Platinum- or Palladium-catalysed Ring-opening Homo- and Co-polymerization of Silicon- and Germanium-bridged [1]Ferrocenophanes

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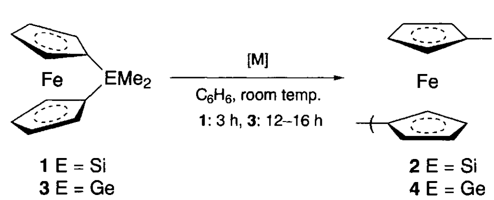
Platinum and palladium complexes catalyse ring-opening homopolymerization of [1]sila- or [1]germa-ferrocenophanes and copolymerization of these two ferrocenophanes under mild conditions to form polymers consisting of 1,1′-ferrocenylene and silylene or germylene units.

In recent years the syntheses and properties of transition-metal-containing polymers have received growing attention.[1] Ferrocene-containing polymers, in particular, are currently under intense scrutiny as they exhibit interesting physicochemical properties that are useful for the development of advanced materials.[2] [1]Ferrocenophanes possess high ring strain with tilted cyclopentadienyl rings. Accordingly, the polymers that contain an alternating 1,1′-ferrocenylene and an inorganic element such as silicon,[3] germanium[4] or phosphorus[5] in the backbone are usually synthesized *via* thermal ring-opening polymerization (ROP) of the corresponding [1]ferrocenophanes at high temperatures. A recent paper by Manners and coworkers[6] has disclosed that anionic ROP of a silicon-bridged [1]ferrocenophane also proceeds under ambient conditions. However, the transition-metal-catalysed ROP of ferrocenophanes has never been explored.[†] We now report that platinum or palladium complexes efficiently promote ROP of silicon- and germanium-bridged [1]ferrocenophanes under exceptionally mild conditions to give high molecular mass polymers and that the new catalysis allows ring-opening copolymerization.

When a mixture of dimethylsilylene-bridged [1]ferrocenophane **1** (0.2 mmol) and $Pt(cod)_2$ (cod = cycloocta-1,5-diene) (0.004 mmol) was dissolved in benzene at room temperature, the solution became highly viscous in less than 30 min.[‡] ^1H NMR spectroscopy of the reaction mixture (after 3 h) showed almost quantitative formation of the polymer **2**. Gel-permeation chromatography (GPC) (using polystyrene as standard and THF as eluent) revealed the polymer as monomodal with a mass average molecular mass (M_w) of 1.7×10^6 and polydispersity (M_w/M_n) of 2.8 (Scheme 1).

Because of the very low solubility of the catalysts (precursors) and the inhomogeneity of the reaction, comparison of catalytic performance among those catalysts tested is not straightforward. However, we can point out the following features (Table 1). As regards activity, the reaction of **1** in the presence of $Pt_2(dba)_3$ or $Pd(dba)_2$ (dba = dibenzylideneacetone) which appeared slightly more soluble than the other catalysts was apparently faster (by visual inspection of the viscosity), but relatively low molecular mass polymers were obtained. The reaction with $Pd(cod)Cl_2$ was extremely rapid and within seconds an insoluble material deposited in the solution. Molecular mass distribution was normally monomodal, but was broad compared with polymers obtained by thermal or anionic methods. Polymer **2** from the $Pt(cod)Cl_2$-catalysed reaction, however, showed two fractions with M_w (M_w/M_n) of 1.0×10^6 (1.5) for the first fraction and 7×10^4 (3.0) for the second (first : second = 34 : 66). Thus, depending on the nature of the catalyst, ROP of **1** affords variant molecular mass polymers. Phosphine–metal complexes such as $M(PPh_3)_4$ or $M(PPh_3)_2Cl_2$ (M = Pt or Pd) did not promote ROP even under heating at 70 °C.



