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Ring-Opening Polymerization of 19-Electron [2]Cobaltocenophanes: A Route to High-Molecular-Weight, Water-Soluble Polycobaltocenium Polyelectrolytes

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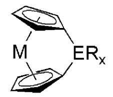
Strained metallocenophanes **1** and related species with π-hydrocarbon ligands are of increasing interest with respect to their reactivity, electronic structures, and use as precursors of functional metallopolymers **2** via ring-opening polymerization (ROP).[1,2] Currently, the most well developed area concerns the synthesis, reactions, and ROP of [1]- and [2]ferrocenophanes. In particular, ROP of 18-electron silicon-bridged[1] [1]ferrocenophanes (**1**, M = Fe, ER_x = SiR_2) provides a route to polyferrocenylsilanes (**2**, M = Fe, ER_x = SiR_2),[3] which have attracted attention as redox-active components of photonic crystal displays,[4] capsules with redox-tunable permeability,[5] redox-responsive surfaces,[6] precursors to magnetic and catalytically active ceramics,[7,8] plasma-etch resists for nanopatterning applications,[9] and self-assembled or crystalline materials.[10] The use of the ROP approach to access new polymer systems based on metals other than iron is much less developed and is currently restricted to materials based on Ru, Ti, V, and Cr.[1] In this paper, we report the successful ROP of dicarba[2]cobaltocenophane **3**. This provides a route to high-molecular-weight polycobaltocenium polyelectrolytes, an unusual class of air-stable, water-soluble redox-active polyelectrolytes.[11,12]



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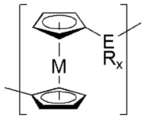

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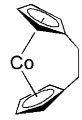

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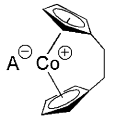
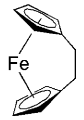


4a A = Cl
4b A = PF$_6$



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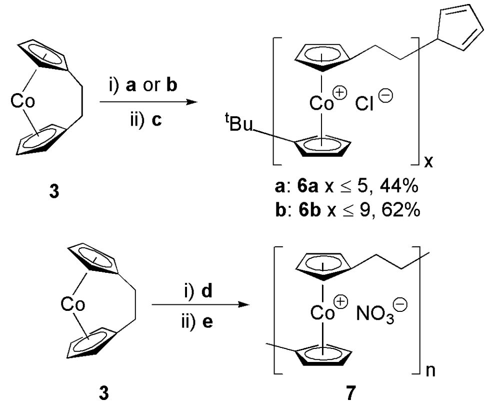
Although accounts of the synthesis and characterization of several [2]cobaltocenophanes have appeared in the literature,[13,14] to date there have been no reports on their successful ROP. High-molecular-weight, easily processed polycobaltocenes are desirable synthetic targets, as their redox activity, which involves cationic 18-electron and neutral 19-electron states, should complement that of polyferrocenes, where neutral 18-electron and cationic 17-electron forms participate. In addition, the most stable 18-electron polycobaltocenium form would be expected to readily afford hydrophilic materials, which are more difficult to access for ferrocene analogues. Furthermore, recent studies of intervalence charge transfer between metal centers in model complexes have suggested that metal−metal interactions in polycobaltocenes should be enhanced relative to those in the corresponding ferrocene systems.[15]

We have previously shown that sila[1]ferrocenophanes undergo photocontrolled living anionic polymerization via an Fe−Cp (Cp = cyclopentadienyl) bond-cleavage mechanism in the presence of mild nucleophiles such as M[C_5H_4R] (M = Li, Na; R = H, Me, ^{t}Bu).[16,17] Our attempts to induce photocontrolled ROP of the 18-electron cobaltoceniumphane **4b** using similar methods under a variety of conditions were unsuccessful and led only to unreacted monomer.[18]

The Co−Cp bond would be expected to be weakened in the corresponding 19-electron [2]cobaltocenophane **3**, which has previously been shown by X-ray crystallography to possess a larger dihedral angle (α) between the planes of the Cp ligands, and thus larger intrinsic ring strain, than analogous 18-electron species [α = 27.1(4)° for **3**,[13] 21.4(2)° for **4a**,[13] and 21.6(4)° for **5**[19]]. Cobaltocenophane **3** was combined with 0.1 equiv of Li[^{t}BuC$_5$H$_4$] in THF and irradiated with UV light for 1 h at 20 °C (Scheme 1, top). At the end of the irradiation period, the suspension, indicative of the presence of insoluble oligomers or polymers, was quenched with degassed methanol and treated with a saturated aqueous solution of NH_4Cl in air to oxidize the resulting material to its cobaltocenium form. After purification by column chromatography, yellow oligocobaltocenium **6a** ($DP_n \le 5$) was isolated in 44% yield based on **3**.[20]

Scheme 1. Syntheses of **6a**, **6b**, and **7**[a]



[a] Conditions: (a) hν, 0.1 equiv of Li[^{t}BuC$_5$H$_4$], THF, 1 h; (b) 0.1 equiv of Li[^{t}BuC$_5$H$_4$], THF, 16 h; (c) NH_4Cl, H_2O, O_2, 16 h; (d) 140 °C, 1 h; (e) NH_4NO_3, MeOH/H_2O, O_2, 16 h.

