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## Poly-linked cyclopentadienide ions

## II \*. Synthesis and properties of the tetracyclopentadienylmethane tetraanion

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## Abstract

The title tetraanion (**1d**) has been synthesized via ferrocenyl derivatives. Dynamic  $^1\text{H}$  NMR spectroscopy indicates the most stable conformation of **1d** and the barrier to internal rotation of cyclopentadienide rings.

## 1. Introduction

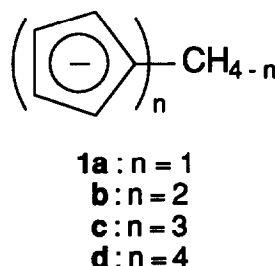
Poly-linked cyclopentadienide ions with a structure of the type,  $(c\text{-C}_5\text{H}_4^-)_n\text{CH}_{4-n}$  ( $n = 1$  (**1a**),  $n = 2$  (**1b**),  $n = 3$  (**1c**), and  $n = 4$  (**1d**); Fig. 1) are suitable for the study of the interaction between cyclopentadienide rings. Of such hydrocarbon polyanions, the monoanion **1a** [2], the dianion **1b** [3], and the trianion **1c** [1] have been synthesized. The tetraanion **1d** is a member of the group of systems of the type  $\text{R}_4\text{Z}$ , with increased symmetry.

## 2. Results and discussion

Cyclopentadienylmethane and bis(cyclopentadienyl)methane, precursors of **1a** and **1b**, have been easily prepared in a variety of ways, including the reactions of cyclopentadienide ion with halomethanes and dihalomethanes, respectively [2,4]. In contrast, tris(cyclopentadienyl)methane, a precursor of **1c**, was first synthesized by the construction of the carbon atom skeleton using ferrocenyl derivatives followed by the reductive cleavage reaction of the ferrocenyl groups [1].

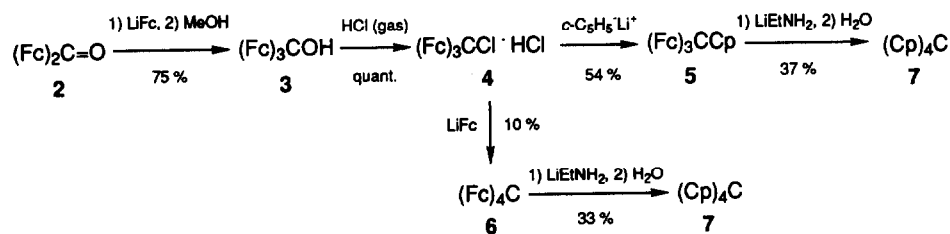
The reaction of diferrocenyl ketone (**2**) [5] with lithioferrocene [6] gave rise to triferrocenylmethanol (**3**) [5] which was chlorinated with HCl gas to afford triferrocenylmethyl hydrodichloride (**4**) [7] (Scheme 1). The hydrodichloride **4** reacted with lithium cyclopentadienide to produce cyclopentadienyltriferrocenylmethane (**5**) [7]. The similar reactions of **4** or triferrocenylmethyl perchlorate with lithioferrocene [6] provided tetraferrocenylmethane (**6**). Both **5** and **6** were converted to tetracyclopentadienylmethane (**7**) by the reductive cleavage reaction of the ferrocenyl groups by lithium-ethylamine [8].

The structure of **7** was determined from the spectral data (Table 1). The  $^{13}\text{C}$  NMR spectra indicated that **7** is a mixture of isomers, possibly five in number, as shown in Fig. 2. The composition of isomers of **7** did not change over time, indicating that [1,5]-sigmatropic

Fig. 1. Poly-linked cyclopentadienide ions **1a**–**d**.

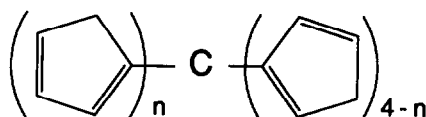
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\* For Part I, see ref. 1.



