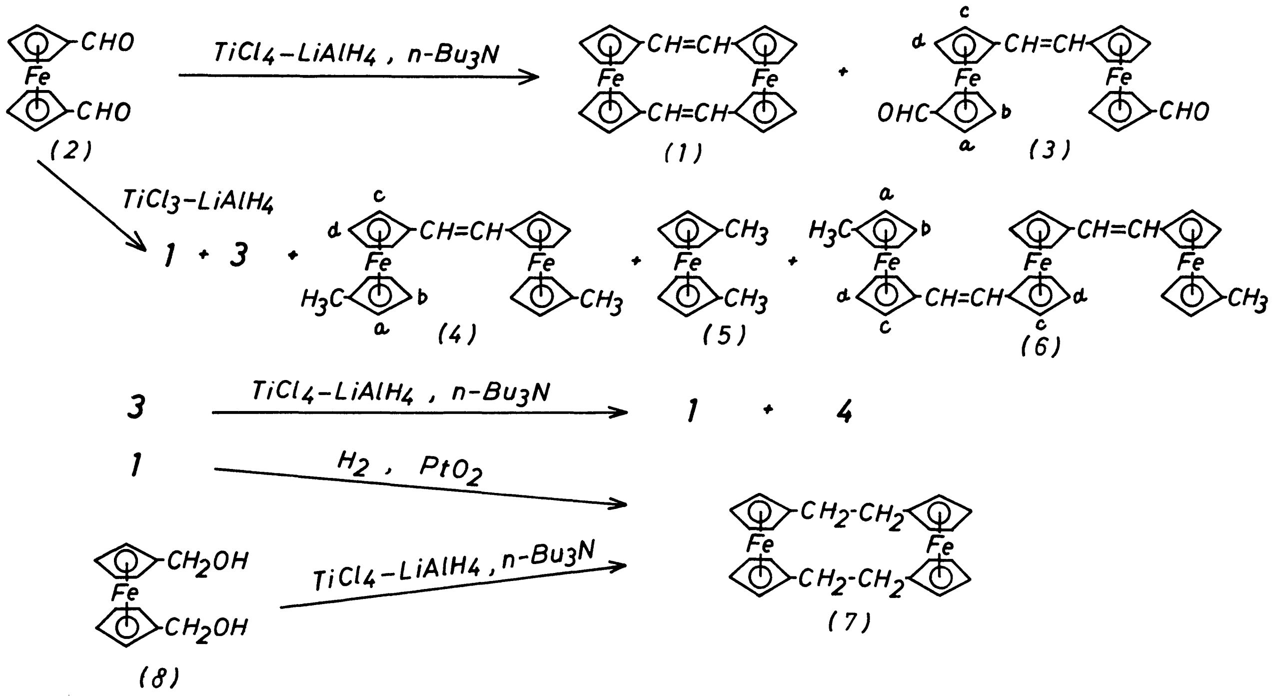
[2,2]Ferrocenophane-1,13-diene (1) was synthesized *via* the intermolecular coupling of ferrocene-1,1'-dicarbaldehyde (2) with $TiCl_4$-$LiAlH_4$. The catalytic hydrogenation of 1 led to the formation of [2,2]ferrocenophane (7). An alternate approach to the synthesis of 7, involving the reductive coupling of 1,1'-bis(hydroxymethyl)-ferrocene with $TiCl_4$-$LiAlH_4$ is described.

In contrast to the active interest in cyclophane compounds generally, the [m,n]-ferrocenophane system[1)] has received little attention, the only compounds of this class which have been described being [0,0]ferrocenophane,[2)] [1,1]ferrocenophane,[3,4)] [1,1]-ferrocenophane-1,12-dione,[4)] [2,2]ferrocenophane-1,13-diyne,[5)] [4,4]ferrocenophane,[3a,6)] bis(*as*-indacenyliron),[7)] and [2,2](1,2)ferrocenophane.[8)] In this communication, we wish to report the synthesis of [2,2]ferrocenophane-1,13-diene (1), in which the two olefinic groups are held rigidly over one another and can be brought into reaction either photochemically or through the agency of organometallic reagents.