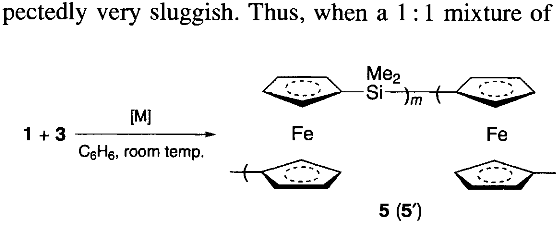
Scheme 1

Table 1 Platinum- or palladium-catalysed polymerization of **1** or **3**

	2		**4**	
[M]	M_w (M_w/M_n)	Yield (%)	M_w (M_w/M_n)	Yield (%)
$Pt(cod)_2$	1.7×10^6 (2.8)	92	1.1×10^6 (5.2)	91
$Pt(cod)Cl_2$	1.1×10^6 (1.5) 7.0×10^4 (3.0)	87		
$Pt_2(dba)_3$	3.0×10^5 (3.7)	95	2.3×10^5 (9.7)	79
$Pd(dba)_2$	1.5×10^5 (4.4)	87		
$Pd(cod)Cl_2$	(Rapid polymerization, insoluble polymer)			

The ROP of [1]germaferrocenophane **3** was also promoted by phosphine-free platinum or palladium catalysts. For instance, the $Pd(cod)Cl_2$-catalysed polymerization was very rapid and gave an insoluble polymer as observed for **1** (see above). However, depending on the catalyst, the polymerization behaviour differs slightly from that of **1**; the reaction in the presence of $Pt(cod)_2$ or $Pt_2(dba)_3$ required an extremely long induction period (> 12 h), after which smooth polymerization took place.

Copolymerization of **1** and **3** was also possible (Scheme 2). However, the reaction carried out using $Pt(cod)_2$ was unexpectedly very sluggish. Thus, when a 1 : 1 mixture of **1** and **3**



Scheme 2

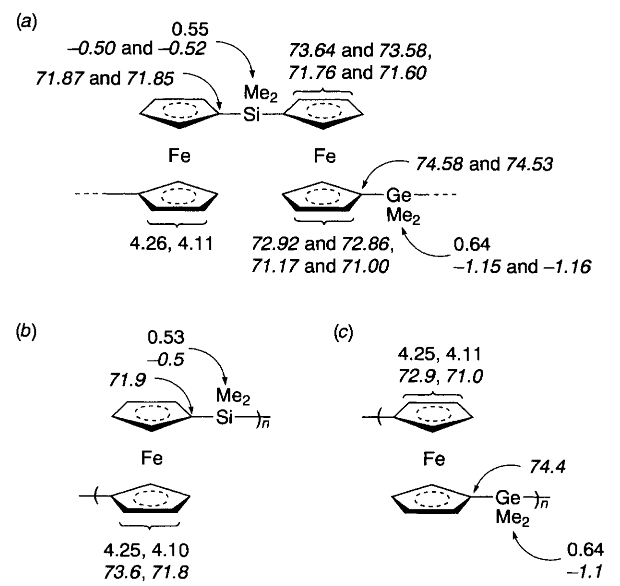


Fig. 1 NMR data of copolymer **5′** (*a*) in comparison with the homopolymers **2** (*b*) and **4** (*c*) (^1H and ^{13}C signals are shown in plain and italic fonts, respectively)