[ Fc = ferrocenyl, Cp = cyclopentadienyl ]

Scheme 1.

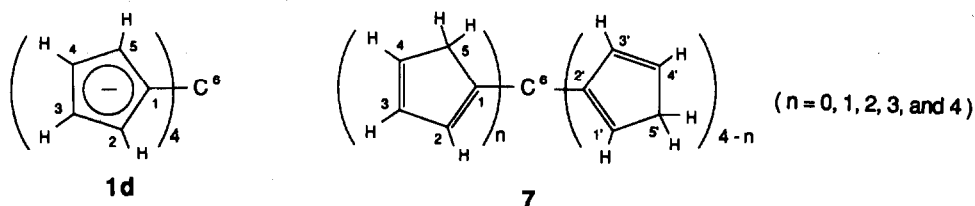


$n = 0, 1, 2, 3, \text{ and } 4$

Fig. 2. Five isomers for 7.

shift of hydrogen was probably fast under the synthetic conditions. The hydrocarbon 7 was in the form of colourless crystals with a narrow melting point range (97.0 ~ 97.6°C) in spite of being a mixture of isomers, soluble in the usual organic solvents, and stable for at least several days at ambient temperature and for at least one month at  $-78^\circ\text{C}$ . The  $\epsilon$  value for 7 is

TABLE 1. NMR spectral data for 1d and 7<sup>a</sup>



Compound	<sup>1</sup> H NMR ( $\delta$ /ppm) <sup>b</sup>		<sup>13</sup> C NMR ( $\delta$ /ppm) <sup>c</sup>	
	$-40^\circ\text{C}$	$-110^\circ\text{C}$	$-50^\circ\text{C}$	$-95^\circ\text{C}$
1d <sup>d</sup>	5.43(s, 8H, H-3, 4) 5.58(s, 8H, H-2, 5)	4.90(s, 4H, H-2 or 5) 5.28(s, 4H, H-3 or 4) 5.50(s, 4H, H-3 or 4) 6.14(s, 4H, H-2 or 5)	49.4(s, C-6) 100.1(d, C-3, 4) 101.4(d, C-2, 5) 139.4(s, C-1)	49.0(s, C-6) 100.0(d, C-3, 4) 101.3(d, C-2, 5) 139.5(s, C-1)
7	3.01(s, 8H, H-5, 5') <sup>e</sup> 5.94 ~ 6.49 (m, 12H, H-2, 3, 4, 1', 3', 4') <sup>e</sup>		40.6, 40.8, 40.9 (t, C-5, 5') <sup>e</sup> 43.0, 43.1 (s, C-6) <sup>e</sup> 125.8, 127.8, 127.9, 129.6, 131.6, 131.8, 131.9 (d, C-2, 1') <sup>e</sup> 135.3, 135.5, 135.8 (d, C-3, 4, 3', 4') <sup>e</sup> 149.9, 150.9, 151.8, 151.9, 152.8 (s, C-1, 2') <sup>e</sup>	

<sup>a</sup> With a JEOL GSX-270 FT-NMR instrument, in THF with a capillary containing CD<sub>3</sub>OD unless otherwise noted. <sup>b</sup> 270 MHz. <sup>c</sup> 68 MHz.

<sup>d</sup> Counter cations: Li<sup>+</sup>. <sup>e</sup> In CDCl<sub>3</sub> at  $+24^\circ\text{C}$ .

