Priority communication

First synthesis and X-ray crystal structure of 1,2-(1,1'-ferrocenediyl)ethene

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Abstract

The ethene-bridged ferrocenophane, 1,2-(1,1'-ferrocenediyl)ethene, has been prepared in six steps from ferrocene using a Stevens rearrangement as the key step to construct the strained bridge.

Keywords: Ferrocenophane; Strained alkene; Ferrocene

There has been a renaissance in the synthesis of metal-containing polymers since the discovery by Manners in 1992 that strained ferrocenophanes undergo ring opening polymerisation to give soluble high molecular weight polymers with skeletal iron atoms [1,2]. These polymers exhibit interesting electronic properties as adjacent iron centres show cooperative interactions which can be tuned by adjusting the nature of the bridge [3].

We have recently become interested in preparing π-conjugated ferrocenyl polymers as they should show enhanced cooperative interactions and may act as excellent hole transport materials. Analogous conjugated organic polymers [e.g. polyacetylene and poly(p-phenylenevinylene) (PPV)] are of considerable commercial interest as they can act as the light-emitting layer in a polymeric LED [4,5]. Unfortunately, synthetic routes to conjugated metal-containing polymers are scarce, the best known examples are the poly(platinaynes) prepared by Hagihara et al. in the late 1970s [6]. These rigid rod polymers form ordered liquid crystalline phases in solution and possess third order non-linear optical properties that may be useful in device technology [7].

One of the best methods for preparing conjugated organic polymers of well defined structure is the ring opening metathesis polymerisation (ROMP) of strained alkenes [8]. By comparison, the ROMP of strained organometallic monomers is relatively unexplored. One recent report describes the preparation of low molecular weight poly(ferrocenylenedivinylene) by the ROMP of
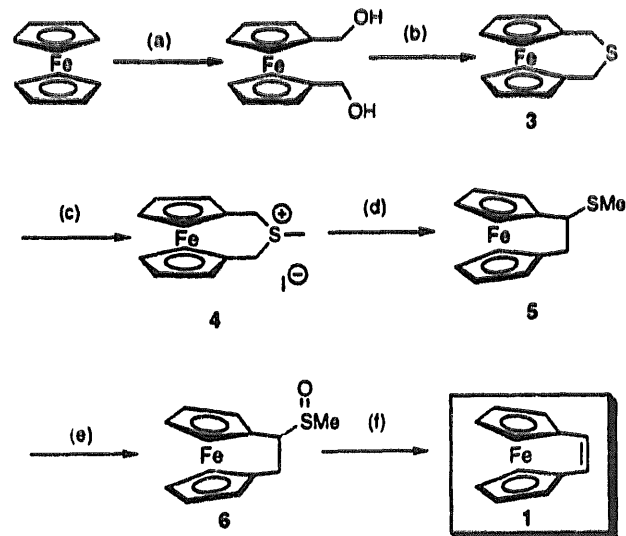
Reagents: (a) i BuLi, DMF; ii NaBH₄ 86% (b) H₂S, AcOH (96%) (c) MeI (90%) (d) NaH, THF (79%) (e) Dimethyl dioxirane (51%) (f) Heat, nonane (5-10%).

Scheme 1. Synthesis of 1,2-(1,1'-Ferrocenediyl)ethene 1.

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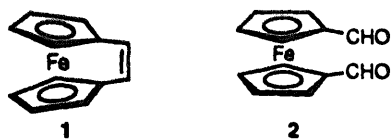
1,4-(1,1'-ferrocenediyl)-1-butene. This study showed that the level of ring strain is the critical factor in determining whether an unsaturated ferrocenophane will undergo ROMP [9]. In this paper we describe the synthesis and solid state structure of the prototypical, and most highly strained, conjugated ferrocenophane, 1,2-(1,1'-ferrocenediyl)ethene 1.

The most obvious route to 1 is by McMurry coupling

of the corresponding dialdehyde 2 especially because this transformation has been used to prepare strained alkenes and cycloalkenes of almost any ring size [10,11].

