Synthesis and Ring-opening of 1,2-Digerma[2]ferrocenophane Catalyzed by Palladium or Platinum Complexes

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1,2-Digerma[2]ferrocenophane (**1**) was prepared and was fully characterized by spectroscopic methods. Palladium or platinum complexes-catalyzed ring-opening polymerization of **1** under mild conditions yielded high molecular weight poly(ferrocenyltetramethyldigermane) in good yields.

Recently, considerable interest has been focused on polymers having a regular alternating arrangement of a group 14 element σ unit and a π-system in the backbone in view of their novel properties and potential applications.[1-8] Particularly, ferrocenes may serve as an interesting π system in the σ-π alternating copolymers because transition metal-containing polymers are expected to have high thermal stability, tunable redox characteristics, and possibly novel magnetic and charge transport properties.[9-14] Such properties are often difficult or impossible to achieve with organic polymers. As part of our program to explore the synthesis and properties of new classes of polygermanes, we herein describe the preparation, structural characterization, and ring-opening polymerization (ROP) of 1,2-digerma[2]ferrocenophane catalyzed by palladium or platinum complexes.

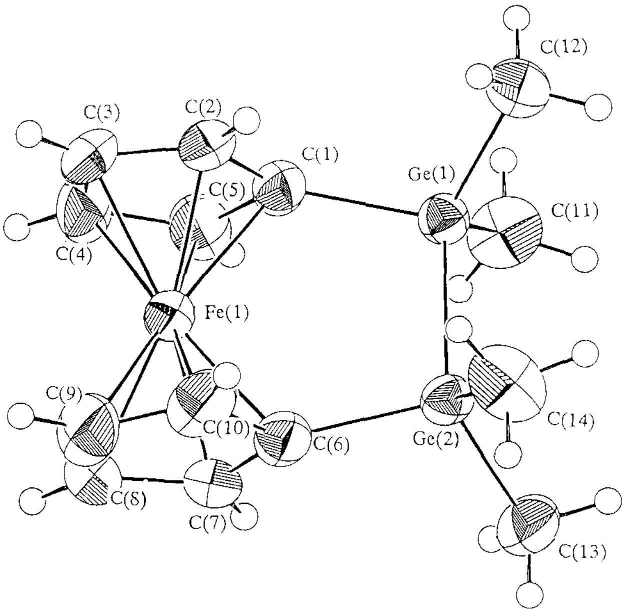


Figure 1. Structure of **1** in the crystal. Selected bond lengths [Å] and angles [°]: Ge(1)-Ge(2) 2.418(1), Ge(1)-C(1) 1.946 (5), Ge(1)-C(11) 1.956 (6), Ge(2)-C(6) 1.959 (5), Ge(2)-C(13) 1.952 (6), Ge(2)-C(14) 1.949 (7); Ge(2)-Ge(1)-C(1) 101.8 (2), Ge(2)-Ge(1)-C(11) 113.4 (2), Ge(2)-Ge(1)-C(12) 115.3 (3), C(1)-Ge(1)-C(11) 108.8 (3), C(1)-Ge(1)-C(12) 107.9 (3), C(11)-Ge(1)-C(12) 109.2 (3), Ge(1)-Ge(2)-C(6) 101.4 (2), Ge(1)-Ge(2)-C(13) 114.3 (3), Ge(1)-Ge(2)-C(14) 113.2 (3), C(6)-Ge(2)-C(13) 108.7 (3), C(6)-Ge(2)-C(14) 109.0 (3), C(13)-Ge(2)-C(14) 109.7 (3).

1,2-Digerma[2]ferrocenophane (**1**) was prepared by the reaction of dilithioferrocene-TMEDA (TMEDA=tetramethylenediamine) with 1,1,2,2-tetramethyl-1,2-dichlorodigermane.[15] The compound **1** was a reddish-orange, moisture-stable, and thermally stable crystalline material. The structure of **1** was confirmed by ^{1}H, ^{13}C NMR, and mass spectroscopy.[16] The X-ray structure of **1** was also determined. A view of the molecular structure of **1** is shown in Figure 1. The molecular structure of **1** reveals some slight and typical deformations as shown in Figure 2.