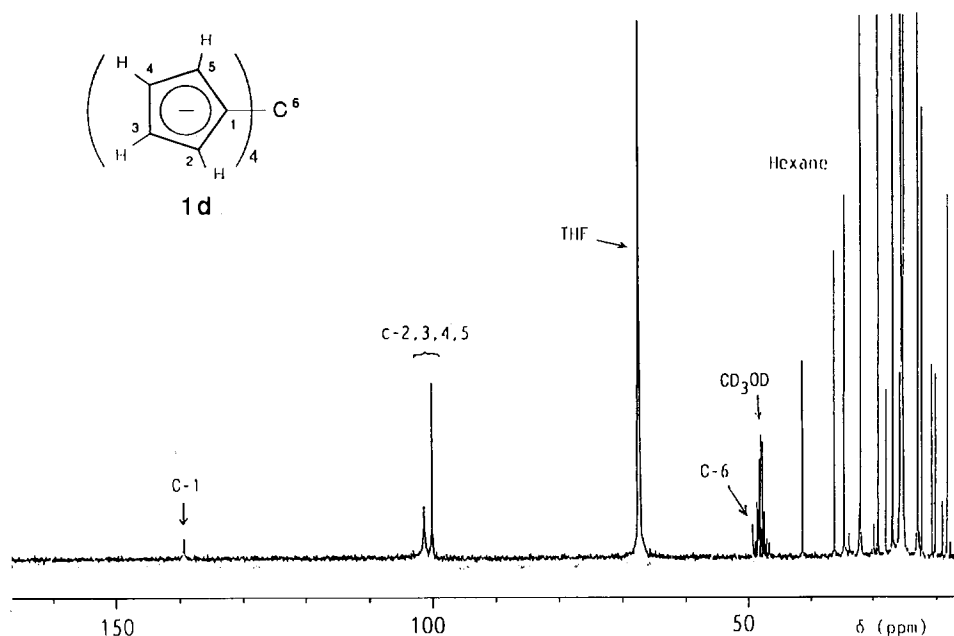


Fig. 3.  $^{13}\text{C}$  NMR spectrum of tetracyclopentadienylmethane (**1d**) tetraanion at  $-50^\circ\text{C}$  (68 MHz, THF, lock solvent:  $\text{CD}_3\text{OD}$ ,  $\delta$  in ppm).

approximately four times that for  $c\text{-C}_5\text{H}_6$  ( $\epsilon$  3400 [9],  $\lambda_{\text{max}}$  (hexane) 238.5 nm [10]).

The reaction of **7** with four or more equivalents of  $^n\text{BuLi}$  in THF at  $-78^\circ\text{C}$  under argon or vacuum produced instantly the tetraanion **1d** (Table 1 and Figs. 3

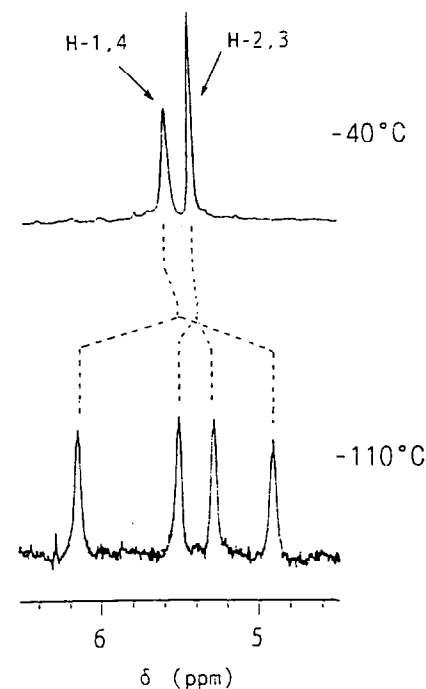


Fig. 4. Temperature dependent  $^1\text{H}$  NMR spectrum of tetracyclopentadienylmethane tetraanion (**1d**) at indicated temperature (270 MHz, THF, lock solvent:  $\text{CD}_3\text{OD}$ ,  $\delta$  in ppm).

and 4). In solution **1d** was pale yellow and stable for at least three days under the synthetic conditions and was treated with  $\text{CD}_3\text{OD}$  at  $-70^\circ\text{C}$  to yield quantitatively tetrakis(deuteriocyclopentadienyl)methane (**8**). [1,5]-Sigmatropic shift was not observed. On warming to ambient temperature, the **1d** solution formed a white precipitate, which was insoluble even in DMSO and when worked up with  $\text{CD}_3\text{OD}$  provided only **8**, which was a mixture of isomers similar to **7**. The precipitation might be attributable to a transformation into an aggregated form of the tetraanion. The solubility of  $\text{CH}_3\text{M}$  ( $\text{M} = \text{Li}, \text{Na}, \text{and K}$ ) is known to decrease with an increase in the degree of aggregation [11].