However, it has previously been shown that treatment of ferrocene dicarboxaldehyde 2 to low valent titanium gave intermolecular coupling products (dimers and ferrocenophane-dimers) in preference to intramolecular coupling [12]. We therefore focussed our attention on ring contraction methods and considered the application of the Ramberg–Bäckland reaction [13] as again this transformation has been used to prepare strained alkenes, e.g. cyclobutenes [14]. The known sulfide 3 [15] was prepared as shown in Scheme 1. However, we were unable to effect α-chlorination on either the sulfide or the corresponding sulfone under a variety of
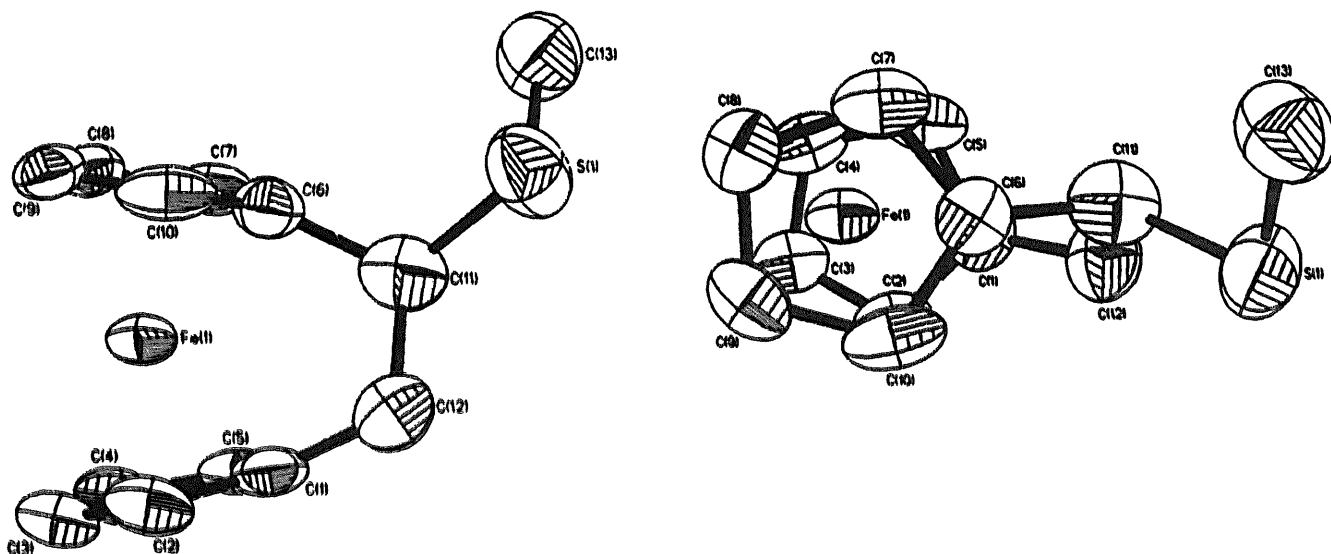

Fig. 1. Side and aerial view of methylthio-1,2-(1,1'-ferrocenediyl)ethane 5.
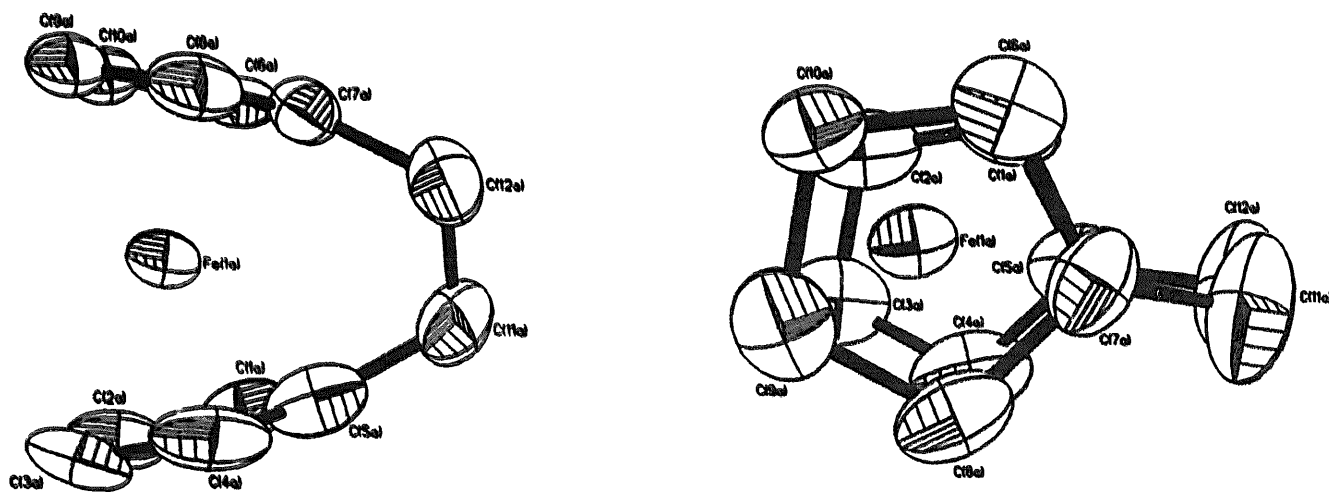

