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# Synthesis, Characterization, and Polymerization of New Ferrocene–Fluorene Complexes. A Novel High-Molecular-Weight Conjugated Polymer with Pendant Ferrocene Groups

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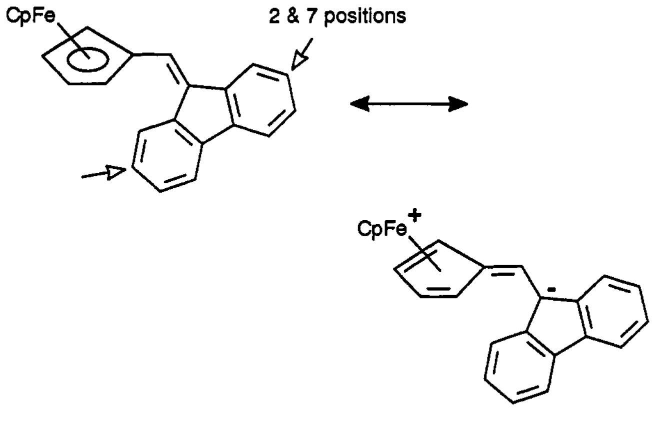
Ferrocenecarboxaldehyde was successfully condensed with fluorene derivatives to afford a series of new complexes, $\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4CH{=}(9\text{-fluorenyl})\}$ (where fluorenyl = 2-bromo-9-fluorenyl (**1a**), 2,7-dibromo-9-fluorenyl (**2a**), 2-nitro-9-fluorenyl (**3**)). The ferrocene–fluorenyl derivatives **1a** and **2a** were converted to the formyl, tributylstannyl, diformyl, and bis(tributylstannyl) complexes (**1b**, **1c**, **2b**, and **2c**, respectively). Complexes **1b** and **2b** were characterized by single-crystal X-ray molecular structures. The fluorenyl ring systems were tilted out of the $\eta^5\text{-}C_5H_4$ plane by 39°. Treatment of **1c** and **2c** with $I_2$ afforded the mono- and diiodofluorenyl complexes **1d** and **2d**, respectively. The reactivity of complexes **2a–d** was explored. The alkynylation (alkyne, $L_2PdCl_2$, CuI, $PPh_3$) of **2a** was an extremely poor reaction, giving little or no cross-coupling. Complex **2b** did not undergo the Knoevenagel polycondensation with bis(cyanoacetate) comonomers. Treatment of **2c** with acid chlorides under Stille cross-coupling conditions afforded ketone product, and iodobenzene showed no cross-coupling. Complex **2d** did copolymerize very cleanly with 2,5-diethynyl-1,4-bis(decyloxy)benzene using palladium catalysis to afford a soluble, high-molecular-weight conjugated polymer (**4**). A model compound (**5**) was prepared from cross-coupling **1d** with 2,5-diethynyl-1,4-bis(decyloxy)benzene. For compound **5** we observed two oxidation events, one at +0.11 V and the other at +0.71 V (relative to the ferrocene/ferrocenium couple). Cyclic voltammetry of polymer **4** showed one, very reversible oxidation event at +0.13 V.

## Introduction

Transition-metal-containing polymeric materials represents an important and active area of materials chemistry.[1] Ferrocene-containing polymers have been utilized in a broad range of applications, ranging from batteries[2] to nonlinear optical (NLO) materials.[3] Ferrocene has long been recognized to stabilize α-carbocations[4] and can serve as an excellent donor for an NLO-phore.[5] With this in mind, we envisioned that fluorenylferrocenes



would be an interesting new class of NLO-phores. With the placement of electron-withdrawing groups at the 2- and 7-positions the complex would model the λ-organic NLO-phores designed by Watanabe and co-workers.[6] Subsequent incorporation into a polymer backbone would give rise to an "accordion" NLO polymeric material with alternating apexes fixed.[7] In principle, this should facilitate the alignment process by predisposing part of the polymer backbone into the desired orientation.

In the drawing above the resonance structure on the right sacrifices one "cyclopentadienyl anion" to generate

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[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1993.

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[2] (a) Iwakura, C.; Kawai, T.; Nojima, M.; Yoneyama, H. *J. Electrochem. Soc.* **1987**, *134*, 791. For other examples of typical ferrocene polymers see: (b) Zhan-Ru, L.; Gonsalves, K.; Lenz, R. W.; Rausch, M. D. *J. Polym. Sci. A* **1986**, *24*, 347 and references cited therein. (c) Singh, P.; Rausch, M. D.; Lenz, R. W. *Polym. Bull.* **1989**, *22*, 247 and references cited therein.

[3] Wright, M. E.; Toplikar, E. G. *Macromolecules* **1992**, *25*, 1838.

[4] For example see: Zou, C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 7578. Also see 2b in this paper.

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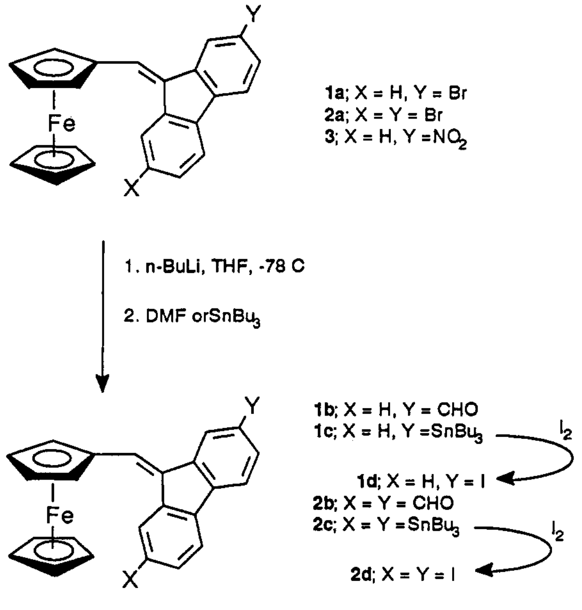
**Scheme I**



the fluorenyl carbanion; hence, there should be little net loss in aromaticity. This "no net loss of aromaticity" has recently been exploited by Marder and co-workers in designing NLO-phores with large hyperpolarizabilities.[8]

This paper presents details concerning the preparation and characterization of several new ferrocene–fluorenyl complexes, a study of their chemistry, and incorporation of this new monomeric unit in the backbone of a conjugated organic polymer.