In the 270 MHz  $^1\text{H}$  NMR spectrum of **1d**, the ring proton signals appear as two slightly broad singlet peaks at  $-40 \sim -50^\circ\text{C}$  (Fig. 4), although they should be considered theoretically as a pattern of  $\text{AA}'\text{BB}'$ . On lowering the temperature below  $-70^\circ\text{C}$  both signals broaden and eventually each splits reversibly to two

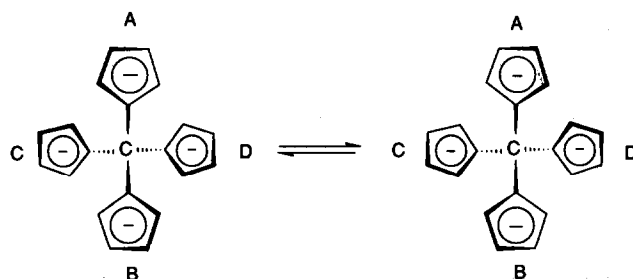


Fig. 5. Stable conformations of tetraanion **1d**.

equivalent slightly broad peaks at  $-110^{\circ}\text{C}$  (Table 1 and Fig. 4; the coalescence temperature is *ca.*  $-95^{\circ}\text{C}$ ). The signals for the protons at 2,5-positions might split more widely than those for the protons at 3,4-positions since the former could be more strongly influenced by the adjacent rings than the latter. Such NMR spectra indicate that, at the most stable conformation of the tetraanion, a set of two cyclopentadienide rings (A, B, C and D; Fig. 5) should be inclined at a constant angle ( $\theta$ ) from the perpendicular to the plane which contains the two *ipso*-carbon atoms and the central  $sp^3$  carbon atom and that two such stable conformers should undergo an interconversion by the rotation of cyclopentadienide rings (Fig. 5), although the effect of the counter cations is not known. The force field MMP2 calculations for tetraphenylmethane ( $\theta = 5^{\circ}$ ) as a model compound support the spectrometric results for the tetraanion **1d**. These spectral changes correspond to the rotation of cyclopentadienide rings becoming slower on the NMR time scale. By the line-shape analysis [12] of the spectral changes, the barrier to rotation ( $E_a$ ) is estimated to be  $8.1 (\pm 0.5)$  kcal/mol and  $\Delta H^{\ddagger}$ ,  $\Delta S^{\ddagger}$ , and  $\Delta G^{\ddagger}$  are  $7.5 (\pm 0.5)$  kcal/mol,  $-5.0 (\pm 2.0)$  e.u., and  $9.0 (\pm 1.0)$  kcal/mol (at  $25^{\circ}\text{C}$ ), respectively. The  $E_a$  value for **1d** is almost identical with those, 7.6 and 8 kcal/mol, for  $(c\text{-C}_5\text{H}_4)_3\text{CH}$  [1] and  $\text{Ph}_3\text{CH}$  [13] respectively. The rotation might proceed via a correlative three-ring-flip transition state which resembles the two-ring-flip one for  $\text{Ph}_3\text{CH}$  [13] and  $(c\text{-C}_5\text{H}_4)_3\text{CH}$  [1]. The ion pair structure of the tetraanion will be discussed in a forthcoming paper.

