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Preliminary communication

Cross-conjugated polymers via condensation of a zirconocene alkynyl(benzyne) derivative generated by thermolysis of $Cp_2ZrMe(C_6H_4C{\equiv}CSiMe_3)$ [1]

Shane S.H. Mao, T.D. Tilley *

Department of Chemistry, University of California at Berkeley, Berkeley, CA 94720-1460, USA

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Abstract

The complex $Cp_2ZrMe(C_6H_4C{\equiv}CSiMe_3)$ (4) has been synthesized by reaction of $Cp_2ZrMeCl$ and $LiC_6H_4C{\equiv}CSiMe_3$ (generated in situ from reaction of ^nBuLi with $BrC_6H_4C{\equiv}CSiMe_3$ at −95°C). Thermolysis of 4 in THF afforded an unsaturated, organometallic polymer $[Cp_2Zr(C_6H_3C{=}CSiMe_3)]_n$ (7) in ca. 80% yield (M_w/M_n = 4000/2000). Polymer 7 was investigated as a synthon for other unsaturated polymers. It reacts with hydrochloric acid to form a new phenylene-1,1-vinylene polymer $[-C(=CHSiMe_3)-1,4-C_6H_4-]_n$ (8), and with sulfur dichloride to give poly(1-trimethylsilyl-2-benzo[b]thiophene) (9). Thermolysis of two similar compounds, $Cp_2ZrMe(C_6H_4C{\equiv}CCH_3)$ (5) and $Cp_2ZrMe(C_6H_4C_6H_4C{\equiv}CSiMe_3)$ (6), did not give polymers.

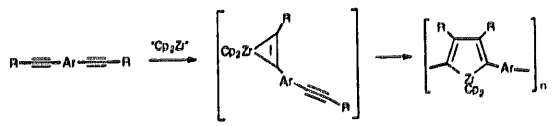
Keywords: Silicon; Zirconium; Zirconocene; Polymers; Benzene; Alkyne

1. Introduction

In recent years, considerable effort has been devoted to the synthesis of new conjugated polymers with potential applications as electrically conducting materials in batteries, chemical sensors, light emitting diodes, and non-linear optical materials [1]. As such applications develop, it becomes more desirable to access specific charge-transporting capabilities, as defined by the polymer's band gap, ionization potential and/or electron affinity [1d,1e]. A potentially useful strategy for fine-tuning these properties involves use of versatile 'synthetic intermediate' structures which may be derivatized in numerous ways. We have recently described such an approach, based on incorporation of zirconacyclopentadiene units into the backbone of a conjugated polymer (Eq. (1), Ar = aromatic linker) [2]. Such polymers possess reactive zirconacyclopentadiene structures which may be converted into a variety of other conjugated residues (butadienyl, phosphole, thiophene, aromatic, etc.) [2c,d]. The intermolecular coupling of diynes by zirconocene presumably occurs by formation of an intermediate zirconacyclopropene complex, which undergoes condensation with a second equivalent of alkyne to give the final zirconacyclopentadiene unit (Eq. (1)) [3]. A related process involves coupling of a zirconocene benzyne complex with an alkyne to produce metallacycles [4]. Here we report attempts to utilize such zirconium-mediated benzyne–alkyne couplings in the synthesis of new polymer structures.

2. Results and discussion

Syntheses of the monomer precursors are outlined in Scheme 1. The palladium-catalyzed coupling of 4-iodobromobenzene or 4,4′-diiodobiphenyl with one equivalent of a terminal alkyne afforded the correspond-



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* Corresponding author.

[1] Dedicated to Professor Robert Corriu in recognition of his many contributions to organosilicon chemistry.