Fig. 2. Side and aerial view of 1,2-(1,1'-ferrocenediyl)ethene 1.

conditions or to effect the Ramburg–Bäckland reaction directly using in situ methods [16]. We therefore considered an alternative ring contraction method, the Stevens rearrangement [17] as this method has been used to prepare cyclophanes [18]. Alkylation of **3** followed by treatment with base was successful and gave the strained ethane-bridged ferrocenophane **5** in good yield. Oxidation of the sulfide moiety in the presence of the strained ferrocene was initially problematic due to competitive oxidation of the iron but was eventually successful using one equivalent of dimethyl dioxirane [19]. Finally, elimination of the sulfoxide in refluxing nonane (150°C) under a stream of nitrogen (to remove sulphenic acids) gave the ethene bridged ferrocenophane **1**. The high temperature required for the elimination is presumably an indication of the increased strain in the product.

The product was purified by sublimation and recrystallisation from cold heptane gave **1** as red blocks. However, the only crystals that were suitable for X-ray analysis were co-crystals of **1** and **5**, derived from heating a mixture of **5** and **6**. Fortunately, this allowed us to obtain data on both **5** and **1** and the structures are shown below [20].

The X-ray structure of **5** reveals significant strain in the ferrocene unit: the tilt angle of the cyclopentadienyl units is 21.7° and the iron atom is shifted to one side of the cyclopentadienyl ring to maintain its η^5-coordination (see Fig. 1).

The X-ray structure of **1** reveals its aesthetic simplicity and shows that there is significantly more strain in the ferrocene unit: the tilt angle of the cyclopentadienyl rings is slightly greater (22.6°) and again the iron atom is shifted away from the line between the ring centroids (see Fig. 2).

Strained ferrocenophanes undergo thermally induced ring opening polymerisation. The driving force for polymerisation is the release of ring strain, a quantity that can be measured by the tilt of the cyclopentadienyl rings [1]. If they are tilted at more than 15° from parallel then the formation of polymer is favoured. The tilt angles of the cyclopentadienyl rings in **5** and **1** are 21.7° and 22.6° respectively, both of which are considerably higher than the minimum required and suggest that polymerisation will be favoured at high temperature.

Previous crystallographic studies of [1] ferrocenophanes suggest that there is an interaction between the iron centre and the bridging atom at distances which range from 2.68 Å in the silane bridged complexes to 2.77 Å in the phosphine bridged systems [22]. A similar interaction is possible between the iron atom and the unsaturated bridge of **1**; whereas no interaction is possible in the ethane bridged complex **5**. It is clear that there is no iron–ethene interaction in the [2] ferrocenophane **1**, as the iron atoms in **1** and **5** are at very similar distances from the centre of C11a–C12a (2.77 Å) and C(11)–C(12) (2.78 Å), respectively.

In summary, we have developed a synthesis of the highly strained ethene bridged [2] ferrocenophane **1** and are currently working on the ring opening metathesis polymerisation reactions of the strained alkene.

