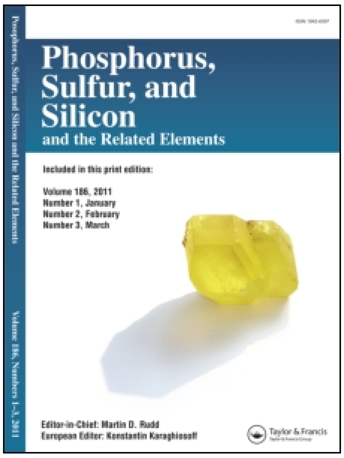

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Ring-Opening Polymerization (ROP) OF [1] and [2]Metallocenophanes

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To cite this Article Nelson, James M. , Lough, Alan J. and Manners, Ian(1994) 'Synthesis and Ring-Opening Polymerization (ROP) OF [1] and [2]Metallocenophanes', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 361 — 362
To link to this Article: DOI: 10.1080/10426509408021857
URL: http://dx.doi.org/10.1080/10426509408021857

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93–94, pp. 361–362
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SYNTHESIS AND RING-OPENING POLYMERIZATION (ROP) OF [1] AND [2]METALLOCENOPHANES

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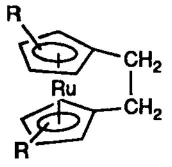
Abstract The ring-opening polymerization of strained, ring-tilted [n]ferrocenophanes (n = 1, 2) represents a new and versatile route to well-defined, soluble and high molecular weight polymers containing skeletal iron atoms. This paper will focus on our efforts to extend this work to species containing different transition metals such as ruthenium.

INTRODUCTION

In contrast to [n]ferrocenophanes, few [n]ruthenocenophanes have been prepared and none with fewer than 3 bridging atoms has been reported to date.[1] In an effort to increase the strain and hence polymerizability of these [n]metallocenophanes (n = 1, 2), we have recently explored the possibility of including a larger metal atom, ruthenium, into these systems.

ROP BEHAVIOR OF [1]- AND [2]RUTHENOCENOPHANES

The reaction of $Li_2[C_5H_4CH_2]_2$ with the Ru(II) complex cis-$RuCl_2(DMSO)_4$ yielded the hydrocarbon-bridged monomer **1** (R = H), the first example of a [2]ruthenocenophane.[1] This monomer was studied crystallographically and the tilt angle was found to be 29.6(5)°, the largest found for any neutral iron-group [n]metallocenophane reported to date. When heated in the melt at 220°C samples of these highly strained monomers **1** (R = H, Me) become viscous and then immobile, producing poly(ruthenocenylethylene)s **2**.[1]



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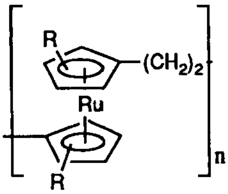

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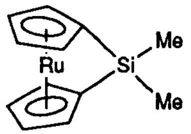

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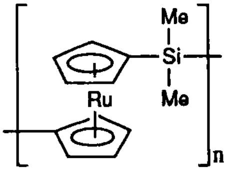

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Attempts to extend this chemistry to other ruthenocenophanes led to the synthesis of the disilane-bridged [2]ruthenocenophane Ru(η-$C_5H_4SiMe_2)_2$ **3** and bis(disilane)-bridged [2][2]ruthenocenophane Ru(η-$C_5H_3(SiMe_2)_2)_2$ **4** containing two disilane bridges by reaction of the appropriate dilithium salt with cis-Ru(DMSO)$_4$Cl$_2$ in THF.[2] Compounds **3** and **4** do not undergo thermal ring-opening polymerization at temperatures in excess of 350 °C. In an effort to explain these dramatic differences in polymerization behavior between **3**, **4** and **1** (R = H, Me), the molecular structures of **3** and **4** were determined by single crystal X-ray diffraction. The disilane-bridged [2]ruthenocenophane **3** was found to possess an angle between the planes of the cyclopentadienyl rings of 7.8(5)° whereas the double-strapped [2]ruthenocenophane **4** was found to be more strained (tilt angle = 12.9(2)°) than **6**. Based on the smaller tilt angles associated with **3** and **4** compared to **1**, it is thought that these disilane based [2]ruthenocenophanes are insufficiently strained to undergo ROP.

Recently, in preliminary experiments, the first silicon-bridged [1]ruthenocenophane has been synthesized in low yields via the reaction of the dilithium salt $Li_2[(C_5H_4)_2SiMe_2]$ with cis-$RuCl_2(DMSO)_4$ in THF. The yellow compound **5** (which is formed together with the ROP product **6**) can be sublimed under high vacuum (at 70 °C) and the identity of this species was verified by ^{1}H-NMR.[3] This shows a characteristically large spacing between the resonances for the protons on the cyclopentadienyl rings which is normally associated with highly strained [1]metallocenophanes. Further work is underway aimed at developing the ROP chemistry of these [1]ruthenocenophane systems.

REFERENCES

1. J.M. Nelson, A.J. Lough, I. Manners, Angew. Chem. Int. Ed. Engl., 33, 989 (1994) and references cited therein.
2. J.M. Nelson, A.J. Lough, I. Manners, Organometallics, 13,(1994), in press.
3. ^{1}H-NMR (200 MHz) of **5** (C_6D_6): δ = 5.15 (t, 4H, Cp), 4.62 (t, 4H, Cp), 0.30 ppm (s, 6H, Si-Me);