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# Synthesis of Poly(arylene cobaltacyclopentadienylene)s, a New Class of Organometallic $\pi$-Conjugated Polymers, by Metallacycling Polymerization and Their Physical Properties

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Reaction of $Cp'Co(PPh_3)_2$, where $Cp' = \eta^5$-cyclopentadienyl (Cp) or $\eta^5$-*n*-hexylcyclopentadienyl (hexCp), with conjugated diacetylenes, $RC{\equiv}C{-}A{-}C{\equiv}CR$, where A = *p*-phenylene, *p*-fluorophenylene, *p*-2,5-difluorophenylene, or 4,4′-biphenylene and R = H or Me affords new organometallic polymers, $[-C_4R_2\{CoCp'(PPh_3)\}-A-]_n$ (**1**−**6**) involving linearly $\pi$-conjugated chains. The polymers are insoluble when Cp′ = Cp but soluble in common organic solvents when Cp′ = hexCp. It is suggested by the results of reactions of $(hexCp)Co(PPh_3)_2$ with $PhC{\equiv}CH$ and $PhC{\equiv}CMe$ that stereoregularity favorable to $\pi$-conjugation, i.e., connection of cobaltacyclopentadienylene moieties at 2,5 position is higher when R = Me compared to when R = H. The cobaltacyclopentadiene polymers undergo quasi-reversible oxidation and irreversible reduction at low temperatures. The oxidation potential is not significantly changed, but the reduction potential shifts considerably in the positive direction for the polymers compared to monomeric cobaltacyclopentadienes. The polymers' bandgap energies (as estimated from visible spectra) are between 2.1 and 2.3 eV. Photoconductivity is observed for $[-C_4Me_2\{Co(hexCp)(PPh_3)\}-C_6H_4-]_n$ (**6e**).

The physical and chemical properties of linearly and highly $\pi$-conjugated conducting organic polymers are often a function of the chemical nature of the repeating units.[1] Many efforts have been directed at discovering new materials with high electronic conductivity,[2] small bandgap energy,[3] high chemical stability when doped,[4] dramatic redox-based color changes,[5] good solubility,[6] low melting point (good fusibility),[7] electroluminescence,[8] and so on, effort aiming at a different application. One group of electronically functional polymers of recent interest is based on incorporation of d-transition metals into the polymer structure. Examples include polymetallocenylene,[9] poly(metalyne),[10,11] poly(metallophthalocyanine),[12] polydecker sandwich compounds,[13] thiolate complex polymers,[14] cyclobutadienecobalt complex polymers,[15] and others.[16] In such transition-metal complex polymers, molecular orbital interactions between metal atoms via ligands have often yielded intrinsically conducting properties.

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[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1996.

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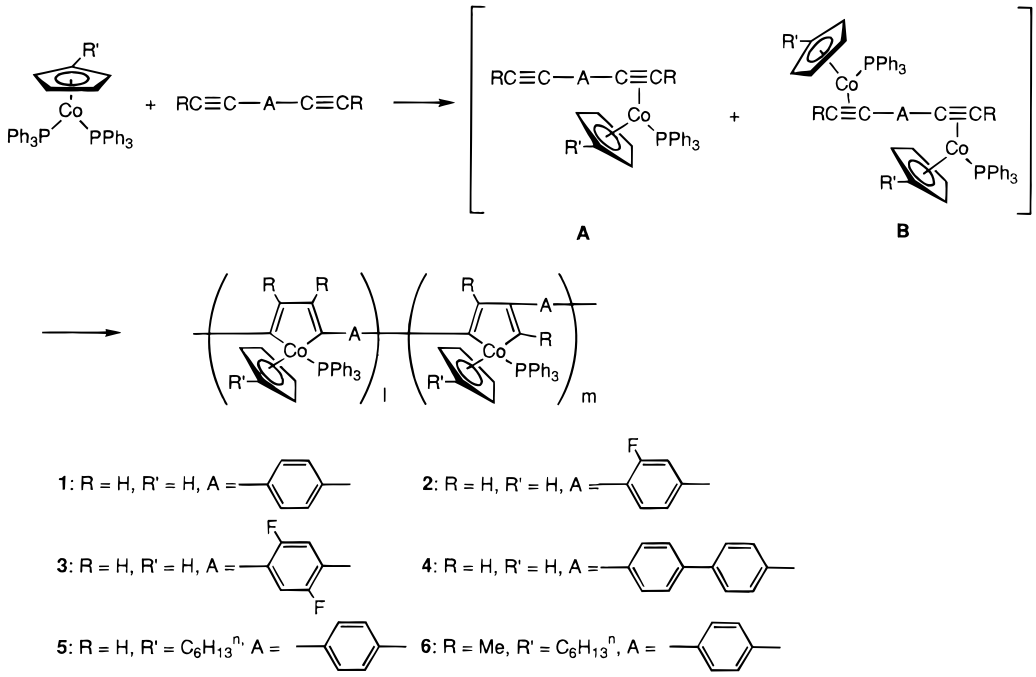
**Scheme 1**