## Results and Discussion

**Monomer Synthesis and Structural Analysis.** To initiate the development of ferrocene–fluorenyl-based polymeric materials, we have prepared a series of mono- and disubstituted fluorenyl complexes by condensing 2-bromofluorene, 2,7-dibromofluorene, and 2-nitrofluorene with ferrocenecarboxaldehyde to afford **1a**, **2a**, and **3**, respectively, all in reasonable yield.[9] In the case of 2-nitrofluorene the base used is potassium *tert*-butoxide, and for the bromofluorenes, lithium diisopropylamide (LDA). Complexes **1a** and **2a** undergo clean halogen–metal exchange by treatment with *n*-BuLi in tetrahydrofuran (THF) at −78 °C and are then converted to their respective formyl[10] and tributylstannyl[11] derivatives by treatment with DMF and $Bu_3SnCl$, respectively, in moderate yield (Scheme I). Oxidative cleavage of the aryl–tin bond with $I_2$ affords the mono- and diiodo complexes in good yield (Scheme I).

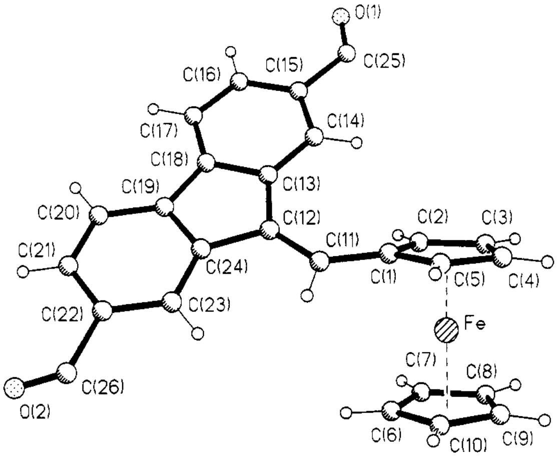


**Figure 1.** Drawing of complex **2b** with labeling scheme. The aldehyde groups were disordered in the structure and modeled with partial occupancy. One of the two possible structures is displayed.

**Table I. Summary of Crystallographic Data for Single-Crystal X-ray Structures of Complexes 1b and 2b**

| param | complex **1b** | complex **2b** |
|---|---|---|
| formula | $C_{25}H_{18}FeO$ | $C_{26}H_{18}FeO_2$ |
| color; habit | red plates cut to size | red plates cut to size |
| cryst size (mm) | 0.4 × 0.3 × 0.5 | 0.3 × 0.4 × 0.3 |
| cryst syst | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1/c$ |
| unit cell dimens | | |
| $a$ (Å) | 9.488(5) | 7.402(2) |
| $b$ (Å) | 7.592(2) | 9.929(2) |
| $c$ (Å) | 25.168(5) | 25.168(5) |
| $\beta$ (deg) | 90.84(3) | 93.84(2) |
| cell vol (Å$^3$) | 1812.8(10) | 1901.6(7) |
| $Z$ | 4 | 4 |
| fw | 390.2 | 418.2 |
| $D_{calcd}$ (g/cm$^3$) | 1.43 | 1.46 |
| abs coeff (cm$^{-1}$) | 8.43 | 8.13 |
| diffractometer used | Siemens P3 | Siemens P3 |
| radiation | Mo K$\alpha$ ($\lambda$ = 0.710 73 Å) | Mo K$\alpha$ ($\lambda$ = 0.710 73 Å) |
| temp (K) | ambient | ambient |
| $2\theta$ range (deg) | 3.0–50.0 | 3.0–50.0 |
| scan type | $2\theta$–$\theta$ | $\omega$ |
| scan speed (deg/min) | variable; 3.0–14.6 | variable; 3.0–14.6 |
| no. of indep rflns | 3211 ($R_{int}$ = 0.76%) | 3356 ($R_{int}$ = 1.26%) |
| no. ov obsd rflns | 2287 ($F > 3.5\sigma(F)$) | 2657 ($F > 3.0\sigma(F)$) |
| refinement method | full-matrix least squares | full-matrix least squares |
| weighting scheme | $w^{-1} = \sigma^2(F) + 0.0004F^2$ | $w^{-1} = \sigma^2(F) + 0.0010F^2$ |
| no. of params refined | 245 | 280 |
| final $R$ indices (obs data) | $R$ = 5.01%, $R_w$ = 5.47% | $R$ = 3.11%, $R_w$ = 4.18% |
| goodness of fit | 1.64 | 0.97 |
| largest diff peak (e/Å$^3$) | 0.49 | 0.23 |

A structural study was initiated to determine the orientation of the fluorenyl ring and possibly reveal any bond distortions (*i.e.* bond alteration or averaging). Single-crystal X-ray molecular structures were completed for complexes **1b** and **2b**. A drawing of **2b** is displayed in Figure 1 and a summary of the crystallographic data for both structures presented in Table I.[13] The fluorenyl-ring system is 39 (±1)° out of plane with the $\eta^5$-$C_5H_4$ ring in both complexes. This is different from what we have observed previously in the vinyl–ferrocene systems, where the nature of the substituent appeared to control the

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(6) Watanabe, T.; Kagami, M.; Yamamoto, H.; Kidoguchi, A.; Hayashi, A.; Sato, H.; Miyata, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*(3), 88.

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(8) Marder, S. R.; Beratan, D. N.; Cheng, L.-T. *Science* **1991**, *252*, 103–106 and references cited therein.

(9) Condensation reactions of ferrocenecarboxaldehyde were first reported by: Barben, I. K. *J. Chem. Soc.* **1961**, 1827.

(10) The reaction of lithium reagents with DMF to produce aldehydes is an established procedure: Wakefield, B. J. *Organolithium Methods*; Academic Press: New York, 1988.

(11) For a general review of organostannane reagents, including synthetic routes to the reagents, see: Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987.

(12) Jung, M. E.; Light, L. A. *Tetrahedron Lett.* **1982**, *23*, 3851. Chen, S.-M. L.; Schuab, R. E.; Grudzinskas, C. V. *J. Org. Chem.* **1978**, *43*, 3450.

(13) Position fractional coordinates and anisotropic thermal parameters for non-hydrogen atoms, bond lengths and angles, and hydrogen atom positions (calculated, riding model) have been deposited with the Cambridge Data Base.

