Polyferrocenylene Persulfides

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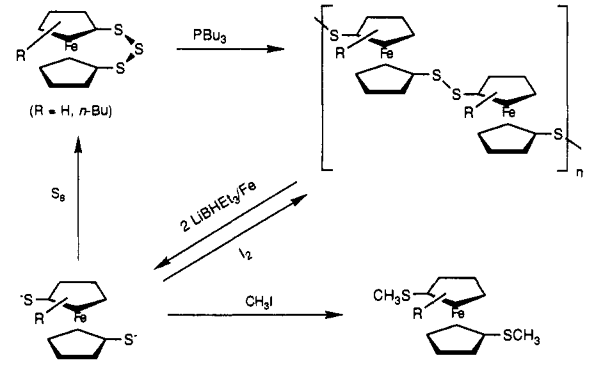
Organometallic polymers are of interest as they promise to combine the processing characteristics of organic polymers with the properties common for transition metals (magnetism, redox, and electrical conduction). However, the development of organometallic polymer chemistry has been slow because of solubility problems, in part, as well as the incompatibility of many organometallic compounds with organic polymerization protocols.[1,2] The present contribution is founded on the fact that persulfides (S–S) are versatile building blocks in many kinds of polymers, viz., cystine-containing proteins, vulcanized rubber, and many inorganic solids (e.g., iron pyrite). We generate our organometallic persulfide polymers by the new process of desulfurization-induced ring-opening polymerization.

Trithiaferrocenophane, $Fe(C_5H_4)_2S_3$ (fcS_3), has been the subject of numerous studies since its synthesis by Smart and Davison in 1971.[3,4] We found that the addition of 1 equiv of PBu_3 to a CH_2Cl_2 solution of fcS_3 resulted in the formation of a bright orange precipitate of $[fcS_2]_n$ together with CH_2Cl_2-soluble $SPBu_3$.[5] The reaction occurs in seconds (25 °C), and the precipitate forms in virtually quantitative yield. The solid was characterized by Raman spectroscopy (λ_{exc} = 514.5 nm, ν_{S-S} = 469 cm^{-1}) and its CP MAS ^{13}C NMR spectrum, which showed only two signals, one at 77 ppm for the two types of *C*H centers and a less intense signal at 87 ppm for the *C*S centers. Scanning electron microscopy (SEM) revealed a morphologically (30000×) and compositionally (2S:Fe, based on energy dispersive X-ray analysis) homogeneous material.[6] Previous work provides evidence for the formation of the biferrocene $[fcS_2]_2$ by the adventious oxidation of 1,1′-$fc(SH)_2$;[7] however, our experiments suggest that the majority of this material is polymeric $[fcS_2]_n$.[8]

Further study of $[fcS_2]_n$ has been limited by its insolubility. Soluble ferrocenylene persulfide polymers can however be obtained from *n*-$BufcS_3$, prepared from the commercially available *n*-butylferrocene. Smart and Davison's procedure was followed by chromatography with silica gel/hexanes to give orange, viscous *n*-$BufcS_3$. Based on ^1H NMR analysis of one of its derivatives (see below), this material consists of a 1:7 mixture of 1,2,1′ and 1,3,1′ isomers. We have also prepared the red liquid *n*-$BufcSe_3$, and it appears that a number of substituted analogues can also be prepared.

Scheme I



Rapid addition of 0.9 equiv of PBu_3 to a hexane solution of *n*-$BufcS_3$ resulted in the precipitation of a dark orange oil of [*n*-$BufcS_2]_n$. After 10 min, the product was washed with hexanes, resulting in >80% yield. The factors which influence the molecular weights are not well understood, but our procedure routinely gives samples with M_w values of 40 000 (n = 160), with molecular weights ranging from 7000 to >150 000.[9] The polymer is highly soluble in THF, CH_2Cl_2, and CS_2. Its ^1H NMR spectrum together with its reactivity confirm that it is indeed comprised of (C_5H_4S)(*n*-$BuC_5H_3S)Fe$ subunits. Thermogravimetric analysis (He atmosphere) shows that the polymer begins to decompose only above 230 °C. Evaporation of CH_2Cl_2 solutions of [*n*-$BufcS_2]_n$ affords translucent yellow-orange flexible films which appear as smooth featureless films when examined at magnifications of 10000× or more by electron microscopy.

A copolymer of the type $[fcS_2]_n$[*n*-$BufcS_2]_m$ was prepared by the addition of PBu_3 to a CH_2Cl_2 solution which was equimolar in the respective trithiaferrocene precursors. This copolymer (M_w = 25 000) contains the fc and *n*-Bufc subunits in a 53:47 ratio, and it is less soluble in CH_2Cl_2 than [*n*-$BufcS_2]_n$.