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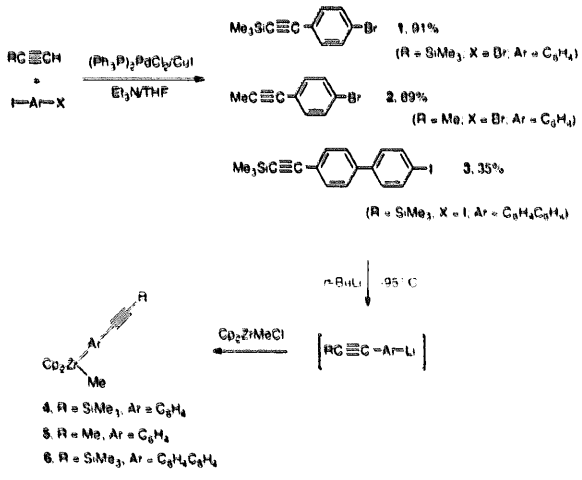
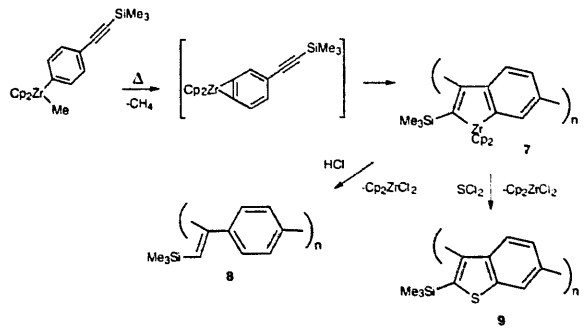
ing alkynylaryl derivatives RC≡C–Ar–X (**1–3**) [5]. Addition of one equivalent of ^{n}BuLi to a THF solution of **1**, **2** or **3** at −95°C produced the lithium reagents LiArC≡CR, which are thermally unstable (decomposing at −78°C within a few hours) but can be generated and used in situ at −95°C for the preparation of complexes **4–6**. These complexes are typically contaminated by impurities (resulting from competing thermal decomposition of the lithium reagents), which are difficult to remove completely by recrystallizations. As compound **4** is extremely soluble in pentane (ca. 2 g ml^{-1}), it can be isolated as an analytically pure, yellowish solid. In contrast, complexes **5** and **6** have solubilities similar to those of the impurities, and so could not be isolated in greater than about 95% purity (by ^{1}H and ^{13}C NMR spectroscopy). The spectroscopic data for compounds **4**, **5** and **6** are similar, and consistent with the structures given in Scheme 1 [6].

Compounds **4–6** are highly air- and light-sensitive. At room temperature, **5** and **6** are stable over extended periods, whereas **4** decomposes to a red solid by loss of methane (vide infra). Samples of **5** and **6** (each containing about 5% impurity) decompose at 85°C by elimination of methane (by ^{1}H NMR spectroscopy) to low molecular weight materials with $M_n < 1000$ (by gel permeation chromatography (gpc); polystyrene standards). Clean formation of higher molecular weight polymers may be inhibited by the impurities that are present in samples of these monomers.

Thermolysis of **4** at 70°C results in a color change from pale yellow to deep red over 1 h, and methane evolution is observed as bubbles in the solution. Monitoring the reaction by ^{1}H NMR spectroscopy (benzene-d_6 solution) revealed the rapid disappearance of **4** and formation of methane. Thermolysis of a concentrated THF solution of **4** (ca. 2 M) at 85°C for 36 h afforded a red polymer **7** in 83% yield (M_w/M_n = 4000/2000; Scheme 2). Prolonged heating of the solution did not



Scheme 1.



Scheme 2.

result in an increase in the molecular weight and, as expected, lowering the monomer concentration decreased the molecular weight significantly (M_w/M_n = 1600/1000 for a monomer concentration of 0.5 M). Similar results were obtained with cyclohexane solvent (M_w/M_n = 3800/1900).

Red polymer **7**, which is air-sensitive and soluble in common organic solvents, was purified by fractionation (precipitation by addition of a benzene solution to an excess of pentane). The ^{1}H NMR spectrum of **7** consists of broad peaks at 0.1, 6.1, 6.6, and 7.1 ppm (integrated ratio 9:10:1:2), which are assigned to the trimethylsilyl, cyclopentadienyl, and aromatic groups, respectively [7a]. Hydrolysis of **7** with concentrated hydrochloric acid afforded the colorless, phenylene-1,1-vinylene polymer **8** (M_w/M_n = 2700/1700) in 80% yield, along with a quantitative yield of zirconocene dichloride (Scheme 2) [7b].