In this paper we present a new class of transition-metal complex polymers wherein the framework of the polymer is $\pi$-conjugated and in part composed of cobaltacyclopentadienes.[17] This class of polymers is, to our knowledge, the first example of d-transition-metal-containing heterocyclic $\pi$-conjugated polymers. In these polymers, the cobaltacyclopentadiene ring with its d-block heteroatom is structurally analogous to the rings found in other representative $\pi$-conjugated polymers, such as poly(pyrrole) and poly(thiophene),[1] which contain p-block heteroatoms. It has been shown both theoretically and experimentally that the electronic properties of the $\pi$-conjugated system (i.e., ionization potential and bandgap) are definitively dependent on the type of heteroatoms in the $\pi$-system.[1] Less aromaticity of the cobaltacyclopentadiene (as compared with thiophene or pyrrole) has been indicated by crystallographic data showing alternating short−long−short carbon−carbon bonds in the metallacycle[18] and by molecular orbital calculations denoting slight back-donation to the $\pi^*$ orbital of the $C_4R_4$ moiety in the metallacycle.[19] Our primary interest in the cobaltacyclopentadiene polymers is to probe the effect that a d-transition-metal heteroatom has on the $\pi$-system and electronic properties of a conducting polymer.

Synthesis of the cobaltacyclopentadiene polymers has been accomplished by a new type of polymerization scheme, MCP, that is based on succesive metallacyclization reactions and that has been described in a preliminary fashion elsewhere.[20−24] Endo et al. have reported the similar MCP reactions independently.[25] In this paper, details of the synthesis making efforts on increasing the degree of polymerization, regioselectivity favorable to $\pi$-conjugation, and solubility in common solvents are described with characterization and physical properties of six cobaltacyclopentadiene polymers. A preliminary result on photoconductivity of a cobaltacyclopentadiene polymer is also reported.

## Results and Discussion

**Synthesis of Insoluble Cobaltacyclopentadiene Polymers.** We first attempted the synthesis of $\pi$-conjugated cobaltacyclopentadiene polymers by the reaction of $\mathrm{CpCo(PPh_3)_2}$ with diacetylenes, $\mathrm{HC{\equiv}C{-}A{-}C{\equiv}CH}$ with A = *p*-phenylene, *p*-fluorophenylene, *p*-2,5-difluorophenylene, and 4,4′-biphenylene. It has been reported that thermally stable cobaltacyclopentadiene complexes, $\mathrm{Cp(PPh_3)[\overline{CoCR{=}CR{-}CR{=}CR}]}$, are formed by double additions of acetylene, $\mathrm{RC{\equiv}CR}$, to $\mathrm{CpCo(PPh_3)_2}$.[26] This suggests that successive additions of a diyne, $\mathrm{HC{\equiv}C{-}A{-}C{\equiv}CH}$, to $\mathrm{CpCo(PPh_3)_2}$ would give linearly $\pi$-conjugated organometallic polymers with the structure $[-\mathrm{C}\{\overline{\mathrm{CoCp(PPh_3)\}{=}CH{-}CH{=}C}}\mathrm{{-}A{-}}]_n$ (Scheme 1) if the addition occurred regioselectively, and also if A were none or a $\pi$-conjugated moiety. As for the regioselectivity of metallacyclization, Wakatsuki et al. have shown the rule that the acetylenic carbon bearing a bulky group becomes the α-carbon of the metallacyclopenta-