The S–S bonds in $[RfcS_2]_n$ polymers are oxidizing while the ferrocene centers are reducing. The oxidative nature of the persulfide bonds was demonstrated by cleavage of $[RfcS_2]_n$ (R = H, Bu) with 2 equiv of $LiBHEt_3$ (Scheme I). The resulting red solutions of $RfcS_2^{2-}$ can be methylated (MeI) to give $Rfc(SMe)_2$; the 400-MHz ^1H NMR analysis of this derivative is used to determine the ratio of the two possible regioisomers of $(BuC_5H_3S)(C_5H_4S)Fe$. Solutions of $RfcS_2^{2-}$ can also be sulfurized (S_8) to give $RfcS_3$ and oxidized (I_2) to regenerate the polymer. Few polymers can be cleaved by reduction and regenerated upon reoxidation (elemental tellurium has this property).

Cyclic voltammetry showed that [*n*-$BufcS_2]_n$ undergoes oxidation at $E_{1/2}$ = 563 and 882 mV vs Ag/AgCl.[10] The oxidations are chemically reversible based on the similarity of the anodic and cathodic currents (i_c/i_a). Coulometry at 600 mV shows that the first wave corresponds to removal of 1e$^-$/2Fe. We propose that this first oxidation occurs at alternating Fe sites in the polymer chain;[11] a similar $\Delta E_{1/2}$ of 290 mV is observed for $[(C_5H_5)Fe(C_5H_4)]_2S$.[12] Bromine oxidation of CS_2 solutions of $[RfcS_2]_n$ gives black soluble species with the empirical formula $[RfcS_2Br_x]_n$, where $x \approx 0.5$.

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(5) **[fcS$_2$]$_n$**, Anal. Calcd for $C_{10}H_8FeS_2$: C, 48.40; H, 3.25; Fe, 22.51; S, 25.84. Found: C, 48.50; H, 3.30; Fe, 22.39; S, 25.85. **BufcS$_3$**: ^1H NMR ($CDCl_3$) δ 3.70–4.60 (m, 7 H), 2.34 (m, 2 H), 1.47 (m, 2 H), 1.35 (m, 2 H), 0.92 (t, J = 7.3, 3 H); ^1H–^1H and ^1H–^{13}C NMR correlation data will be presented in the full report; Raman 610, 450, 370 cm^{-1}; EI MS (70 eV) 336 (M$^+$). Anal. Calcd for $C_{14}H_{16}FeS_3$: C, 50.00; H, 4.80; Fe, 16.61; S, 28.60. Found: C, 50.35; H, 4.97; Fe, 16.06; S, 28.66 **BufcSe$_3$**: ^1H NMR ($CDCl_3$) δ 3.70–4.60 (m, 7 H), 2.33 (m, 2 H), 1.48 (m, 2 H), 1.35 (m, 2 H), 0.92 (t, J = 7.3, 3 H); EIMS m/z = 478 (M$^+$). Anal. Calcd for $C_{14}H_{16}FeSe_3$: C, 35.25; H, 3.38; Fe, 11.71; S, 49.66. Found: C, 35.58; H, 3.52; Fe, 10.01; S, 49.23. **[BufcS$_2$]$_n$**: ^1H NMR ($CDCl_3$) δ 4.15 (s, 3 H), 4.09 (s, 4 H), 2.18 (s, 2 H), 1.38 (m, 2 H), 1.28 (m, 2 H), 0.87 (t, J = 6.6 Hz, 3 H); Raman (film) 470 cm^{-1}. Anal. Calcd for $C_{14}H_{16}FeS_2$: C, 55.27; H, 5.30; Fe, 18.36; S, 21.08. Found: C, 55.34; H, 5.45; Fe, 18.13; S, 20.89. **Bufc(SMe)$_2$**: ^1H NMR (major isomer, $CDCl_3$) δ 3.90–4.30 (m, 7 H), 2.25 (m, 2 H), 2.07 (s, 3 H), 2.05 (s, 3 H), 1.42 (m, 2 H), 1.27 (m, 2 H), 0.87 (t, J = 7.2 Hz, 3 H); EIMS (70 eV) 334 (M$^+$). Anal. Calcd for $C_{16}H_{22}FeS_2$: C, 57.48; H, 6.63; Fe, 16.71; S, 19.18. Found: C, 57.32; H, 6.68; Fe, 16.50; S, 19.31.

(6) Hitachi microscope operating at 20 kV with a Link EDX system.

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(8) Conclusive evidence for the existence of ferrocenes linked by persulfides is presented: Herberhold, M.; Brendel, H.-D.; Nuyken, O.; Pöhlmann, T. *J. Organomet. Chem.* **1991**, *413*, 65. These workers prepared the oligomers RSfcS[SfcS]$_n$SfcSR (n_{av} = 1) by the addition (AIBN, 3 days, 60 °C) of $fc(SH)_2$ to norbornadiene.

(9) GPC analyses: 7.5 mm × 30 cm Varian GMH6 GPC column (crosslinked polystyrene) with a 7.5-cm H6 guard column; CH_2Cl_2 eluting at 1.5 mL/min.

