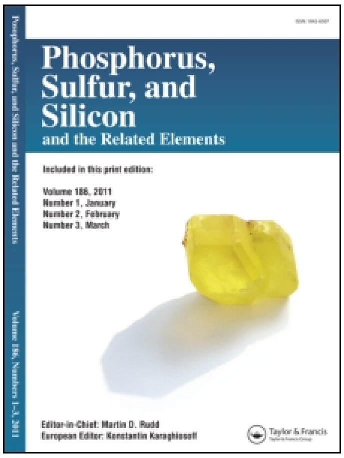

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HIGHLY STRAINED METALLOCENOPHANES: SYNTHESIS AND RING-OPENING OF SULFUR-, SELENIUM- AND BORON- BRIDGED [1]FERROCENOPHANES

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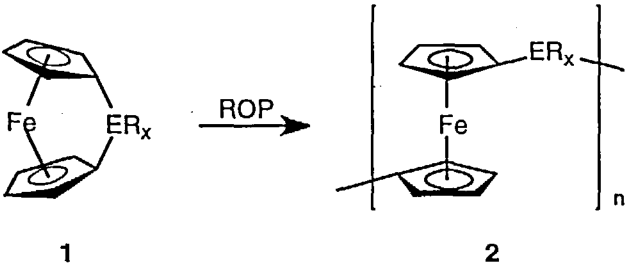
Abstract The limits of cyclopentadienyl ring-tilting in [1]ferrocenophanes are explored with the incorporation of group 16 elements and a first row element. In this paper the synthesis and ring-opening polymerisation (ROP) behaviour of highly strained chalcogen- and boron- bridged [1]ferrocenophanes will be described.

INTRODUCTION

[1]Ferrocenophanes have attracted attention because of their interesting structures, reactivity, and very recently their use as precursors to novel transition-metal-based polymers via ring-opening polymerisation (ROP) reactions.[1] For example, silicon-bridged [1]ferrocenophanes (**1**, $ER_x = SiMe_2$) have recently been used as precursors to polyferrocenylsilanes (**2**, $ER_x = SiMe_2$) via ROP.[2] The

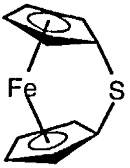
main driving force in the polymerisation of such species is the presence of ring strain resulting from the considerable tilting of the cyclopentadienyl ligands bound to iron. The synthesis and ROP of species containing phosphorus (**1**, ER_x = PR), germanium (**1**, ER_x = GeR_2) and tin (**1**, ER_x = Sn^tBu_2) have also recently been reported.[3] The incorporation of chalcogens and first row elements, initially thought to be too strained to exist, represents a potential means to prepare new organometallic polymers.



CHALCOGEN BRIDGED [1]FERROCENOPHANES

The sulfur-bridged [1]ferrocenophane **3** was prepared by the low temperature reaction of dilithioferrocene•TMEDA (TMEDA = tetramethylethylenediamine) with $(PhSO_2)_2S$.[4] Characterization of the purple compound (**3**) by ^1H NMR revealed a characteristic large separation between the α and β cyclopentadienyl protons ($\Delta\delta = 0.65$ ppm). The ^{13}C NMR spectrum of **1** showed a highly upfield shifted *ipso* carbon resonance of 14.3 ppm, reflecting the strain present in this species. Further evidence for strain present in this species was provided by X-ray crystallography which revealed a remarkable tilt angle (α) of 31.05(10)°.[4]

Extension of this synthetic methodology to a selenium bridged [1]ferrocenophane **4** was accomplished by the reaction of dilithioferrocene•TMEDA with $Se(S_2CNEt_2)_2$.[5] Compound **4** was characterized by ^1H and ^{13}C NMR spectroscopy, and the latter exhibited resonances for three types of carbon atom, including the *ipso*-carbon, which was observed at 5.6 ppm. The ring-tilt (α) was 26.4°, which although less than in **3**, indicates a significant amount of strain for this species.



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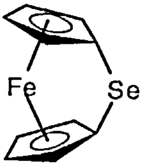

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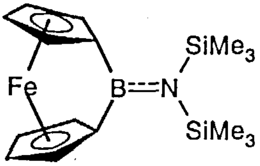
BORON-BRIDGED [1]FERROCENOPHANES

First row and group 13 elements have, until now, not been incorporated into the bridge of a [1]ferrocenophane. The first example of a boron-bridged [1]ferrocenophane **5** was synthesized from the reaction of dilithioferrocene•TMEDA and $Cl_2BN(SiMe_3)_2$.[6] Compound **5**, owing to the small size of the boron atom, possesses the largest tilt-angle [α = 32.4(2)°] for any [n]ferrocenophane. The high degree of strain present in this species is also reflected in the large separation between the α and β Cp protons (Δδ = 0.51 ppm).



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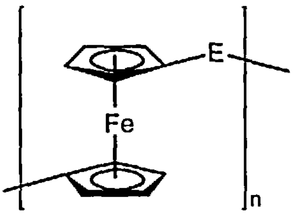
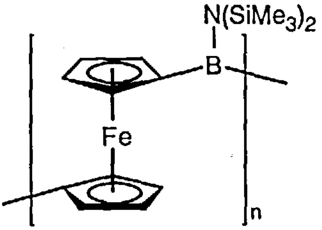
ROP BEHAVIOUR OF NEW [1]FERROCENOPHANES

Since these new [1]ferrocenophanes possess highly strained structures, thermal ROP was expected to result in the formation of poly(ferrocene)s. Indeed, studies of the thermal behaviour of **3**, **4**, and **5** by differential scanning calorimetry (DSC) revealed large exotherms at ca. 140 °C, 130 °C and 190 °C respectively, attributed to the ROP process. However, the resulting poly(ferrocenylsulfides) **6a**, poly(ferrocenylselenides) **6b**, and poly(boraferrocenes) **7** were insoluble in common organic solvents.



6a (E = S)
6b (E = Se)



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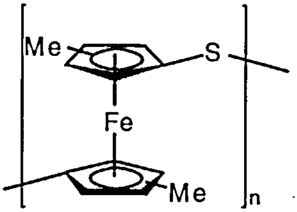
In an attempt to overcome this insolubility problem, the Cp-dimethylated sulfur-bridged [1]ferrocenophane was prepared. This species was isolated as a mixture of isomers, of which one crystallized and structural characterization revealed a tilt angle of 31.46(8)°.[5] Heating this species at 160 °C resulted in the formation of a beige powdery poly(ferrocenylsulfide) **8** which was soluble in THF and benzene. Analysis of the polymeric product by gel permeation chromatography (GPC) gave an estimate of the weight average molecular weight (M_w = 10,900) and polydispersity index (PDI = 1.84).[5] Cyclic voltammetric analysis of **8** gave a redox coupling of ca. 0.32 V, which is considerably larger than that of **2** (ER_x = $SiMe_2$) for which a value of 0.24 V has been established.



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