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New Route to Unsaturated Organosilicon Polymers and Macrocycles Based on Zirconocene Coupling of 1,4-MeC≡C(Me$_2$Si)C$_6$H$_4$(SiMe$_2$)C≡CMe

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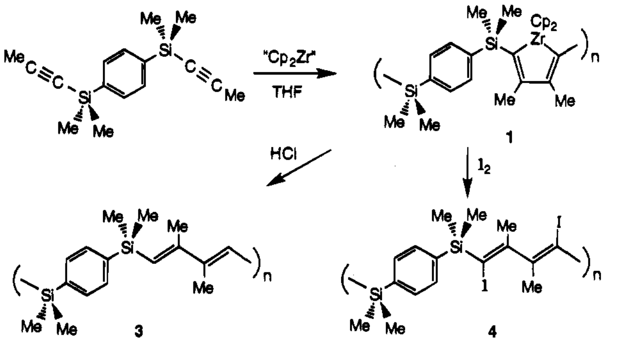
Substantial efforts in materials chemistry target the construction of "supramolecular" structures based on electroactive chains or segments which can mediate charge transport. Macromolecules with σ, π, or σ/π conjugation have been used in the design of rechargeable batteries, light-emitting diodes, photovoltaic cells, electrochromic devices, and as light weight conducting, electrophotographic, and nonlinear optical materials.[1] Macrocycles with delocalized structures have also attracted attention as components in molecular electronic devices, as building blocks for electroactive networks, and for their molecular recognition properties.[2] A new synthetic approach to metal-containing, electroactive polymers is based on the metal-induced coupling of diynes RC≡CR′C≡CR to polymers possessing metallacyclopentadiene groups in the main chain. Two groups have recently reported the synthesis of cobaltacyclopentadiene polymers by this method,[3] and we have been exploring analogous couplings to zirconocene-containing polymers. Zirconacyclopentadiene residues in the polymer backbone may significantly influence the electronic properties of the polymer and should provide versatile chemical pathways for placement of a variety of conjugated groups (dienes, aromatic heterocycles) into a delocalized chain.[4] Here we report some of our initial results in employing this strategy, which demonstrate the utility of a single diyne, 1,4-MeC≡C(Me$_2$Si)C$_6$H$_4$(SiMe$_2$)C≡CMe, as a synthon for high-yield conversions to various polymers and macrocycles. On the basis of literature precedent, σ/π-conjugated polymers containing isolated silylene units are expected to be slightly delocalized and dopable to a semiconducting state.[5]

Generation of a slight excess of "zirconocene" (by addition of 2 equiv of *n*-BuLi to Cp$_2$ZrCl$_2$ at −78 °C and then warming to room temperature)[6] in the presence of 1,4-MeC≡C(Me$_2$Si)C$_6$H$_4$(SiMe$_2$)C≡CMe resulted in formation of yellow polymer **1**, isolated in 90% yield by fractionation from benzene/pentane solution (Scheme 1).[7] This polymer (M_w/M_n = 13 000/4600 vs polystyrene standards) is soluble in most organic solvents, and thin films are readily cast from THF solutions. Refractionation of the polymer by addition of a benzene solution to pentane separated polymer of higher molecular weight (M_w/M_n = 17 000/8000; 62% yield). Spectroscopic data[7] are consistent with the structure shown in Scheme 1 and reflect regiospecific coupling to afford 2,5-zirconacyclopentadiene rings in the polymer backbone. In particular, the ^{1}H and ^{13}C NMR shifts for **1** closely correspond to those for the model complex 2,5-bis(dimethylphenylsilyl)-3,4-dimethylzirconacyclopentadiene (**2**).[7] The λ_{max} value for **1** (228 nm) is at somewhat lower energy than the λ_{max} value for **2** (214 nm), suggesting only slight conjugation between monomer units in **1**, as would be expected for *cis*-diene units and a σ/π system of this type.