(10) 1 mM CH_2Cl_2 soln (0.1 M NBu_4PF_6); porous carbon working electrode, 100 mV/s.

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To summarize, the process of desulfurization-induced ring-opening polymerization provides access to a family of redox-active polymers with novel processing characteristics. The method relies on the following characteristics of the trithiaferrocenophanes: (i) one S atom in the $RfcS_3$ is particularly reactive toward conventional S-abstracting reagents; (ii) monomeric $RfcS_2$ would be strained since the S–S bond cannot easily span the inter-ring separation; and (iii) once the S–S linkage is cleaved, the C_5H_4SR rings can rotate freely.

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All-Cis Catalytic Hydrogenation of Polynuclear Aromatic Hydrocarbons by Group 5 Metal Aryloxide Compounds

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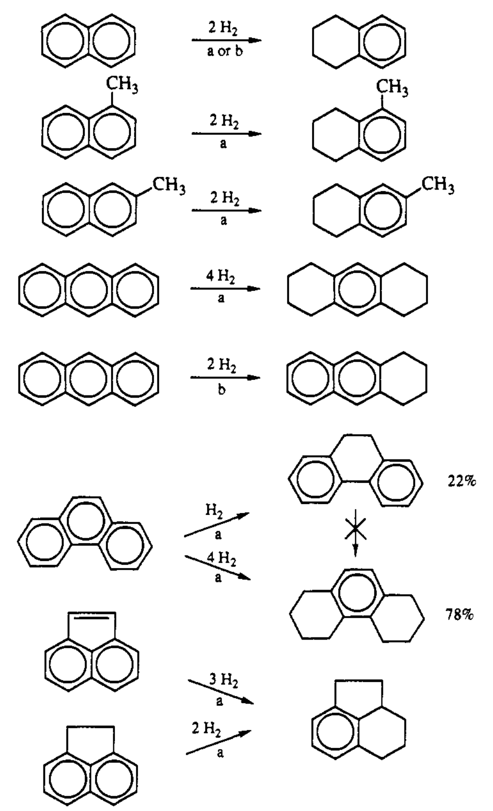
Despite the immense success that has been achieved in the field of homogeneous catalytic hydrogenation of olefin,[1-3] the related field of arene hydrogenation has been underdeveloped.[4-7] We wish to report here our discovery of a new series of arene hydrogenation catalysts. These systems exhibit not only a significant amount of regioselectivity but an extremely high degree of stereoselectivity.[8]

Scheme I[a]



[a] Reaction conditions: (a) [**1**] = 0.1 mmol, C_6H_{12} (3 mL), H_2 (1200 psi), 80 °C, 24 h; (b) [**2**] = 0.1 mmol, C_6H_{12} (3 mL), H_2 (1200 psi), 90 °C, 24 h. GC/MS analysis of the reaction mixture from hydrogenation of naphthalene by **1** showed tetralin, 95.5%, *cis*-decalin, 4.5%, and <0.3% *trans*-decalin.

The niobium tris(4-methylbenzyl) compound $Nb(OC_6H_3Ph_2\text{-}2,6)_2(CH_2C_6H_4\text{-}4Me)_3$ (**1**)[9] acts as a catalyst precursor for the hydrogenation of benzene and a variety of polynuclear aromatic hydrocarbons. A solution of **1** (0.1 mmol) in neat C_6D_6 solvent (3 mL) was found to produce $C_6D_6H_6$ (10% conversion) after being exposed to H_2 (1200 psi, 80 °C) for 24 h.[10] Hydrolysis of the resulting solution showed that the $Nb\text{-}CH_2C_6H_4\text{-}4Me$ groups in **1** had undergone hydrogenolysis to produce *p*-xylene, while the aryloxide ligands had undergone hydrogenation to 2,6-dicyclohexylphenoxide groups.[7a] Solutions of **1** in cyclohexane will carry out the efficient hydrogenation of a variety of polynuclear aromatic hydrocarbons (Scheme I). Typical reaction conditions consist of a solution of **1** (0.1 mmol) in cyclohexane (3 mL) with 20 equiv of aromatic substrate heated at 80 °C under 1200 psi of hydrogen. After 24 h, most of the substrates are hydrogenated to the indicated products (Scheme I) in >95% yield (NMR analysis). Anthracene was found to yield 1,2,3,4,5,6,7,8-octahydroanthracene exclusively with no detectable 9,10-dihydroanthracene. Phenanthrene is hydrogenated by **1** at a slower rate (90% conversion) than the other substrates to produce a mixture of 9,10-dihydrophenanthrene (22%) and 1,2,3,4,5,6,7,8-octahydrophenanthrene (78%). The fact that 9,10-dihydrophenanthrene is not hydrogenated by **1** indicates that this product ratio is kinetic in origin. 1-Methyl- and 2-methyl-

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