reacted in the presence of Pt(cod)$_2$ [(**1** + **3**) : Pt = 50 : 1], the *reaction did not* reach completion even after two days. Surprisingly, ^{1}H NMR spectroscopy of the reaction mixture showed that the conversion of **1** (20%) was less than that of **3** (65%) and that the ratio of SiMe$_2$ (m) to GeMe$_2$ (n) in the resulting copolymer **5** was *ca.* 1 : 3.§ In view of the high reactivity of **1** in the homopolymerization and the necessity of a long induction period for the homopolymerization of **3** (see above), this observation appeared quite abnormal. On the other hand, when the reaction was carried out using Pt$_2$(dba)$_3$, a smooth copolymerization reaction took place with complete conversion in 4 h. The copolymer **5′** showed a rather broad profile (M_w = 6.8 × 10^5; M_w/M_n = 13.5) in GPC. Spectral and analytical data¶ clearly indicate that **5′** is a 1 : 1 copolymer (m : n = 1 : 1) of **1** and **3**. ^{1}H NMR spectroscopy showed two broad resonances at δ 4.11 and 4.26 for cyclopentadienyl ring protons (Ge- and Si-bound cyclopentadienyl ring protons display signals at nearly the same chemical shifts[3a,4]), and two well resolved resonances at δ 0.55 and 0.64 corresponding to dimethylsilylene and dimethylgermylene, respectively (Fig. 1). ^{13}C NMR spectroscopy was more informative and suggested that **5′** was a random copolymer; each carbon of the cyclopentadienyl rings displayed two resonances of almost equal intensity, clearly indicating that the cyclopentadienyl rings were located in two different environments in the global structure of the polymer chain (*i.e.* block and alternating segments).

In conclusion, platinum or palladium complexes have been found to be powerful catalysts that promote ROP of [1]sila- or [1]germa-ferrocenophane under mild conditions. Although the mechanistic details are yet to be clarified, the new procedure is useful to synthesize homo- and co-polymers of [1]ferrocenophanes. Further studies are aimed at understanding the nature of the ROP, extention of the scope and properties of the resulting (co)polymers.

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Footnotes

† Reactivity of the Si–C bond of [1]silaferrocenophanes can be compared with that of 1-silacyclobutanes. Recently, we observed that phosphine-free platinum complexes catalyse the ROP of a 1-silacyclobutane and that phosphine–platinum complexes promote the dimerization (*J. Am. Chem. Soc.*, 1995, **117**, 8873).

‡ *General procedure*: A mixture of **1** or **3** (0.2 mmol) and a metal complex (**1** or **3** : metal = 50 : 1) was placed in a dried and argon-purged glass tube containing a magnetic bar and 0.5 ml of benzene was added under stirring (stirring was not necessary after the reaction mixture became homogeneous in colour). After the solution became viscous, it was allowed to stand for 2–3 h prior to analysis. The colour of the reaction mixture changed from red to brown except in the reaction with Pt(cod)$_2$ which turned to orange. The reaction mixture was dissolved in benzene (2 ml), filtered and the polymer was precipitated into hexane (20 ml). The spectral data of **2** and **4** were consistent with reported data.[3a,4]

§ The reaction was carried out in C$_6$D$_6$ and followed by NMR. The initial ratio (< 10 min) of m : n in **5** was 1 : 2 and the conversion of **1** and **3** was 7 and 13%, respectively. As the conversion increased (**1**, 20%; **3**, 65%), the ratio of m : n decreased to 1 : 3. This indicates that the reaction was initiated by **1** and in the propagation step the reactivity of **3** was higher than that of **1**.

¶ *Spectral and analytical data* for **5′**: ^{1}H NMR (300 Mz, C$_6$D$_6$) δ 4.26 (br, pseudotriplet, 8 H, C$_5$H$_4$), 4.11 (br, 8 H, C$_5$H$_4$), 0.64 (s, 6 H, GeMe$_2$), 0.55 (s, 6 H, SiMe$_2$); ^{13}C NMR (75.4 Mz, C$_6$D$_6$) δ 74.58 and 74.53 (2 C, *ipso*-CGe), 73.64 and 73.58 (4 C, SiC$_5$H$_4$), 72.92 and 72.86 (4 C, GeC$_5$H$_4$), 71.87 and 71.85 (2 C, *ipso*-CSi), 71.76 and 71.60 (4 C, SiC$_5$H$_4$), 71.17 and 71.00 (4 C, GeC$_5$H$_4$), −0.50 and −0.52 (2 C, SiMe$_2$), −1.15 and −1.16 (2 C, GeMe$_2$); ^{29}Si NMR (59.6 Mz, C$_6$D$_6$) δ −6.28.

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