Table II. Summary of UV-Vis Data

| compd | solvent | $\lambda_{max}$ (nm) [$\epsilon \times 10^3$] | compd | solvent | $\lambda_{max}$ (nm) [$\epsilon \times 10^3$] |
|---|---|---|---|---|---|
| **1a** | $CH_2Cl_2$ | 494 [2.93] | **3** | $CH_2Cl_2$ | 512 [6.76] |
| **1b** | $CH_2Cl_2$ | 498 [6.36] | | EtOH | 506 |
| **2a** | $CH_2Cl_2$ | 502 [3.01] | | hexanes | 492 |
| **2b** | $CH_2Cl_2$ | 522 [6.50] | | | |

planarity of the system.[14] The exo double bond (C11–C12) is distorted from planarity by 7–9° (defined by C13–C12–C11–C1). The two structures do not show significant differences in their C1–C11 and C11–C12 bond distances (**1b**, 1.450(6), 1.354(6) Å; **2b**, 1.458(3), 1.340(3) Å; respectively). We would anticipate that contribution of a dipolar structure to the ground-state configuration would lead to a shortening of the C1–C11 bond and lengthening of the C11–C12 bond.[15]

From the data presented in Table II it is quite evident that the electron-withdrawing groups have an effect on the metal to ligand charge transfer (MLCT) band.[16] These data imply that there is indeed a meaningful interaction between the iron center and the fluorenyl-ring system. The observation of a solvatochromic effect for **3** (hexane → $CH_2Cl_2$, red shift of 20 nm) is consistent with a dipolar excited state. It is worth noting that the change in dipole moment ($\mu_{\text{ground state}} - \mu_{\text{excited state}}$), which is often indicated by a solvatochromic shift, can be used to estimate the hyperpolarizability of a given material.[17]

**Monomer Reactivity and Polymer Synthesis.** By analogy with our recent success in preparing ferrocenyl polymers via a Knoevenagel polycondensation,[18] we treated **2b** with a bis(cyanoacetate) comonomer. Regardless of the base employed, the reaction afforded a complicated mixture of products, none of which displayed the expected and distinctive cyanocinnamate vinyl proton resonance.[19] A model study using **1b** and ethyl cyanoacetate again gave a complicated mixture of products. The product mixture is yellow, and this suggests that some type of reaction is occurring which isolates the fluorenyl ring from the ferrocene. Michael addition at the C11 vinyl carbon would represent such an event.

The palladium-catalyzed cross-coupling of **2a** with phenylacetylene was found to lead to decomposition of the acetylene and recovery of **2a**.[20] In another model study we employed **2c** in the Stille cross-coupling reaction with acid chlorides.[21] This reaction leads to the formation of the ketone, but also several additional byproducts. With so many side reactions we deemed the reaction unsuitable as a polymerization technique.

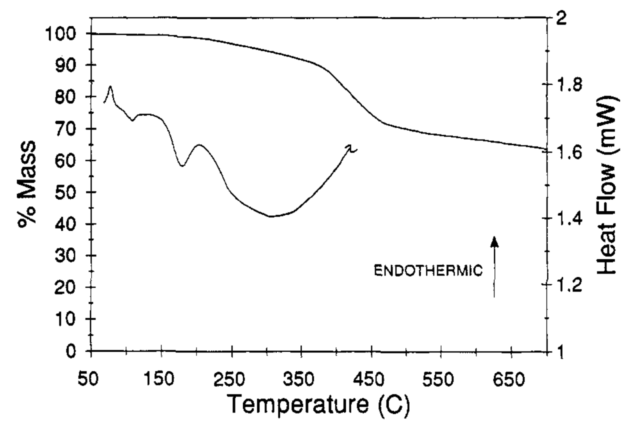
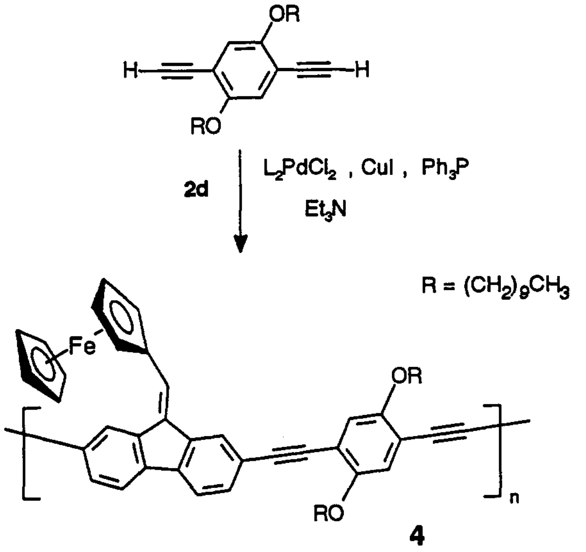


**Figure 2.** TGA and DSC plots for copolymer **4**. In both analyses the samples were heated at 10 °C/min under an atmosphere of nitrogen.

Scheme II



We did find that the iodo derivatives undergo facile palladium/copper-catalyzed alkynylation (Scheme II).[22] Copolymer **4** is produced in high yield and purity ($M_n$ = 67 000, polydispersity 3.8). In some polymerization runs the alkyne comonomer underwent slight decomposition, producing imbalanced stoichiometry, which in turn produces a low-molecular-weight polymer with fluorenyl iodide end caps ($M_n$ = 7000, average degree of polymerization 10). Copolymer **4** is soluble in common organic solvents and casts very tough, free-standing films.

The thermal behavior and stability of copolymer **4** was measured using TGA and DSC (Figure 2). In the DSC scan we observe a small endothermic transition (possibly a melting point), then an exothermic event, and finally an endothermic event. The middle event is likely some type of organizational process (*e.g.* crystallization).[23] Stopping the DSC scan at 250 °C, cooling the sample, and then reheating the sample to 250 °C showed no exo- or

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[14] Wright, M. E.; Toplikar, E. G. *Macromolecules* **1992**, *25*, 6050.

[15] A similar structural analysis was reported for a series of donor–acceptor organic molecules: Graham, E. M.; Miskowski, V. M.; Perry, J. W.; Coulter, D. R.; Stiegman, A. E.; Schaefer, W. P.; Marsh, R. E. *J. Am. Chem. Soc.* **1989**, *111*, 8771.