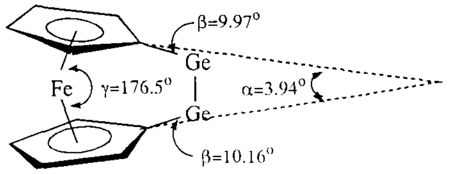


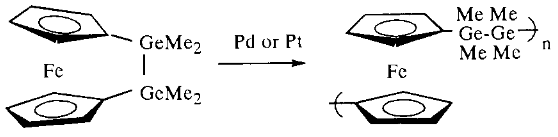
Figure 2. Distorsion in **1** defining angles α, β, and γ.

The cyclopentadienyl rings are almost parallel (with a tilt angle α of 3.9° towards the bridge) and adopt a nearly eclipsed conformation (with a twist angle τ of 5.0°). Both the C(1)-Ge(1) and the C(6)-Ge(2) distances (av 1.96 Å) and the Me-Ge-Me angles (av 109.5°) are in the expected ranges.

Previous work has shown that palladium or platinum complexes undergo oxidative addition of a germanium-germanium bond.[17-19] It therefore is of interest to investigate whether transition-metal catalyzed ROP of **1** will also be possible. Indeed, we found that reaction of **1** with small quantities of Pd(acac)$_2$ (acac=acetylacetonato), Pd(dba)$_2$ (dba=dibenzylideneacetone), and PtCl$_2$(cod) (cod=1,5-cyclooctadiene) in benzene or hexane afforded the poly(ferrocenyldigermane) **2** in all cases.[20] These results are summarized in Table 1.

In a typical experiment, a benzene (1 ml) solution of **1** (0.2 mmol) was stirred at room temperature in an argon-purged sealed tube in the presence of Pd(acac)$_2$ (4 mol%). The conversion of **1** and formation of **2** were monitored by ^{1}H NMR. The solution became highly viscous in 50 h. The molecular weight (M_w) of polymer **2** was determined by GPC to be 5.0 x 10^5 with polydispersity (M_w/M_n) of 1.7 (Scheme 1). The polymer **2** is highly soluble in common organic solvents such as dichloromethane, chloroform, benzene, and THF. NMR spectroscopy revealed that the polymer **2** comprises digermanylene and ferrocene units which alternate in a regular repetitive form.

Under similar reaction conditions, Pd(PPh$_3$)$_4$, PdCl$_2$(PPh$_3$)$_2$, Pt(PPh$_3$)$_4$, Pt(acac)$_2$, and Pt(dba)$_2$ catalysts could not promote



1 **2**

Scheme 1.

ROP of **1**.

Thermal ROP and anionic living ROP of **1** could not also be achieved under various conditions. Similar results on ROP of 1,2-disila[2]ferrocenophane have been reported.[21,22]

Thermal and transition metal complexes catalyzed ROP of [1]ferrocenophanes containing germanium as bridging element also proceed.[23-26]

Table 1. The ring-opening polymerization of compound **1** catalyzed by palladium or platinum complexes

Complex	Conditions	$M_w \times 10^4$	M_w/M_n	Yield/%
$Pd(acac)_2$	r.t., 50 h	40	1.7	68
$Pd(dba)_2$	r.t., 50 h	50	1.8	45
$PtCl_2(cod)$	r.t., 70 h	2	2.6	70

acac=acetylacetonato. dba=dibenzylideneacetone. cod=1,5-cyclooctadiene.

In conclusion, we have demonstrated that [2]ferrocenophane **1** polymerizes in the presence of palladium or platinum complexes. The Ge-Ge bond of **1** undergoes a facile oxidative addition reaction of a Pd(II) or Pt(II) complexes. The detailed studies on the catalytic transformations of **1** are in progress.

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16 **1**: ^1H NMR (δ in $CDCl_3$) 0.52 (s, 12H), 4.18 (pseudo tr, J=1.65 Hz, 4H), 4.53 (pseudo tr, J=1.65 Hz, 4H); ^{13}C NMR (δ in $CDCl_3$) -3.3, 44.8, 72.3, 75.9; MS M^+ 389.
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