Acknowledgement

References and notes

[1] I. Manners, *Adv. Organomet. Chem.*, **37** (1995) 131.
[2] I. Manners, *Chem. Br.*, **32** (1996) 46.
[3] D.A. Foucher, C.H. Honeyman, J.M. Nelson, B.Z. Tang, and I. Manners, *Angew. Chem., Int. Ed. Engl.*, (1993) 1709.
[4] P.L. Burn, A. Kraft, D.R. Baigent, D.D.C. Bradley, A.R. Brown, R.H. Friend, R.W. Gymer, A.B. Holmes, and R.W. Jackson, *J. Am. Chem. Soc.*, **115** (1993) 10117.
[5] A. Wu and M.-A. Kakimoto, *Adv. Mat.*, **7** (1995) 812.
[6] N. Hagihara, K. Sonogashira, and S. Takahashi, *Adv. Polym. Sci.*, **41** (1981) 149.
[7] M.S. Khan, N.A. Pasha, A.K. Kakkar, P.R. Raithby, J. Lewis, K. Fuhrmann, and R.H. Friend, *J. Mater. Chem.*, **2** (1992) 759.
[8] R.H. Grubbs and W. Tumas, *Science*, **243** (1989) 907.
[9] C.E. Stanton, T.R. Lee, R.H. Grubbs, N.S. Lewis, J.K. Pudelski, M.R. Callstrom, M.S. Erickson and M.L. McLaughlin, *Macromolecules*, **28** (1995) 8713.
[10] J.E. McMurry, *Chem. Rev.*, **89** (1989) 1513.
[11] A. Furstner and A. Hupperts, *J. Am. Chem. Soc.*, **117** (1995) 4468.
[12] T. Izumi, I. Shimizu, and A. Kasahara, *Kenkyu Hokoku-Asahi Garasu Gijutsu Shoreikai*, **38** (1981) 223; *Chem. Abs.*, **97**, 216400f.
[13] J. Clough, in B.M. Trost and I. Fleming (eds.), *Comprehensive Organic Synthesis*, Vol. 3, Pergamon, Oxford, 1991, pp. 861.
[14] R.W. Alder, P.R. Allen, and E. Khosravi, *J. Chem. Soc., Chem. Commun.*, (1994) 1235.
[15] A. Ratajczak and M. Dominiak, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **23** (1975) 255.
[16] T.L. Chan, S. Fong, Y. Li, T.O. Man, and C.D. Poon, *J. Chem. Soc., Chem. Commun.*, (1994) 1771.
[17] I.E. Markó, in B.M. Trost and I. Fleming, (eds.), *Comprehensive Organic Synthesis*, Vol. 3, Pergamon, Oxford, 1991, p. 913.
[18] V. Boekelheide, P.H. Anderson, and T.A. Hylton, *J. Am. Chem. Soc.*, **96** (1974) 1558.
[19] C.W. Jones, J.P. Sankey, W.R. Sanderson, M.C. Rocca, and S.L. Wilson, *J. Chem. Res.-S.*, (1994) 114.
[20] Crystal data for $C_{25}H_{24}Fe_2S$: $M = 468.20$, crystallises from heptane as red blocks; crystal dimensions $0.55 \times 0.33 \times 0.22$ mm^3. Monoclinic, $a = 25.63(2)$, $b = 7.428(4)$, $c = 23.36(2)$ Å, $\beta = 115.55(5)°$ $U = 4013(4)$ Å^3, $Z = 8$, $D_c = 1.550$g cm^{-3}, space group $C2/c$, Mo-Kα radiation ($\bar{\lambda} = 0.71073$ Å), μ(Mo Kα) = 1.558 mm^{-1}, $F(000) = 1936$.
[21] Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 45°$ on a Siemens P4 diffractometer by the omega scan method. Of the 3363 reflections measured, all of which were corrected for Lorentz and polarisation effects (but not for absorption), 1718 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$ The structure was solved

by direct methods and refined by full matrix least squares methods on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0622$ ($wR_2 = 0.1772$, for all 2622 data, 253 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms, Minimum and maximum final electron density -0.404 and 0.618e A^{-3}. A

weighting sch me $w = 1/[\sigma^2(F_c^2) + (0.0737 * P)^2 + 22.0158 * P]$ where $P = (F_0^2 + 2 * F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93 as implemented on the Viglen 486dx computer.

[22] J. Silver, J. Chem. Soc., Dalton Trans., (1990) 3513.