[16] Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979; Chapter 1.

[17] DeMartino, R. N.; Choe, E. W.; Khanarian, G.; Haas, D.; Lesile, T.; Nelson, G.; Stamatoff, J.; Stuetz, D.; Teng, C. C.; Yoon, H. In *Nonlinear Optical and Electroactive Polymers*; Prasad, P. N., Ulrich, D. R., Eds.; Plenum Press: New York, 1988; pp 169–188. Paley, M. S.; Harris, J. M.; Looser, H.; Baumert, J. C.; Bjorkland, G. C.; Jundt, D.; Twieg, R. J. *J. Org. Chem.* **1989**, *54*, 3774.

[18] Wright, M. E.; Mullick, S. *Macromolecules* **1992**, *25*, 6045. Wright, M. E.; Sigman, M. S. *Macromolecules* **1992**, *55*, 6055.

[19] The vinyl proton for the β-ferrocenyl-α-cyanoacrylates is typically at δ 8.1 ppm. In the past we have found the chemical shift to be very consistent for both monomeric and polymeric materials.

[20] The homocoupling of alkynyl–aryl halide monomers was carried out by: Trumbo, D. L.; Marvel, C. S. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 2311. The alkynyl cross-coupling reaction conditions employed were developed by: Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

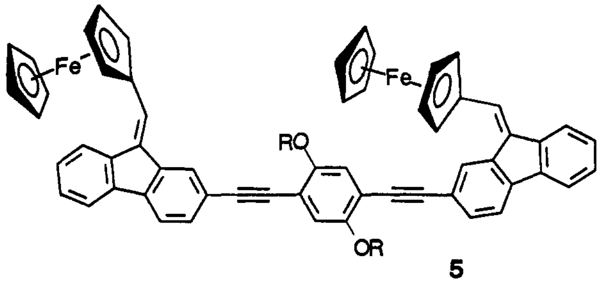
[21] Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 3636; *J. Org. Chem.* **1979**, *44*, 1613.

[22] The dialkynyl monomer was prepared according to the procedure of: Schulz, R. C.; Giesa, R. *Makromol. Chem.* **1990**, *191*, 857–867.

[23] If this is a crystallization process, then the melting point of the material is higher than the observed decomposition point. Other typical processes ($T_m$, $T_g$, solvent loss) would be endothermic. In addition, solvent loss is not corroborated by a decrease in sample weight (TGA). The exact nature of this exothermic event is unclear at this time.

endothermic events. A film of 4 was heated under nitrogen and viewed using a polarizing microscope. We did not observe any apparent phase transitions from 40 to 200 °C. An endothermic event, which begins at ~350 °C, is concomitant with a significant weight loss in the TGA (Figure 2). The loss in mass corresponds to removal of two decyl groups per repeating unit. A film of 4 was cast on a sodium chloride plate, and infrared spectra were obtained before and after heating the sample to 400 °C for 30 min. The infrared spectrum after heating does not indicate quinone formation (*i.e.* C=O stretch) but is supportive of the ferrocene–fluorenyl species remaining intact.

We prepared model compound **5** by cross-coupling **1d** with 1,4-diethynyl-2,5-bis(decyloxy)benzene. Complex **5** is isolated as an orange oil and displays spectroscopic data very similar to those of copolymer **4**. Cyclic voltammetry of complex **5** shows two reversible oxidation events, one at +0.11 V (two-electron event) and another at +0.71 V (one electron, peaks relative to the ferrocene/ferrocenium couple). We interpret this to be oxidation of the ferrocenyl[24] units (uncoupled events) followed by a more difficult oxidation of the hydroquinone moiety. Surprisingly, copolymer **4** (low-molecular-weight sample, $M_n$ = ~7000) shows *only a single* and very reversible oxidation event at +0.13 V. Could an extended array of ferrocenium ions be oriented in such manner as to "protect" the hydroquinone polymer backbone from further oxidation? This is an intriguing result and deserves further investigation.



**5**

## Concluding Remarks

Our work has demonstrated the feasibility of preparing ferrocene–fluorenyl systems and that functionalization at the 2- and 7-positions can be carried out with reasonable efficiency. The 2,7-diformyl complex did not undergo the expected Knoevenagel condensation and led to unidentified byproducts. Synthesis of the 2,7-diiodofluorenyl derivative and copolymerization afforded a novel conjugated polymer. The polymer was processable and displayed interesting thermal and cyclic voltammetric behavior. To our knowledge, this is the first conjugated organic polymer backbone to possess pendant ferrocene moieties.

## Experimental Section

**Materials and Methods.** All manipulations of compounds and solvents were carried out by using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents. Spectroscopic measurements utilized the following instrumentation: $^1$H NMR, Varian XL 300; $^{13}$C NMR, Varian XL 300 (at 75.4 MHz). NMR chemical shifts are reported in $\delta$ versus $Me_4Si$ in $^1$H NMR and in assigning the $CDCl_3$ resonance at 77.00 ppm in $^{13}$C spectra. Ferrocenecarboxaldehyde, *n*-butyllithium, 2-nitrofluorene, 2-bromofluorene, 2,7-dibromofluorene, tributyltin chloride, iodine, triphenylphosphine, and copper iodide were purchased from Aldrich Chemical Co. and used as received. $K_2CO_3$ (granular, AR grade, Mallinckrodt) and $Na_2SO_3$ were purchased from Baxter. $(PPh_3)_2PdCl_2$ was prepared by the literature method.[25] Polymer analyses were performed using a Perkin-Elmer TGA7 and DSC7 thermal analysis data station. Elemental analyses were performed at Atlantic Microlab Inc., Norcross, GA.