### 3. Experimental section

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on JEOL model GSX-270 270 MHz and/or JEOL model JNM FX-90Q 90 MHz ( $^1\text{H}$ ) Fourier transform instruments with TMS as an internal standard. IR spectra were taken with a Perkin Elmer model 1640 FTIR spectrophotometer. MPLC was performed with a Chemco chromatograph system composed of a FMI model RP-SY-2 pump and a Merck silica gel 60 column. Melting points were measured on a Yamato model MP-21 apparatus. All procedures were performed under argon.

#### 3.1. Triferrocenylmethanol (**3**)

The lithiation of ferrocene was accomplished using  $^t\text{BuLi}$  [6] rather than  $^n\text{BuLi}$  [5,7], as follows. A  $^t\text{BuLi}$ -pentane solution (2.3 ml, 3.5 mmol) was added to a solution of ferrocene (0.720 g, 3.85 mol) in dry THF (4 ml) with cooling by ice. To the solution, a solution of diferrocenyl ketone (**2**) [1] (0.280 g, 0.700 mmol) in THF (1.5 ml) was added and stirred at ambient tem-

perature for 2 h. After addition of methanol (2 ml) and the usual work-up, the product was washed repeatedly with hot hexane to provide **3** (0.300 g, 75% yield (lit., [5], 53%); m.p.  $161.5\text{--}162.5^{\circ}\text{C}$  (lit., [5],  $160\text{--}162^{\circ}\text{C}$ )) as reddish yellow crystals.

#### 3.2. Cyclopentadienyltriferrocenylmethane (**5**)

The literature procedures [7] were modified. HCl gas was bubbled into **3** (0.200 g, 0.340 mmol) in dry ether (13 ml) to give triferrocenylmethyl hydrochloride (**4**) as a deep green solid, which was washed with ether and dissolved in DMF (1.5 ml). At  $-70 \sim -60^{\circ}\text{C}$ , the DMF solution was added to a lithium cyclopentadienide solution which was prepared from  $^n\text{BuLi}$ -hexane solution (3.0 ml, 5.1 mmol) and freshly depolymerized cyclopentadiene (66 mg, 10 mmol) in THF (12 ml). After the usual work-up, the product was separated by MPLC ( $\text{Al}_2\text{O}_3$ ) to afford **5** (0.139 g, 64.0% yield (lit., [7], 66%)) as reddish orange crystals: m.p.  $198 \sim 200^{\circ}\text{C}$  (dec) (lit., [7],  $201.5 \sim 203^{\circ}\text{C}$  (dec));  $^1\text{H}$  NMR (90 MHz/ $\text{CDCl}_3$ )  $\delta$  3.05 (br s, Cp methylene, 2H), 4.00 (s, Fc, 15H), 4.16 (m, Fc, 6H), 4.25 (m, Fc, 6H), and 6.33  $\sim$  7.03 (m, Cp olefinic, 3H);  $^{13}\text{C}$  NMR (23 MHz/ $\text{CDCl}_3$ )  $\delta$  40.4 (Cp methylene), 66.2, 68.6, 68.9, 69.2 (Fc), 98.5 ( $\text{>G<}$ ), 128.0, 130.0, 136.5 (Cp olefinic), and 151.7 (Cp olefinic-*ipso*).

#### 3.3. Tetraferrocenylmethane (**6**)

A monolithioferrocene which was synthesized from ferrocene (1.08 g, 5.78 mmol) and  $^t\text{BuLi}$  (2.3 ml, 3.5 mmol) was mixed with a 4-THF (3 ml) solution, which had been prepared from **3** (0.206 g, 0.353 mmol) as mentioned above, under cooling with ice to produce **6** (26 mg, 10% yield) as orange crystals: m.p.  $185 \sim 188^{\circ}\text{C}$  (dec);  $^1\text{H}$  NMR (90 MHz/ $\text{CDCl}_3$ )  $\delta$  4.00 (s, Fc, 20H), 4.16 (m, Fc, 8H), and 4.35 (m, Fc, 8H);  $^{13}\text{C}$  NMR (23 MHz/ $\text{CDCl}_3$ )  $\delta$  66.2, 68.0, 69.2, 69.7 (Fc), and 105.1 ( $\text{>C<}$ ); IR (KBr) 820, 1000, 1030, 1110, and  $1410\text{ cm}^{-1}$ ; Anal. Found: C 65.40, H 4.89;  $\text{C}_{41}\text{H}_{36}\text{Fe}_4$  calcd.: C 65.47, H 4.82%.

