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Polyhedron 25 (2006) 429–436

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Synthesis and reactivity of [2]ferrocenophanes containing C–Pb and C–Zr bridges

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Received 4 May 2005; accepted 8 July 2005
Available online 1 September 2005

Dedicated to Professor Malcolm Chisholm for his outstanding and scholarly contributions to chemistry.

Abstract

The synthesis, characterization and reactivity of novel carbometalla[2]ferrocenophanes (η-C_5Me_4)Fe(η-C_5H_4)CH_2ER_2 (**14**) and (**15**) (E = Pb, R = Ph or E = Zr, R = (η-C_5H_5)) are reported. Compounds **14** and **15** were prepared by the reaction of the dilithiated species (η-C_5Me_4)Fe(η-C_5H_4Li)CH_2Li · *x*TMEDA with the appropriate dichlorodiorganoplumbane or dichlorozirconocene in low yields (ca. 20%). The Pb species **14** was characterized by ^{1}H and ^{13}C NMR, and MS, however it could not be cleanly separated from pentamethylferrocene. Moreover, it was found that the C–Pb bonds of **14** underwent facile cleavage, and under ambient light or at room temperature, **14** decomposed to Pb_2Ph_6 and pentamethylferrocene. Compound **15**, on the other hand, was stable and readily purified; this species was characterized by ^{1}H and ^{13}C NMR, UV–Vis, MS, and elemental analysis. Single crystal X-ray diffraction studies of this compound revealed the presence of a moderate degree of ring-tilt with a value of $\alpha = -5.5(2)°$ (a negative value is used to denote tilting away from the bridging elements), and a potentially moderate degree of strain due to a large β(Zr) of 31.6(1)° (angle between Cp′(Fe) plane and *ipso*-Cp′–Zr bond). Attempted thermal ring-opening polymerization (ROP) of **15** resulted only in decomposition and attempted transition metal-catalyzed and photolytic ROP were also unsuccessful. The reaction of **15** with HCl · Et_2O resulted in cleavage of the C–Zr bonds, and led to the formation of pentamethylferrocene.

Keywords: Ring-strain; Ferrocenophane; Plumbane; Zirconocene; Ring-opening polymerization

1. Introduction

[1]Ferrocenophanes have been the focus of much recent research due to the ring-strain imposed upon these organometallic species by the bridging of the cyclopentadienyl (Cp) rings by one atom [1–7]. This ring-strain leads to interesting reactivity for these compounds, and has led to their use in surface derivatization methods [8] and ring-opening polymerization (ROP) reactions [3,4]. Since the initial report of the thermal ROP of silicon-bridged [1]ferrocenophanes such as **1** ($(ER_x)_y$ = $SiMe_2$) to yield high molecular weight polymer **2** [3], the polymerization methods have been successfully expanded to include transition metal-catalyzed ROP [9,10], living anionic ROP [11], and photolytic ROP [12]. In addition, the ROP protocol has been extended to include other atoms in the bridge (E = B, P, Ge, Sn, S) [5–7], different metals (e.g., Ru, Cr and Ti) and also alternative π hydrocarbon ligands [6,7]. The resulting ring-opened polymers are attracting considerable attention due to their interesting physical and preceramic properties [13–20], and copolymers incorporating a ferrocene-containing block have intriguing applications in supramolecular chemistry [21,22]. In addition,

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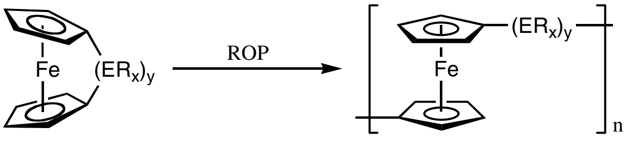
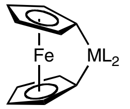
doi:10.1016/j.poly.2005.07.019

polyferrocenylsilanes have recently been used in the area of redox-responsive photonic crystals [23], as etch resists for the nanopatterning of substrates [24] and as precursors to patterned metal catalysts for the growth of carbon nanotubes [25].

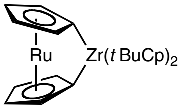


1 **2**

Examples of [1]ferrocenophanes with transition metals in the bridge have also been explored. Broussier et al. [26] reported the synthesis and reactivity of [1]ferrocenophanes (**3**) containing group 4 bridges. Analogues containing titanium, zirconium and hafnium bridges were prepared and single crystal X-ray diffraction of **3b** (L = *t*-BuCp) determined the tilting of the cyclopentadienyl rings to be moderate ($\alpha = 6.0°$). These [1]ferrocenophanes were shown to be reactive towards water and oxygen, in addition to heavier chalcogens leading to insertion of the chalcogen into the *ipso*-Cp–Zr bond [26]. In addition, we recently reported the synthesis of a zirconium-bridged [1]ruthenocenophane (**4**) with a larger tilt angle of the metallocene fragment ($\alpha = 10.4°$) [27].