Reaction of **7** with sulfur monochloride afforded a yellow polymer **9** in 50% yield (M_w/M_n = 2400/1400; Scheme 2), along with one equivalent of elemental sulfur (as measured by by thermal gravimetric analysis (TGA) and elemental analysis). Efforts to separate sulfur from this polymer by either solvent extraction or reaction with Hg failed, perhaps due to an interaction between the elemental sulfur and the polymer chain. To overcome this problem, sulfur dichloride (containing 20% of S_2Cl_2) was used as an alternative reagent to generate polymer **9**, and this resulted in incorporation of less elemental sulfur (only 3.0% by TGA). The ^{1}H and ^{13}C{^{1}H} NMR spectra are consistent with the structure given in Scheme 2 [7c]. The presence of the benzo[b]thiophene group in polymer **9** is supported by the appearance of infrared absorption bands at 1589, 1542, 1510, 1461, 1405 and 1373 cm^{-1} [8]. Note that the poly(2-benzo[b]thiophene) **9** is related to poly(1-benzo[b]thiophene), which has been made by plasma- and electrochemical polymerizations [9,10].

The UV–vis spectra for polymers **7**, **8** and **9** are compared in Fig. 1. Owing to the cross-conjugated nature of these polymers, the observed band gaps are relatively high. Polymer **7** displays a λ_{max} value of ca. 260 nm, and the presence of weaker transitions at ca.

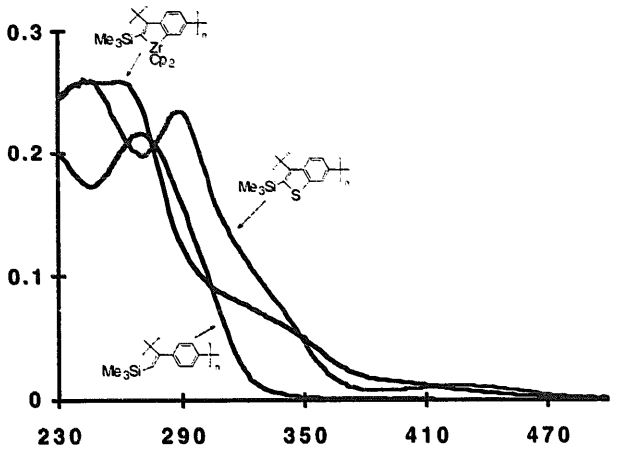


Fig. 1. UV–vis spectra of polymers **7**, **8** and **9**.

320 and 400 nm which may represent ligand-to-metal charge transfer transitions. The spectrum for polymer **9** contains a major absorption at $\lambda_{max} = 288$ nm, which is similar to the λ_{max} value reported for benzo[b]thiophene (294 nm) [8]. Thermal analyses of polymers **8** and **9** revealed onset temperatures for decomposition at 425°C and 410°C respectively.

In conclusion, we have synthesized a low molecular weight polymer (**7**) containing zirconacyclopentadiene units by thermolysis of the single-source precursor molecule $Cp_2ZrMe(C_6H_4C{\equiv}CSiMe_3)$ (**4**). This organometallic polymer has been derivatized to other new polymers containing phenylene-1,1-vinylene and 2-benzo[b]thiophene repeat units. We are currently investigating other routes to polymers which utilize zirconocene benzyne chemistry, in search of polymerizations that provide higher molecular weights and more conjugated structures.