The synthesis of 1 was carried out by means of the reductive coupling of ferrocene-1,1'-dicarbaldehyde (2) with low-valent titanium reagent according to Mukaiyama's procedure.[9)] To a solution of $TiCl_4$ (50 mmol, 9.49 g) in dry THF (200 ml) was added $LiAlH_4$ (26 mmol, 0.97 g) in ice-salt bath. The mixture was refluxed for 20 min under a nitrogen atmosphere to give a deep black solution. To the metal complex solution thus obtained was added dropwise a solution of 2 (10 mmol, 2.42 g) and tributylamine (10 mmol, 1.85 g) in dry THF (100 ml) for 5 h under refluxing. The mixture was refluxed for additional 3 h and quenched with 20% K_2CO_3 aqueous solution. After filtration, the filtrate was extracted with chloroform. The extract was washed with water, and dried over $MgSO_4$. 1,2-Bis(1'-formylferrocenyl)ethylene (3), reddish needles, mp 155-156°C



(44% yield) and 1, reddish yellow needles, mp 235-240°C (decomp.) (7% yield) were obtained after separation by silica-gel column chromatography. Under the same reaction conditions, the reductive coupling reaction of 3 with $TiCl_4$-$LiAlH_4$ gave 1 (43% yield) and 1,2-bis(1'-methylferrocenyl)ethylene (4), reddish needles, mp 159-160°C (3% yield). On the other hand, when two fold amount of the low-valent titanium reagent [$TiCl_4$ (100 mmol)-$LiAlH_4$ (52 mmol)] was used, 2 was converted to a mixture of 1 (14% yield), 4 (4% yield), 1,1'-dimethylferrocene (5), mp 41°C (lit,[10] mp 39-40.5°C) (24% yield), and 1,1'-bis[2-(1'-methylferrocenyl)vinyl]ferrocene (6), reddish needles, mp 168-170°C (decomp.) (20% yield). Furthermore, the reductive coupling of 2 (10 mmol) in dry THF (100 ml) with $TiCl_3$ (40 mmol)-$LiAlH_4$ (20 mmol)[11] led to the formation of the mixture of 1 (2% yield), 3 (7% yield), 4 (23% yield), 5 (24% yield), and 6 (20% yield).

The catalytic hydrogenation of 1 with PtO_2 in dioxane-ethanol afforded [2,2]-ferrocenophane (7), mp 146-148°C, yellowish needles, in 75% yield. The reductive coupling reaction[12] of 1,1'-bis(hydroxymethyl)ferrocene (8) (10 mmol, 2.50 g) with $TiCl_4$ (50 mmol, 9.45 g)-$LiAlH_4$ (26 mmol, 0.98 g) and tributylamine (10 mmol, 1.85 g) in dry THF (200 ml) also afforded 7 in 32% yield.

The structures of these compounds were determined on the basis of NMR, IR and MS spectra and elemental analysis (see Table 1). The low solubility of 1 in common solvents precluded any NMR studies at room temperature, and hence the NMR spectrum of

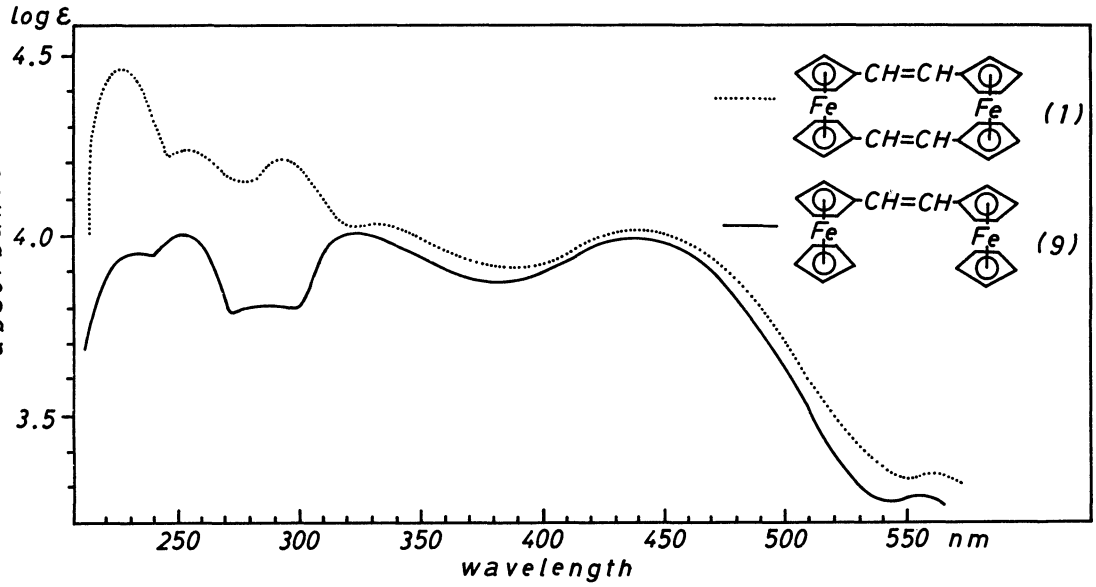


Fig. 1. Electronic spectra of the compounds 1 and 9 in dioxane.