**Preparation of $\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4CH{=}$(2-bromo-9-fluorenyl)$\}$ (1a).** A chilled (−78 °C) THF (30 mL) solution containing freshly distilled diisopropylamine (0.24 g, 2.3 mmol) was treated with *n*-BuLi (1.1 mL, 2.8 mmol) and warmed to 0 °C over a period of 30 min. The mixture was cooled to −78 °C, and 2-bromofluorene (0.57 g, 2.3 mmol) was added. After 5 min ferrocenecarboxaldehyde (0.50 g, 2.3 mmol) was added in one portion and the cooling bath removed. The mixture was stirred for an additional 2 h and then diluted with ether (100 mL). The organic layer was washed with water (2 × 100 mL) and brine (100 mL) and then dried over potassium carbonate. The solvents were removed under reduced pressure. The crude product was subjected to column chromatography (4 × 30 cm) on deactivated alumina. Elution with hexane/ethyl acetate (9/1, v/v) produced two major bands. The first band was reddish purple and was found to be pure **1a** (0.77 g, 76%, mp >300 °C), and the second orange band was unreacted ferrocenecarboxaldehyde. $^1$H NMR ($CDCl_3$): $\delta$ 8.39 (s, 1 H, Ar CH), 8.19, 8.17 (2 s, 1 H, Ar CH), 7.90 (s, 1 H, Ar CH), 7.77–7.70, 7.69–7.68 (2 m, 1 H, Ar CH), 7.59 (dd, $J$ = 8.1, 4.6 Hz, 2 H, Ar CH), 7.51 (s, 1 H, vinyl CH), 7.48–7.43 (m, 2 H, Ar CH), 7.37–7.33 (m, 2 H, Ar CH), 4.73–4.71 (m, 2 H, Cp CH), 4.53 (t, $J$ = 1.8 Hz, 2 H, Cp CH), 4.50 (t, $J$ = 1.8 Hz, 2 H, Cp CH), 4.23 (s, 5 H, Cp CH). $^{13}$C NMR ($CDCl_3$): $\delta$ 141.8, 139.7, 139.5, 139.2, 138.6, 137.1, 136.9, 136.6, 132.3 (aromatic C), 130.3, 129.9, 128.0, 127.9, 127.8, 127.4, 127.1, 126.8, 124.1, 122.8, 20.8, 119.6 (aromatic or vinyl CH), 80.7, 80.6 (*ipso* Cp), 70.8, 70.3, 70.1 (Cp CH), 69.6 (Cp CH). UV–vis ($CH_2Cl_2$): $\lambda_{max}$ 494 nm ($\epsilon$ 2.93 × $10^3$).

**Preparation of $\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4CH{=}$(2,7-dibromo-9-fluorenyl)$\}$ (2a).** A chilled (−78 °C) THF (30 mL) solution containing diisopropylamine (0.24 g, 2.3 mmol) was treated with *n*-BuLi (1.1 mL, 2.8 mmol) and then warmed to 0 °C over a period of 30 min. The reaction mixture was cooled to −78 °C, and 2,7-dibromofluorene (0.76 g, 2.3 mmol) was added in one portion. The mixture was stirred for 5 min, and then ferrocenecarboxaldehyde (0.50 g, 2.3 mmol) was added. The cooling bath was removed, and stirring was continued for 2 h. The mixture was diluted with ether (100 mL) and then washed with water (2 × 100 mL) and finally with brine (100 mL). The organic layer was dried over potassium carbonate and the solvents removed under reduced pressure. The crude product was crystallized from chloroform (reflux temperature down to −25 °C) to give 0.93 g of pure **2a** (77%, mp >300 °C). $^1$H NMR ($CDCl_3$) $\delta$ 8.40 (s, 1 H, Ar CH), 7.88 (s, 1 H, Ar CH), 7.57, 7.55 (2 d, $J$ = 4.0 Hz, 2 H, Ar CH), 7.48–7.44 (m, 3 H, Ar and vinyl CH), 4.72 (t, $J$ = 0.6 Hz, 2 H, Cp CH), 4.56 (t, $J$ = 0.5 Hz, 2 H, Cp CH), 4.24 (s, 5 H, Cp CH). $^{13}$C NMR ($CDCl_3$): $\delta$ 141.6, 138.4, 138.3, 135.9, (Ar C), 131.1, 130.5, 130.1, 129.7, 127.1, 122.8, 120.9, 120.6 (Ar or vinyl CH), 80.1 (*ipso*-Cp), 71.0, 70.6 (Cp CH), 69.7 (Cp CH). UV–vis ($CH_2Cl_2$): $\lambda_{max}$ 504 nm ($\epsilon$ 3.01 × $10^3$). Anal. Calcd for $C_{24}H_{16}Br_2Fe$: C, 55.42; H, 3.10. Found: C, 55.52; H, 3.16.

**Preparation of $\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4CH{=}$(2-nitro-9-fluorenyl)$\}$ (3).** One equivalent of 2-nitrofluorene (0.99 g, 4.7 mmol) was added to a solution of ferrocenecarboxaldehyde (1.0 g, 4.7 mmol) in THF (100 mL) at room temperature. Two mole

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(24) For an excellent treatment of the electrochemistry for organometallic bridged dimers see: Van Order, N.; Geiger, W. E.; Bitterwolf, T. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 5680 and references cited therein. Also see: Kotz, J. In *Topics in Organic Electrochemistry*; Fry, A. J., Britton, W. E., Eds.; Plenum: New York, 1986; pp 100–109.

(25) King, A. O.; Negishi, E.; Villani, F. J., Jr.; Silveira, A., Jr. *J. Org. Chem.* **1978**, *43*, 358.

equivalents of potassium *tert*-butoxide (1.1 g, 9.4 mmol) was added, and the mixture was stirred for 15 min. The mixture was then diluted with ether (100 mL) and run through a flash column (deactivated Al$_2$O$_3$, 1 cm) to remove a heavy black precipitate. The resulting solution was further diluted with ether (50 mL), washed with water (2 × 100 mL) and then brine (100 mL), and dried over K$_2$CO$_3$. The crude product was subjected to column chromatography (2 × 15 cm) on deactivated alumina. Elution with EtOAc/hexanes (1/20, v/v) gave two major bands; the first was a dark purple band, and this was found to be pure **3** (0.38 g, 20%, mp >300 °C). $^1$H NMR (CDCl$_3$): δ 9.16 (s, 1 H, Ar CH), 8.64 (s, 1 H, Ar CH), 8.31–8.22 (m, 2 H, Ar CH), 7.88–7.81 (m, 2 H, Ar or vinyl CH), 7.65–7.63 (m, 1 H, Ar or vinyl CH), 7.46–7.33 (m, 2 H, Ar CH), 4.78–4.76 (m, 2 H, Cp CH), 4.61 (t, *J* = 1.8 Hz, 1 H, Cp CH), 4.56 (t, *J* = 1.8 Hz, 1 H, Cp CH), 4.25 (s, 5 H, Cp CH). $^{13}$C NMR (CDCl$_3$): δ 146.9, 146.6, 145.8, 143.3, 141.5, 140.5, 138.4, 138.2, 137.1, 135.8 (aromatic C), 131.3, 130.4, 130.1, 128.7, 128.5, 128.1, 127.6, 124.3, 122.9, 122.5, 121.0, 120.9, 119.8, 119.5, 115.1 (aromatic or vinyl CH), 80.2, 79.9 (*ipso*-Cp) 71.1, 71.0, 70.6 (Cp CH), 69.7 (Cp CH). UV–vis (CH$_2$Cl$_2$): $\lambda_{max}$ 512 nm (ε 6.76 × 10$^3$).