In order to test whether the oligomerization was dependent on UV irradiation, a control experiment was conducted. Cobaltocenophane **3** was stirred for 16 h in the absence of light at 20 °C under conditions otherwise identical to those discussed above (Scheme 1, top). This also yielded yellow oligocobaltocenium, **6b** ($DP_n \le 9$), in 62% yield based on **3**. The observed chain growth in the absence of light confirmed a weak M−Cp bond, presumably as the unpaired electron in the 19-electron cobaltocenophane occupies an orbital with significant antibonding character. In both reactions, the lower-than-expected DP_n values and the formation of insoluble material suggested that the synthesis of higher-molecular-weight species by anionic polymerization in THF in the presence or absence of light may not be possible.

Thermal ROP of 18-electron species **5** at 300 °C has previously been used to afford high-molecular-weight polymers.[19] We therefore explored a similar approach for 19-electron **3**. A sample of **3** was sealed in an evacuated Pyrex glass tube and heated at 140 °C with constant

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rocking for 1 h. The sample melted and then rapidly became immobile and solidified. The contents of the tube were cooled and then stirred overnight in a 50:50 methanol/water mixture saturated with NH_4NO_3 in air (Scheme 1, bottom).[21] The resulting yellow suspension was then placed in a dialysis tube (MWCO = 14 000) and dialyzed against deionized water for 72 h, at which time the majority of the suspension had dissolved. During the dialysis, no coloration of water outside the dialysis tube was observed, qualitatively ruling out the presence of a significant fraction of low-molecular-weight species. The mixture was filtered and the water removed to yield yellow-green polymer **7** in 47% yield; elemental analyses data for **7** were consistent with polycobaltocenium nitrate. The NMR spectra for **7** were significantly shifted relative to those reported for **4a** and **4b**.[13] The ^{1}H NMR spectrum of **7** (in D_2O) showed two broad resonances at 5.50 and 5.43 ppm associated with the Cp ligands as well as a broad signal at 2.66 ppm associated with the CH_2CH_2 spacer protons (Figure 1). The ^{13}C NMR spectrum was consistent with the assigned structure, showing resonances at 105.1, 84.3, and 84.1 ppm for the Cp rings and 28.0 ppm for the bridging methylenes. The low-energy absorption in the UV−vis spectrum of **7** ($\lambda_{max} = 402$ nm, $\varepsilon = 446$ M^{-1} cm^{-1}) is blue-shifted relative to that in the spectrum of strained **4b** ($\lambda_{max} = 424$ nm, $\varepsilon = 1035$ M^{-1}cm^{-1}) (Figure S1 in the Supporting Information) and is in close agreement with that reported for 1,1′-dimethylcobaltocenium cation ($\lambda_{max} = 403$ nm, $\varepsilon = 306$ M^{-1} cm^{-1}) under similar conditions.[22] The redox activity of **7** was assessed by cyclic voltammetry (Figure S3). In a degassed aqueous solution of 0.1 M KCl, a 2 mM solution of **7** showed a chemically reversible but electrochemically irreversible reduction wave at −0.98 V vs SCE, which is consistent with the electrochemical properties of related cobaltocenium salts under similar conditions.[13,23]

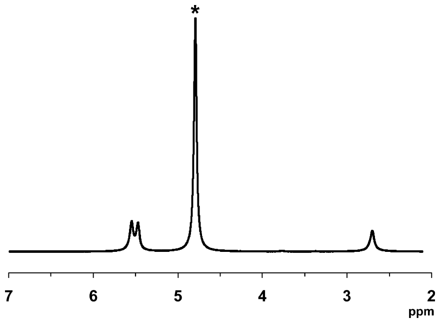

Figure 1. ^{1}H NMR spectrum (500 MHz) of **7** in D_2O. The residual solvent signal is denoted by an asterisk.

In order to estimate the molecular weight of **7**, dynamic light scattering (DLS) experiments in aqueous solution were conducted to compare the hydrodynamic radius (R_H) obtained for **7** with that of polystyrene sulfonate of varying molecular weight.[24] The average R_H of **7** determined by DLS at three different concentrations was ~36 nm (Table S1), which corresponds to a weight-average molecular weight of ~55 000 for sodium polystyrene sulfonate and a DP_w of 198 for **7**.

In summary, ROP routes to polycobaltocenium materials have been developed. Anionic polymerization of the 19-electron cobaltocenophane **3** using Li[^{t}BuC$_5$H$_4$] as initiator resulted in the formation of oligomers with up to nine repeat units. The observation that this process occurs in the absence of light, in contrast to the case for corresponding [1]ferrocenophanes, indicates that the M−Cp bond in 19-electron **3** is intrinsically weaker, presumably because the unpaired electron occupies an antibonding orbital. Thermal ROP of **3** followed by oxidation resulted in high-molecular-weight, water-soluble redox-active polycobaltocenium **7**. Future work will focus on expansion of the ROP process to new monomers and the properties of the new polymers as well as the development of living systems that allow molecular-weight control and access to functional block copolymers.

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Supporting Information Available: Experimental details, UV−vis spectra, and DLS and cyclic voltammogram data for **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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