1 was taken in pyridine-d_5 at 100°C. The olefinic protons (δ 5.09 ppm) in 1 are strikingly shifted to high fields compared with the corresponding protons (δ 6.40 ppm, $CDCl_3$) in a reference compound, 1,2-diferrocenylethylene (9), because the former are situated just above the other olefinic group. The mass spectrum of 1 is completely consistent with the proposed structure. At 70 eV, the most intense peak is that due to the parent ion of m/e 420; the remaining two prominent peaks at m/e 56 and 210, corresponding to Fe^+ and the doubly charged ion.

As seen in the Figure 1, the absorption bands of 1 somewhat shifted to longer wavelength and show an increase of intensity of the bands in 230-320 nm region compared with the spectrum of the reference compound 9. It is probably due to some transannular interaction between olefinic chromopheres.

Table 1. The IR, NMR, and MS spectral data of the compounds.[a)]

Compound	
1	IR: 1635, 940 (trans -CH=CH-), 3095, 800 cm^{-1} (ferrocene ring). NMR (pyridine-d_5, at 100°C): δ 4.36 (br. s, 12H) and 4.53 (br. s, 4H) (ferrocene ring protons), 5.09 ppm (br. s, 4H, olefinic protons). MS: m/e 420 (M^+), 210 (m/2e), 56 (Fe^+).
3	IR: 1680 (-CH=O), 1620, 950 (trans -CH=CH-), 3100, 810 cm^{-1} (ferrocene ring). NMR: δ 4.38 (br. s, 8H, H_b + H_d), 4.53 (m, 4H, H_c), 4.78 (m, 4H, H_a), 6.41

(s, 2H, -CH=CH-), 10.03 ppm (s, 2H, -CH=O). MS: m/e 452 (M^+).

4 IR: 1620, 950 (trans -CH=CH-), 3100, 800 cm^{-1} (ferrocene ring). NMR: δ 1.97 (s, 6H, $-CH_3$), 4.07 (br. s, 8H, $H_a + H_b$), 4.26 (br. s, 4H, H_d), 4.36 (br. s, 4H, H_c), 6.37 ppm (s, 2H, -CH=CH-). MS: m/e 424 (M^+).

6 IR: 1620, 945 (trans -CH=CH-), 3100, 800 cm^{-1} (ferrocene ring). NMR: δ 1.97 (s, 6H, $-CH_3$), 4.07 (br. s, 8H, $H_a + H_b$), 4.28 (br. s, 8H, H_d), 4.36 (br. s, 8H, H_c), 6.40 ppm (s, 4H, -CH=CH-). MS: m/e 634 (M^+).

7 IR: 3100, 800 cm^{-1} (ferrocene ring). NMR: δ 2.48 (s, 8H, $-CH_2-$), 3.98 ppm (br. s, 16H, $H_a + H_b$). MS: m/e 424 (M^+), 212 (m/2e).

a) All compounds gave correct elemental analysis. All IR spectra were measured on KBr disks. NMR spectra were observed in $CDCl_3$ at 90 MHz with TMS as standard, except the spectrum of 1.

References

1) G. B. Shul'pin and M. I. Rybinskaya, Usp. Khim., 43, 1524 (1974).
2) a) F. L. Hedberg and H. Rosenberg, J. Am. Chem. Soc., 91, 1258 (1969);
b) M. D. Rausch, R. F. Kovar, and C. S. Kraihanzel, ibid., 91, 1259 (1969).
3) a) W. E. Watts, J. Am. Chem. Soc., 88, 855 (1966); b) T. J. Katz, N. Acton, and G. Martin, ibid., 95, 2934 (1973).
4) a) W. E. Watts, J. Organomet. Chem., 10, 191 (1967); b) T. H. Barr, H. L. Lentzer, and W. E. Watts, Tetrahedron, 25, 6001 (1969); c) A. Kasahara, T. Izumi, and S. Ohnishi, Bull. Chem. Soc. Jpn., 45, 951 (1972).
5) M. Rosenblum, N. M. Brawn, D. Clappenelli, and J. Tancrede, J. Organomet. Chem., 24, 469 (1970).
6) A. Lüttringhaus and W. Kullick, Angew. Chem., 70, 438 (1958).
7) T. J. Katz and J. Schulman, J. Am. Chem. Soc., 86, 3169 (1964).
8) M. Benedikt and K. Schlögl, Abstracts of VIIIth International Conference on Organometallic Chemistry, p 23 (1977).
9) A. Ishida and T. Mukaiyama, Chem. Lett., 1976, 1127.
10) E. A. Hill and J. H. Richards, J. Am. Chem. Soc., 83, 4216 (1961).
11) J. E. Mc Murry and M. P. Fleming, J. Am. Chem. Soc., 96, 4708 (1974).
12) J. E. Mc Murry and M. Silverstri, J. Org. Chem., 40, 2687 (1975).

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