3a: M = Ti, L = Cp, *t*-BuCp
3b: M = Zr, L = Cp, *t*-BuCp
3c: M = Hf, L = Cp, *t*-BuCp



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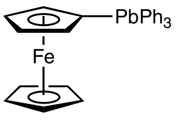
Attempts have also been made to introduce heavy atoms into ferrocenophane structures. Ferrocene was reacted with *n*-BuLi in hexanes to yield a mixture of (η-C_5H_5)Fe(η-C_5H_4Li) and (η-C_5H_4Li)$_2$Fe to which Ph_3PbCl and Ph_2PbCl_2 were added in situ [28]. The products isolated were a mixture of the plumbylferrocene (**5**), and the [1,1′]diplumbylferrocenophane (**6**). These products were characterized by NMR, MS and elemental analysis; however single crystals were not obtained, and no evidence for the formation of a [1]plumbaferrocenophane was reported [28].



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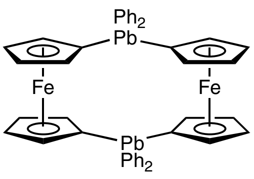

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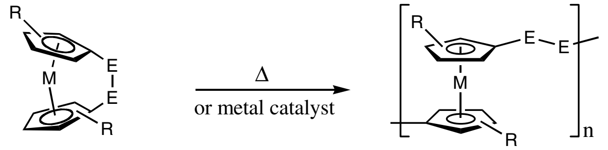
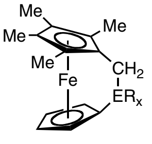
The preparation and reactivity of [1]ferrocenophanes have been well explored over the past few decades, however until recently the area of [2]ferrocenophanes has received comparatively less attention. Previous work has shown that highly strained hydrocarbon-bridged monomers **7** (M = Fe, R = H, Me, $E_2 = CH_2CH_2$) and the analogous [2]ruthenocenophane (**7**) (M = Ru, R = H, $E_2 = CH_2CH_2$), undergo thermal ROP [29,30], whereas ring-opening metathesis polymerization of [2]ferrocenophane (**7**) (M = Fe, R = H, E_2 = CH=CH) has also been described [31]. In contrast, [2]metallocenophanes with Si–Si bridges such as **7** (M = Fe or Ru, $E_2 = SiMe_2SiMe_2$), are relatively unstrained and resist ROP [32], whereas an analogue with a Ge–Ge bridge (**7**: M = Fe, $E_2 = GeMe_2GeMe_2$) has been successfully polymerized [33].



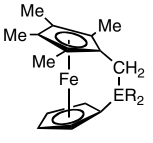
7: M = Fe or Ru,
R = H or Me,
$E_2 = CH_2CH_2$ or CH=CH
$E_2 = SiMe_2SiMe_2$ or $GeMe_2GeMe_2$

8: M = Fe or Ru,
R = H or Me,
$E_2 = CH_2CH_2$ or CH=CH
$E_2 = GeMe_2GeMe_2$

Recently, our group has studied the synthesis and ROP behaviour of [2]ferrocenophanes with unsymmetrical C–E bridges **9**–**13** [34,35]. It was shown for compounds **9**–**11** (E = Si, P, S) as the covalent radius of E was varied, the ring-strain was varied accordingly [34]. The least strained of these species (**9**, $\alpha = 11.8(1)°$) was found to be completely resistant to polymerization under all conditions studied, whereas the more strained species **10** ($\alpha_{avg} = 16.5°$) and **11** ($\alpha = 18.5(1)°$) were found to undergo successful ROP. This work recently prompted us to explore the synthesis and ROP behaviour of the [2]ferrocenophanes **12** and **13**. The presence of weak C–Ge and C–Sn bonds were expected to increase reactivity of group 14 carbo[2]ferrocenophanes, despite the decrease in tilt angle between the cyclopentadienyl rings. It was found however that the C–E bonds of **12** and **13** were insufficiently weak to permit ring-opening polymerization [35].



9 : $ER_x = SiMe_2$
10 : E = P, R = Ph, Mes
11 : ER_x = S



12 : E = Ge, R = Me, Ph
13 : E = Sn, R = Me, *t*-Bu, Mes

In this paper, we report on our attempts to further explore the area of carbon-heteroatom bridged [2]ferrocenophanes via the introduction of heavy main group elements and transition metals into the bridge. We report the synthesis and reactivity of the novel carboplumba[2]ferrocenophane (**14**) and carbozircona[2]ferrocenophane (**15**).