**Preparation of {$^5$-C$_5$H$_5$}Fe{$\eta^5$-C$_5$H$_4$CH═(2-formyl-9-fluorenyl)} (1b).** A chilled (−78 °C) THF solution of **1a** (0.50 g, 1.1 mmol) was treated with *n*-BuLi (0.54 mL, 1.4 mmol). After 10 min an excess of dry DMF (0.26 mL, 3.4 mmol) was added and the cooling bath removed. The mixture was brought to room temperature and hydrolyzed with water (5 mL). It was then diluted with ether (100 mL), washed with water (2 × 100 mL) and then brine (100 mL), and dried over potassium carbonate. The crude product was subjected to column chromatography (2 × 15 cm) on deactivated alumina. Elution with EtOAc/hexanes (1/3, v/v) gave two major bands, the first deep red band being pure **1b** (0.17 g, 39%, mp >300 °C). $^1$H NMR (CDCl$_3$): δ 10.1, 9.97 (2 s, 1 H, CHO), 8.75 (s, 1 H, Ar CH), 8.33 (s, 1 H, Ar CH), 8.28, 8.26 (2 s, 1 H, Ar CH), 7.88–7.83 (m, 3 H, Ar or vinyl CH), 7.64, 7.60 (2 s, 1 H, Ar or vinyl CH), 7.44–7.37 (m, 2 H, Ar CH), 4.76 (s, 2 H, Cp CH), 4.56–4.52 (m, 2 H, Cp CH), 4.24 (s, 5 H, Cp CH). $^{13}$C NMR (CDCl$_3$): δ 192.2, 192.0 (CHO), 145.8, 143.4, 141.2, 140.3, 138.9, 138.1, 137.0, 136.6, 134.9, 134.8, 132.0 (aromatic C), 130.0, 129.2, 128.8, 128.7, 128.2, 128.0, 127.9, 127.4, 125.8, 124.2, 120.8, 120.6, 120.0, 119.8, 119.7 (aromatic or vinyl CH), 80.5, 80.4 (*ipso*-Cp), 70.9, 70.8, 70.5, 70.2, 69.6 (Cp CH). UV–vis (CH$_2$Cl$_2$): $\lambda_{max}$ 498 nm (ε 6.36 × 10$^3$). IR (CH$_2$Cl$_2$): 1684 cm$^{-1}$.

**Preparation of {$\eta^5$-C$_5$H$_5$}Fe{$\eta^5$-C$_5$H$_4$CH═(2,7-diformyl-9-fluorenyl)} (2b).** A chilled (−78 °C) THF (100 mL) solution of **2a** (0.50 g, 0.96 mmol) was treated with *n*-BuLi (1.0 mL, 2.6 mmol). After 10 min an excess of dry DMF (0.45 mL, 5.8 mmol) was added and the cooling bath removed. The mixture was brought to room temperature and hydrolyzed with water (10 mL). It was then diluted with ether (150 mL), washed with water (2 × 150 mL) and then brine (150 mL), and dried over potassium carbonate. The crude product was subjected to column chromatography (2 × 15 cm) on deactivated alumina. Elution with EtOAc/hexanes (1/3, v/v) gave three bands. The first orange band was the monoformyl–monobromo complex and the second, major purple band was the desired diformyl species (0.16 g, 40%, mp >300 °C). $^1$H NMR (CDCl$_3$): δ 10.2 (s, 1 H, C*H*O), 10.0 (s, 1 H, CHO), 8.83 (s, 1 H, Ar CH), 8.38 (s, 1 H, Ar CH), 8.01–7.92 (m, 4 H, Ar CH), 7.76 (s, 1 H, vinyl CH), 4.80 (t, *J* = 1.8 Hz, 2 H, Cp CH), 4.63 (t, *J* = 1.8 Hz, 2 H, Cp CH), 4.27 (s, 5 H, Cp CH). $^{13}$C NMR (CDCl$_3$): δ 192.2, 192.0 (CHO), 144.0, 141.7, 138.4, 136.0 (Ar C), 131.3, 130.7, 129.7, 129.1, 126.0, 121.2, 121.0, 120.3 (Ar C, Ar and vinyl CH), 79.9 (ipso Cp), 71.2, 71.1 (Cp CH), 69.8 (Cp CH). UV–vis (CH$_2$Cl$_2$): $\lambda_{max}$ 522 nm (ε 6.50 × 10$^3$). IR (CH$_2$Cl$_2$): $\nu_{C=O}$ 1693 cm$^{-1}$. Anal. Calcd for C$_{26}$H$_{18}$FeO$_2$: C, 74.66; H, 4.33. Found: C, 74.32; H, 4.39.

**Preparation of {$\eta^5$-C$_5$H$_5$}Fe{$\eta^5$-C$_5$H$_4$CH═[2-(tributylstannyl)-9-fluorenyl]} (1c).** A chilled (−78 °C) THF (100 mL) solution containing **1a** (1.0 g, 2.3 mmol) was treated with *n*-BuLi (1.3 mL, 3.3 mmol) and stirred at −78 °C for 1 h. Tributyltin chloride (0.88 mL, 3.3 mmol) was then added and the cooling bath removed. The mixture was allowed to reach room temperature and was stirred an additional 1 h. The mixture was diluted with ether (100 mL), washed with water (2 × 100 mL) and brine (100 mL), and then dried over K$_2$CO$_3$. The crude product was subjected to column chromatography on deactivated alumina. Elution with EtOAc/hexanes (1/20, v/v) gave one major band (orange), which was found to be **1c** (1.0 g, 68%) contaminated with SnBu$_4$. $^1$H NMR (CDCl$_3$): δ 8.28 (s, 1 H, Ar CH), 8.16, 8.13 (2 s, 1 H, Ar CH), 7.88 (s, 1 H, Ar CH), 7.75–7.61 (m, 2 H, Ar CH), 7.47–7.39 (m, 2 H, Ar or vinyl CH), 7.32–7.24 (m, 2 H, Ar or vinyl CH), 4.69 (t, *J* = 1.4 Hz, 2 H, Cp CH), 4.41 (t, *J* = 1.6 Hz, 2 H, Cp CH), 4.18 (s, 5 H, Cp CH), 1.62–1.21 (m, 12 H, CH$_2$), 1.20–0.98 (m, 6 H, SnCH$_2$), 0.9 (t, *J* = 7 Hz, 9 H, CH$_3$).