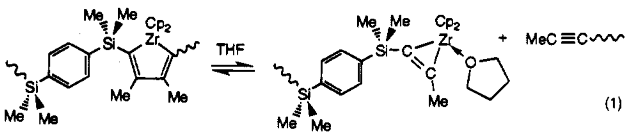
Scheme 1



End-group analysis of **1** by ^{1}H NMR spectroscopy provided a molecular weight for **1** of ca. 28 000. The great disparity between this value and the molecular weight obtained by gel permeation chromatography (GPC) (4600) indicates that some of the polymers formed in this condensation reaction have cyclic structures. The GPC trace for **1** reveals a primarily monomodal molecular weight distribution in addition to a small peak (at ca. M = 1000, Scheme 2), which appeared to correspond to a cyclic oligomer (compound **5**, vide infra) on the basis of its increased yield under more dilute reaction conditions (e.g., 50% for a monomer concentration of ca. 0.1 M).

The synthetic utility of **1** as a reaction intermediate was initially demonstrated by two reactions which are well-known for zirconacyclopentadiene derivatives (Scheme 1).[4] Hydrolysis of **1** (M_w/M_n = 13 000/4600) with concentrated HCl generated a quantitative amount of Cp$_2$ZrCl$_2$ and colorless polymer **3** (94% isolated yield) with little or no degradation of the polymer backbone (M_w/M_n = 12 000/4200). The λ_{max} value for **3** (261 nm) reflects the higher conjugation associated with *trans*-dienyl units. Reaction of **1** with iodine produced the vinyl iodide polymer **4** (M_w/M_n = 8800/5000) in 74% isolated yield.

In investigating the influence of reaction temperature on formation of **1**, we discovered that higher temperatures favor production of the low-molecular-weight species **5**. This is due to depolymerization of the (Me$_2$SiC$_6$H$_4$SiMe$_2$C$_4$Me$_2$ZrCp$_2$)$_n$ chains, as shown by the quantitative (by GPC) conversion of **1** to **5** in refluxing THF (Scheme 2). The depolymerization of **1** to **5**, identified by X-ray crystallography as a trimer, most likely occurs via reversible alkyne-coupling reactions.[8] Thus, the reaction is cleaner and more rapid in THF (vs benzene), probably because THF stabilizes intermediate alkyne complexes in the polymer-cleavage process (eq 1).



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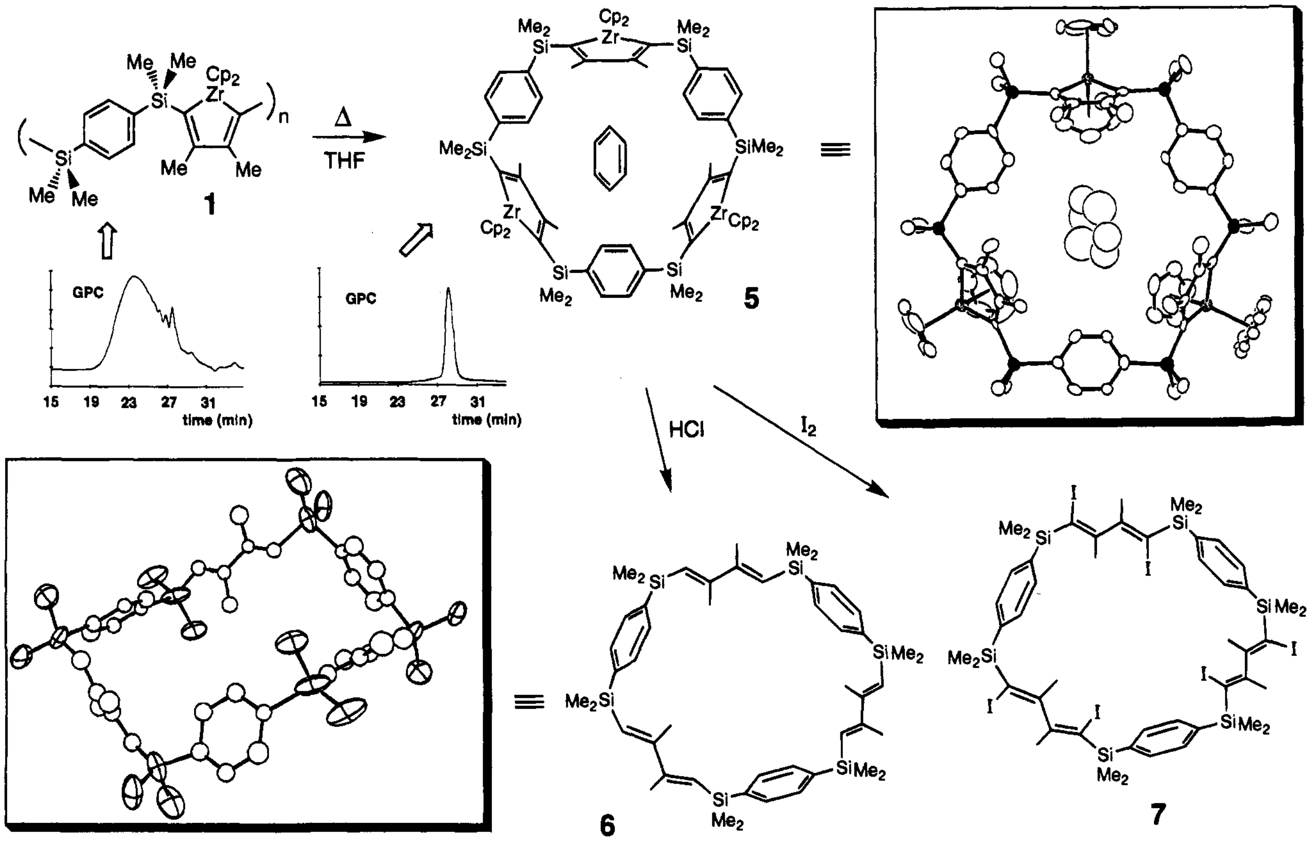
Scheme 2



