CHEMISTRY LETTERS, pp. 67-68, 1994.

A Synthesis of the Cyclic Ferrocene Tetramer $[1]^4$Ferrocenophane

Ulrich T. MUELLER-WESTERHOFF* and Gerhard F. SWIEGERS†
Chemistry Department, University of Connecticut, U-60, Storrs, CT 06269-3060, U.S.A.

The cyclic ferrocene tetramer, $[1]^4$ferrocenophane, may be isolated in a 2.1% yield from a reaction involving the controlled addition of $FeCl_2.1.5THF$ to a dilute solution of the bis(cyclopentadienylmethyl)ferrocene anion.

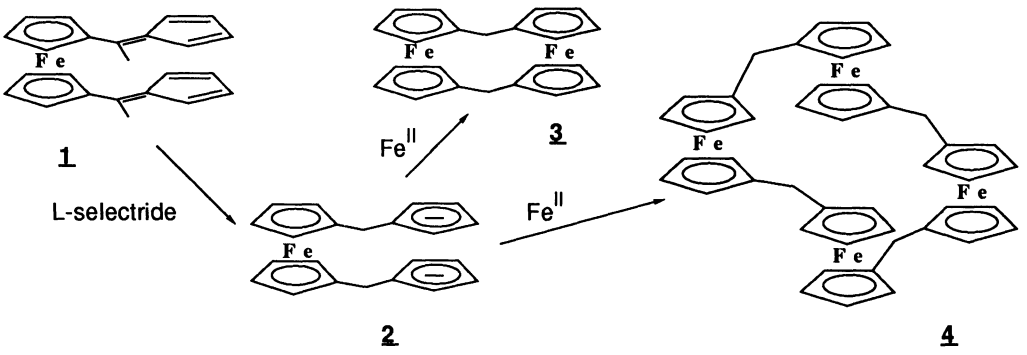
Among the many different ranges of bridged ferrocene containing molecules are the $[m.m]^n$, or $[n]^m$metallocenophanes in which the cyclopentadienyl rings of n ferrocene units are attached by hydrocarbon bridges containing m bridging atoms.1) Examples of such compounds are $[1]^2$, $[1]^3$ and $[1]^4$Ferrocenophane $\{(C_5H_4\text{-}CH_2\text{-}C_5H_4)_xFe_y\ ;\ x = y = 2,3,4\}$.1,2) These compounds are not easily synthesised, even in small yields. We report here a route to the cyclic ferrocene tetramer $[1]^4$ferrocenophane.2)

$[1]^2$Ferrocenophane, **3**, may be prepared using literature procedures;3-5) the material bis(6-fulvenyl)ferrocene, **1**, can be converted to the 1,1'-bis(cyclopentadienyl methyl)ferrocene anion, **2**, by treatment with L-selectride6) under anhydrous, inert atmosphere conditions. Slow addition of $FeCl_2.1.5THF$7) leads to $[1]^2$ferrocenophane, **3**, in up to 40% yield, along with trace amounts of the tetramer (observable using TLC). A simple alteration in the conditions of the addition process led, however, to the production of $[1]^4$ferrocenophane, **4**, as the main isolable product. Thus an increase in the speed of the addition (30 - 40 min) on a more dilute solution (6.8 g $FeCl_2.1.5THF$ in 100 ml THF added to an 800 ml THF solution made up initially with 10 g of **1**) - a deliberate, controlled alteration of the high dilution technique - increased not only the amount of oligomeric materials produced but also the cyclic tetrameric by-product, which could then be isolated in small quantities (0.25 g: 2.1%). The tiny amount of $[1]^2$ferrocenophane also produced was removed, along with ferrocenophane oligomers (the main products), during the extraction, chromatography (the second, yellow, band was collected) and recrystallizations required in the isolation process. Two recrystallizations of the tetrameric product were performed using degassed CCl_4 at temperatures below 30 °C at all times.

The product was characterised by mass spectra (m/z = 792), ^1H NMR (δ (CCl_4) 4.15 ppm {s, 4H, ArH}, 3.75 ppm {s, 1H, $-CH_2-$}) and melting point (darkens at *ca.* 270-272 °C). These results differ significantly from those of **3**. They are also consistent with the earlier finding,2) and with what may be expected for $[1]^4$ferrocenophane [The coalescence of the ring proton NMR resonances is attributable to, and characteristic of increased polymerisation2) and is therefore in accordance with the tetrameric structure proposed]. Elemental analysis is, of course, uninformative as **3** and **4** have the same C:H:Fe ratio's. The cyclic nature of the structure was deduced from the reaction mechanism. The ferrocenophane tetramer is stable as a pure solid, but when

---

†Present address: Research School of Chemistry, Australian National University, Canberra, 0200, A.C.T., Australia.



heated (especially in solution) in the presence of air the tetradione oxidation product is readily formed. For this reason oxygen was excluded from the work-up wherever possible, including the chromatographic separations.$^{3)}$ Further studies on the molecule, including cyclic voltammetry, will be reported elsewhere.$^{8)}$ We have recently produced the tetrameric cyclic [1]^{4}ruthenocenophane analogue as a by-product in the synthesis of [1]^{2}ruthenocenophane.$^{9)}$ It seems likely that a similar procedure could be used to improve yields in their preparation.

References

1) U. T. Mueller-Westerhoff, *Angew. Chem. Int. Ed.*, **25**, 702 (1986), and references therein.
2) T. J. Katz, N. Acton, and G. Martin, *J. Am. Chem. Soc.*, **91**, 2804 (1969), and references therein.
3) A. Cassens, P. Eilbracht, A. Nazzal, W. Prossdorf, and U. T. Mueller-Westerhoff, *J. Am. Chem. Soc.*, **103**, 6367 (1981).
4) U. T. Mueller-Westerhoff, A. Nazzal, and M. Tanner, *J. Organomet. Chem.*, **236**, C41 (1982).
5) T. Izumi, K. Asakura, and A. Kasahara, *Yamagata Daigaku Kiyo, Kogaku*, **20**, 95 (1988).
6) L-Selectride = a mixture of $(i\text{-Bu})_3B$ and LiH. Used as a 1M solution in THF.
7) F. A. Cotton and L. T. Reynolds, *J. Am. Chem. Soc.*, **80**, 269 (1958).
8) In progress.
9) A. L. Rheingold, U. T. Mueller-Westerhoff, and G. F. Swiegers, *Organometallics*, **11**, 3411 (1992). U. T. Mueller-Westerhoff and G. F. Swiegers, *Syn. React. Inorg. Metal-O. Chem.*, **23**, 589 (1993).

(Received September 3, 1993)