**Preparation of {$\eta^5$-C$_5$H$_5$}Fe{$\eta^5$-C$_5$H$_4$CH═(2-iodo-9-fluorenyl)} (1d).** A solution of {$\eta^5$-C$_5$H$_5$}Fe{$\eta^5$-C$_5$H$_4$CH═[2-(tributylstannyl)–9–fluorenyl]} (1.0 g, 1.5 mmol) in THF (40 mL) was cooled to 0 °C in an ice bath, and I$_2$ (0.39 g, 1.5 mmol) was added. The solution was stirred at 0 °C for 30 min and then diluted with ether (40 mL), washed with 10% Na$_2$SO$_3$ (2 × 40 mL) and brine (40 mL), and dried over K$_2$CO$_3$. The solvent was removed under reduced pressure, and the crude product was crystallized from ether/hexanes to give pure **1d** (0.30 g, 40%). $^1$H NMR (CDCl$_3$): δ 8.60 (s, 1 H, Ar CH), 8.19, 8.17 (2 s, 1 H, Ar CH), 8.10 (s, 1 H, Ar CH), 7.72–7.65 (m, 2 H, Ar CH), 7.50–7.43 (m, 3 H, Ar or vinyl CH), 7.37–7.31 (m, 2 H, Ar CH), 4.72 (t, *J* = 1.7 Hz, 2 H, Cp CH), 4.53 (t, *J* - 1.8 Hz, 1 H, Cp CH), 4.49 (t, *J* = 1.8 Hz, 1 H, Cp CH), 4.23 (s, 5 H, Cp CH). $^{13}$H NMR (CDCl$_3$): δ 142.0, 139.8, 139.6, 139.5, 138.9, 137.5, 137.2, 136.4, 136.2, 135.8, 133.0, 132.3, 132.2 (Ar C), 128.7, 128.0, 127.8, 127.4, 127.3, 127.0, 124.1, 121.2, 119.7, 119.6, 119.5 (Ar CH or vinyl CH), 91.9, 91.5 (*ipso*-Cp), 80.8, 80.6, 70.8, 70.3, 70.0, 69.6 (Cp CH). UV–vis (CH$_2$Cl$_2$): $\lambda_{max}$ 494 nm (ε 4.01 × 10$^3$). Anal. Calcd for C$_{24}$H$_{17}$FeI: C, 59.05; H, 3.51. Found: C, 58.81; H, 3.54.

**Preparation of {$\eta^5$-C$_5$H$_5$}Fe{$\eta^5$-C$_5$H$_4$CH═[2,7-bis(tributylstannyl)-9-fluorenyl]} (2c).** A chilled (−78 °C) THF (100 mL) solution containing **2a** (1.0 g, 2.3 mmol) was treated with *n*-butyllithium (1.1 mL, 2.7 mmol) and stirred at −78 °C for 1 h. Tributyltin chloride (0.74 mL, 2.7 mmol) was then added and the cooling bath removed. The mixture was allowed to reach ambient temperature and was stirred an additional 1 h. It was then diluted with ether, washed with water and then brine, and dried over K$_2$CO$_3$. The crude product was subjected to column chromatography on deactivated alumina. Elution with EtOAc/hexanes (1/20, v/v) gave one major band (orange), affording **2c** (1.3 g, 70%) also contaminated with some SnBu$_4$. $^1$H NMR (CDCl$_3$): δ 8.24 (s, 1 H, Ar CH), 7.87 (s, 1 H, Ar CH), 7.68–7.65 (m, 2 H, Ar CH), 7.45–7.37 (m, 3 H, Ar and vinyl CH), 4.71 (t, *J* = 1.7 Hz, 2 H, Cp CH), 4.43 (t, *J* = 1.7 Hz, 2 H, Cp CH), 4.20 (s, 5 H, Cp CH), 1.65–0.78 (m, 54 H, tributyltin CH$_2$ and CH$_3$).

**Preparation of {$\eta^5$-C$_5$H$_5$}Fe{$\eta^5$-C$_5$H$_4$CH═(2,7-diiodo-9-fluorenyl)} (2d).** A chilled (0 °C) THF (40 mL) solution of **2c** (1.0 g, 1.1 mmol) was treated with I$_2$ (0.54 g, 2.1 mmol). The solution was allowed to react at 0 °C for 30 min and then diluted with ether (40 mL). The organic layer was washed with 10% Na$_2$SO$_3$ (2 × 40 mL) and brine (40 mL) and then dried over K$_2$CO$_3$. The solvents were removed under reduced pressure, and the crude product was crystallized from ether/hexanes to give pure **2d** (0.31 g, 48%). $^1$H NMR (CDCl$_3$): δ 8.60 (s, 1 H, Ar CH), 8.08 (s, 1 H, Ar CH), 7.69–7.64 (m, 2 H, Ar CH), 7.47–7.43 (m, 3 H, Ar and vinyl CH), 4.71 (t, *J* = 1.9 Hz, 2 H, Cp CH), 4.56 (t, *J* = 1.8 Hz, 2 H, Cp CH), 4.25 (s, 5 H, Cp CH). $^{13}$C NMR (CDCl$_3$): δ 141.5, 138.8, 138.4 (Ar C), 136.5, 136.3, 135.9, 132.9, 130.8, 129.6, 128.7, 121.3 (vinyl and Ar CH), 80.1 (*ipso*-Cp), 71.0, 70.6 (Cp CH), 69.7 (Cp CH). UV–vis (CH$_2$Cl$_2$): $\lambda_{max}$ 502 nm (ε 3.29 × 10$^3$). Anal. Calcd for C$_{24}$H$_{16}$FeI$_2$: C, 46.94; H, 2.63. Found: C, 47.50; H, 2.72.