Acknowledgements

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[6] (a) Selected spectroscopic data for compound **4**: ^{1}H NMR (benzene-d_6, 400 MHz): δ 0.16 (s, 3 H, $ZrCH_3$), 0.27 (s, 9 H, $SiCH_3$), 5.65 (s, 10 H, C_5H_5), 6.87 (d, 2 H, $J = 8.1$ Hz, C_6H_4), 7.50 (d, 2 H, $J = 8.1$ Hz, C_6H_4). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz): δ 0.29 ($SiCH_3$), 3.10 ($ZrCH_3$), 92.82 ($C{\equiv}CSiMe_3$), 107.64 ($C{\equiv}CSiMe_3$), 111.30 (C_5H_5), 128.50 (C_6H_4), 129.87 (C_6H_4), 135.12 (C_6H_4), 186.71 (C_6H_4). Anal. Found: C, 63.74; H, 6.50. $C_{22}H_{26}SiZr$. Calc.: C, 64.49; H, 6.40%. EIMS: 393 ($M^+ - CH_4$). The isotope pattern for this peak matched that obtained from simulation of the benzyne complex $Cp_2Zr(C_6H_3C{\equiv}CSiMe_3)$. (b) For compound **5**: ^{1}H NMR (benzene-d_6, 400 MHz): δ 0.19 (s, 3 H, $ZrCH_3$), 1.73 (s, 3 H, $C{\equiv}CCH_3$), 5.69 (s, 10 H C_5H_5), 6.91 (d, 2 H, $J = 8.0$ Hz, C_6H_4), 7.45 (d, 2 H, $J = 8.0$ Hz, C_6H_4). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz): δ 4.22 ($Zr{-}CH_3$), 35.09 ($C{\equiv}CCH_3$), 81.62($C{\equiv}C$), 84.53 ($C{\equiv}C$), 111.38 (C_5H_5), 128.50 (C_6H_4), 129.27 (C_6H_4), 135.12 (C_6H_4), 184.67 (C_6H_4). EIMS: $M^+ = 351$, 335 (most intense peak, $M^+ - CH_4$). The isotope patterns for these peaks were in good agreement with those obtained from simulations. (c) For compound **6**: ^{1}H NMR (benzene-d_6, 400 MHz): δ 0.27 (s, 9H, $SiCH_3$), 0.28 (s, 3 H, $ZrCH_3$), 5.75 (s, 10 H, C_5H_5), 7.07 (d, 2 H, $J = 8.0$ Hz, C_6H_4), 7.36 (d, 2 H, $J = 8.0$ Hz, C_6H_4), 7.46 (d, 2 H, $J = 8.0$ Hz, C_6H_4), 7.58 (d, 2 H, $J = 8.0$ Hz, C_6H_4). EIMS: $M^+ = 486$, 470 ($M^+ - CH_4$, most intense peak). The isotope patterns for these peaks were in good agreement with those obtained from simulations.

[7] (a) Data for polymer **7**: ^{1}H NMR (benzene-d_6, 400 MHz): δ 0.1 (br, 9 H, $SiCH_3$), 6.1 (br, 10 H, C_5H_5), 6.6 (br, 2 H, C_6H_3), 7.1 (br, 1 H, C_6H_3). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz): δ 3.1 (br, $SiCH_3$), 112.5 (br, C_5H_5), 125.9 (C_6H_3), 129.7 (C_6H_3), 136.7 (C_6H_3), 160.6 (C_6H_3), 183.8 (C_6H_3), 203 (C_6H_3). $M_w/M_n = 4000/2000$. Anal. Found: C, 63.27; H, 6.02. $C_{21}H_{22}SiZr$. Calc.: C, 64.07; H, 5.63%. (b) Data for polymer **8**: ^{1}H NMR (benzene-d_6, 400 MHz): δ 0.09 (br, 9 H, $SiCH_3$), 6.42 (br, 1 H, C=CH), 7.18 (br, 2 H, C_6H_4), 7.35 (br, 2 H, C_6H_4). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz): δ 0.24 (br, $SiCH_3$), 127.36 (C_6H_3), 128.83, 129.84 (C=CH), 129.91 (C_6H_3), 142.49, 142.72, 157.01. $M_w/M_n = 2700/1700$. Anal. Found: C, 75.33; H, 8.32. $C_{11}H_{14}Si$. C, 75.79; H, 8.09%. Calc.: (c) Data for polymer **9**: ^{1}H NMR (benzene-d_6, 400 MHz): δ −0.01 (br, 9 H, $SiMe_3$), 6.63 (s, 1 H, C_6H_3), 7.00 (s, 2 H, C_6H_3). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz): δ 0.00 (br, $SiCH_3$), 130.4 (C_8H_3S), 134.0 (C_8H_3S), 137.5 (C_8H_3S), 141.8 (C_8H_3S), 151.0 (C_8H_3S). $M_w/M_n = 2400/1400$. Anal. Found: C, 55.36; H, 5.40. $C_{11}H_{12}S_2Si$. Calc.: C, 55.88; H, 5.12%.

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