#### 3.4. Tetracyclopentadienylmethane (**7**)

A mixture of **5** (0.250 g, 0.400 mmol) and lithium powder (0.450 g, 0.0652 mol) in ethylamine (60 ml) was stirred at  $0^{\circ}\text{C}$  for 100 min. After addition of cold methanol and water, the product was separated by preparative TLC ( $\text{Al}_2\text{O}_3$ ) to provide **7** (40 mg, 37% yield) as crystals colourless. **7**: m.p.  $97.0 \sim 97.6^{\circ}\text{C}$ ; high resolution mass spectrum  $m/e$  calcd for  $\text{C}_{21}\text{H}_{20}$  272.1566; found 272.1567 [14\*]; UV (THF)  $\lambda_{\text{max}}$  246

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

nm ( $\epsilon$  12200); IR (KBr disk)  $\nu$  3071, 2880, 1598, 1378, 1353, 901, and 726  $\text{cm}^{-1}$ ; NMR table.

In a similar manner, **7** (65 mg, 0.24 mmol) was also obtained from **6** (537 mg, 0.729 mmol) with 33% yield.

### 3.5. Tetracyclopentadienylmethane tetraanion (**1d**)

A  $n\text{-BuLi}$ -hexane solution (0.12 ml, 0.21 mmol) was mixed with **7** (13 mg, 0.044 mmol) in THF (0.5 ml) in an NMR sample tube with a capillary containing  $\text{CD}_3\text{OD}$  as a lock solvent at  $-78^\circ\text{C}$  under argon to give a pale yellow solution. The tube was sealed and the NMR spectra were measured (Table 1 and Figs. 3 and 4). The **1d** solution was stable for at least three days under the synthetic conditions. The addition of  $\text{CD}_3\text{OD}$  to the **1d** solution yielded only tetrakis(deuteriocyclopentadienyl)methane (**8**) (11 mg, 85% yield): high resolution mass spectrum  $m/e$  calcd for  $\text{C}_{21}\text{H}_{16}\text{D}_4$  276.1816; found 276.1813;  $^1\text{H}$  NMR (90 MHz/ $\text{CDCl}_3$ )  $\delta$  3.01 (s, 4H) and 5.90 ~ 6.42 (m, 12H). On warming to room temperature, the **1d** solution formed a white precipitate which was insoluble on being cooled again to  $-78^\circ\text{C}$  and even in DMSO and worked up with  $\text{CD}_3\text{OD}$  to afford **8** in 90% yield.

Mixing of **7** (27 mg, 0.099 mmol) with  $t\text{-BuOK}$  (67 mg, 0.60 mmol) in THF- $d_8$  (0.7 ml) at  $-78^\circ\text{C}$  under vacuum produced a slightly yellow precipitate which

was insoluble in THF,  $\text{CH}_3\text{CN}$ , and DMSO and treated with methanol to give **7** (24 mg, 89% yield).

### References and notes

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- 14 Such peaks as  $m/e$  207 ( $\text{M}^+ - \text{C}_5\text{H}_5$ ), 142 ( $\text{M}^+ - 2\text{C}_5\text{H}_5$ ), 77 ( $\text{C}_6\text{H}_5$ ), and 65 ( $\text{C}_5\text{H}_5$ ) were detected in addition to the parent peak.