**Preparation of Polymer 4.** A 25-mL Schlenk tube was charged with **2d** (70 mg, 0.11 mmol), 1,4-bis(decyloxy)-2,5-diethynylbenzene (53 mg, 0.12 mmol), (PPh$_3$)$_2$PdCl$_2$ (2 mg, 3 mol %), CuI (1 mg, 6 mol %), PPh$_3$ (2 mg, 6 mol %), and triethylamine (5 mL) under nitrogen. The mixture was warmed to 50 °C with stirring for 2 h and then diluted with dichloromethane (100 mL). The organic layer was washed with 10%

NaCN (100 mL), water (2 × 100 mL), and brine (100 mL) and then dried over $K_2CO_3$. The solvents were removed, and the polymer was washed with ether (5 mL) and then dried under reduced pressure at 65 °C for 24 h (53 mg, 61%). $^1H$ NMR ($CDCl_3$): $\delta$ 8.49–8.46 (br s, 1 H, Ar CH), 8.01–7.97 (br s, 1 H, Ar CH), 7.76–7.72 (m, 2 H, Ar CH), 7.61–7.54 (m, 3 H, Ar CH), 7.12, 7.09, 7.06, 7.02 (4 br s, 2 H, Ar CH), 4.80–4.78 (m, 2 H, Cp CH), 4.59–4.55 (m, 2 H, Cp CH), 4.26 (br s, 5 H, Cp CH), 4.14–4.03 (m, 4 H, $CH_2O$–), 1.95–1.84 (m, 4 H, $CH_2$), 1.61–1.51 and 1.31–1.23 (2 m, 28 H, $CH_2$), 0.85–0.83 (m, 6 H, $CH_3$). IR ($CH_2Cl_2$): $\nu$(alkyne) 2206 $cm^{-1}$. UV–vis ($CH_2Cl_2$): $\lambda_{max}$ 514 nm ($\epsilon$ 5.39 × $10^3$). Anal. Calcd for $[C_{58}H_{64}FeO_2]_n$: C, 81.39; H, 7.59. Found: C, 79.42; H, 7.72.

**Preparation of Model Complex 5.** A 25-mL Schlenk tube was charged with **1d** (70 mg, 0.14 mmol), 1,4-bis(decyloxy)-2,5-diethynylbenzene (61 mg, 0.14 mmol), $(PPh_3)_2PdCl_2$ (3 mg, 3 mol %), CuI (2 mg, 6 mol %), $PPh_3$ (2 mg, 6 mol %), and triethylamine (10 mL) under nitrogen. The mixture was warmed to 50 °C with stirring for 2 h and then diluted with dichloromethane (100 mL). The organic layer was washed with 10% NaCN (100 mL), water (2 × 100 mL), and brine (100 mL) and then dried over $K_2CO_3$. The residue was subjected to column chromatography, with EtOAc/hexanes (1/4, v/v) as the eluent, to afford spectroscopically pure **5** as an orange oil (0.14 g, 87%). $^1H$ NMR ($CDCl_3$): $\delta$ 8.60 (s, 1 H, Ar CH), 8.45 (s, 1 H, Ar CH), 8.21, 8.18 (2 s, 1 H, Ar CH), 7.97 (s, 1 H, Ar CH), 7.82–7.69 (m, 4 H, Ar CH), 7.57–7.52 (m, 4 H, Ar and possible vinyl CH), 7.37–7.32 (m, 4 H, Ar and possible vinyl CH), 7.12, 7.08, 7.05, 7.01 (4s, 2 H, Ar CH), 4.78, 4.73 (2 m, 4 H, Cp CH), 4.53–5.52 (m, 2 H, Cp CH), 4.50–4.48 (m, 2 H, Cp CH), 4.23 (s, 10 H, Cp CH), 4.13–4.02 (m, 4 H, $CH_2O$–), 1.61–1.40, 1.35–1.18 (2 m, 34 H, aliphatic $CH_2$), 0.90–0.81 (m, 6 H, aliphatic $CH_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 153.6 (Ar–oxy carbon), 140.4, 140.0, 138.0, 137.5, 137.3, 136.8, 132.8, 132.6, 131.2, 130.7, 127.8, 127.6, 127.3, 127.2, 124.2, 122.8, 121.4, 121.3, 119.9, 119.5, 117.0, 114.1 (Ar C, Ar and vinyl CH), 96.0, 86.0, 81.0 (Cp CH), 70.9, 70.7, 70.1, 69.9, 69.7, 69.5 (Cp CH and $OCH_2$), 31.9, 29.7, 29.6, 29.5, 29.4, 26.1, 22.7 ($CH_2$), 14.1 ($CH_3$).

**X-ray Diffraction Studies.** Crystals suitable for X-ray analysis were grown by slow evaporation of benzene solutions containing **1b** and **2b**. Pertinent data for the X-ray studies, including crystal, collection, and final solution data, are summarized in Table I. Crystals were mounted on the tip of a glass fiber and secured by epoxy cement. Intensity data were collected at ambient temperature on a Siemens P3 diffractometer, and data were processed on a MICROVAX 3100 computer using SHELXTL PLUS (version 4.0) software. The intensities of two check-reflections were measured for every 100 reflections of data collected. No decay was observed (100 ± 4%). The structures were initially solved using direct methods, and remaining atoms were located using difference Fourier maps. Neutral atomic scattering factors internal to SHELXTL PLUS were used. Final refinement was by full-matrix least-squares minimization of $\Sigma[w(F_o - kF_c)]^2$ with weights $w = 1/[\sigma^2(F) + 0.0004F^2]$ (for **2b** the weighting factor was fixed at $0.001F^2$). All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were refined with constrained geometrical ("riding" on the carbons to which they are attached) and isotropic thermal parameters. For **2b**, the C=O group was disordered and was refined using two models. The occupancy factors for O1 and O1′ were 0.75 and 0.25, respectively, and for O2 and O2′ they were both 0.50. The structures were refined to final *R* values given in Table I.

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**Supplementary Material Available:** Tables giving structure determination summaries, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1b** and **2b** and a figure showing the structure of **1b** (17 pages). Ordering information is given on any current masthead page.

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