Air-sensitive, yellow crystals of **5** were grown from a THF/ether solution containing a slight amount of benzene. These crystals contain 3.5 equiv of somewhat disordered benzene molecules per macrocycle, one of which is located near the center of the ring, in closest contact with the dienyl methyl substituents. The trimeric ring (Scheme 2)[7] is approximately planar, with five of the six Si atoms in a plane, and one displaced by 0.86 Å in the direction of the zirconocene groups, which all protrude from the same face of the ring and lie outside of the perimeter. The slight bending in the ring appears to result merely from crystal-packing forces. The phenyl groups are all roughly coplanar with the Si atoms of the ring, while the dienyl rings are strongly tilted with respect to this plane. The linkages between the Si atoms are approximately linear, and the cavity size may be described by transannular Si· · ·Si distances of 12.87, 13.41, and 13.42 Å. In toluene-d_8 solution at −78 °C, two resonances for the $SiMe_2$ groups were observed in the ^1H NMR spectrum, but warming the solution resulted in coalescence of these resonances ($T_c = -37$ °C; $\Delta G^{\ddagger} = 10.9$ kcal mol^{-1}), apparently by rotation of the zirconacyclopentadiene units about the Si· · ·Si axes, which flips the six Cp ligands from one side of the ring to the other.

Hydrolysis of **5** converted the metallacycle rings to *trans*-dienyl units with formation of colorless **6** (98%), which crystallizes from acetonitrile without incorporation of solvent (Scheme 2).[7] Molecules of **6** adopt cyclohexane-like chair conformations and are stacked in columns along the *a* direction. These chairs are somewhat irregular in shape, as indicated by inequivalent transannular Si−Si distances of 14.22, 11.81, and 12.75 Å.

Iodinolysis of **5** gave the functionalized macrocycle **7** in 75% isolated yield (Scheme 2; trimeric by mass spectroscopy). The ^1H and ^{13}C NMR spectra of **7** indicate the presence of four isomers (presumably rotamers) with inequivalent SiMe resonances, which do not coalesce up to 90 °C.[7]

In conclusion, we have described simple synthetic procedures for the incorporation of unsaturated zirconacyclopentadienyl rings into a polymer chain, which is a versatile and efficient precursor to macrocycles and other polymers. In particular, the high-yield macrocycle syntheses are remarkable in that routes to macrocycles are generally associated with low yields.[2a] The efficient conversion of polymer **1** to macrocycle **5** is attributed to the facile reversibility of alkyne coupling, which provides a low-energy pathway to the thermodynamic product. We are currently investigating the generality of the diyne coupling method described here and will soon report on extensions to polymers and macrocycles with all-carbon-based π systems.[9]

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Supplementary Material Available: Experimental procedures and characterization data for polymers and compounds, tables of crystal, data collection, and refinement parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates, and other views of the structures (41 pages); listings of observed and calculated structure factors (89 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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