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diene.[27] In the diacetylenes that we employed, the small terminal group, H, would effect the regioselective metallacyclization at 2,5 positions, and an aromatic moiety inserted between the two carbon−carbon triple bonds would be effective to lessen structural resistance to polymerization due to bulky ligands such as triphenylphosphine around the metallacycle.[18,28]

The reaction between $CpCo(PPh_3)_2$ and *p*-diethynylbenzene in toluene at room temperature was monitored by GPC. A solution of *p*-diethynylbenzene was added dropwise to a solution of $CpCo(PPh_3)_2$ over 8 min, and then sampling of the solution for the analysis began. The color of the reaction mixture changed from dark red to green after the addition of several drops of the solution of *p*-diethynylbenzene, and further changed to dark brown after more than half of the solution of *p*-diethynylbenzene was added. Black precipitates had been already formed at the wall of the flask by the time all of the solution of *p*-diethynylbenzene was added. With time, the amount of black precipitate increased and the color of the solution faded. This "two-step" color change suggests that monoacetylene complexes are formed at the first stage, and then further additions of acetylenic moieties to the monoacetylene complexes yield polymeric cobaltacyclopentadiene complexes, in much the same way as observed in the formation of monomeric cobaltacyclopentadiene complexes by Yamazaki, Wakatsuki, and co-workers.[27,29]

At any given point during the polymerization reaction, GPC was used to monitor both the molecular weight of the longest polymer formed so far (Figure 1A) and the molecular weight of the most abundant polymer in the reaction mixture at that time (Figure 1B). Because polymer precipitates had already formed during the 8 min of reactant mixing, the first GPC sample (at time zero in Figure 1) already shows the presence of polymers with highest and most abundant molecular weights of $8 \times 10^3$ and $1 \times 10^3$, respectively, based on polystyrene standards. Both molecular weights increased with time and reached to $8 \times 10^4$ and $3 \times 10^3$, respectively, after 4 h and remained essentially unchanged thereafter. This indicates that the solubility of the polymer is limited by the degree of polymerization and the insoluble polymer would have the molecular weight more than $8 \times 10^4$ based on the polystyrene standard. Results of similar analyses indicate that the lower limits of molecular weight of insoluble polymers would be $5 \times 10^4$, $1 \times 10^4$, and $4 \times 10^4$ for **2**, **3**, and **4**, respectively.

The reaction of $CpCo(PPh_3)_2$ with 4,4′-diethynylbiphenyl was carried out at various mole ratios, *x*, of $CpCo(PPh_3)_2$ to diacetylene in benzene at room temperature or in toluene at 4 °C under argon or nitrogen. The reaction in benzene at room temperature afforded dark brown and moderately gelatinous precipitates and dark reddish-brown films on the wall of glass vessels within a few hours when *x* was around 1. The formation of precipitates in toluene at 4 °C was slower than in benzene, and the product was powdery and colored with a tint of violet. These precipitates were collected by filtration and thoroughly washed with benzene or toluene, dried and used for the characterization. Yields of the insoluble product, **4**, depend on *x* as represented in Table 1. Yields are maximized when the mole ratio, *x*, is near unity regardless of whether the reaction is carried out in benzene at room temperature or toluene at 4 °C, as can be expected from the equation of the MCP process. Reactions of other diacetylenes with CpCo$(PPh_3)_2$ also gave insoluble polymeric products with dark red or dark brown colors, **1**−**3**, in moderate yields, 65−80% (Table 1) using a mole ratio of unity.

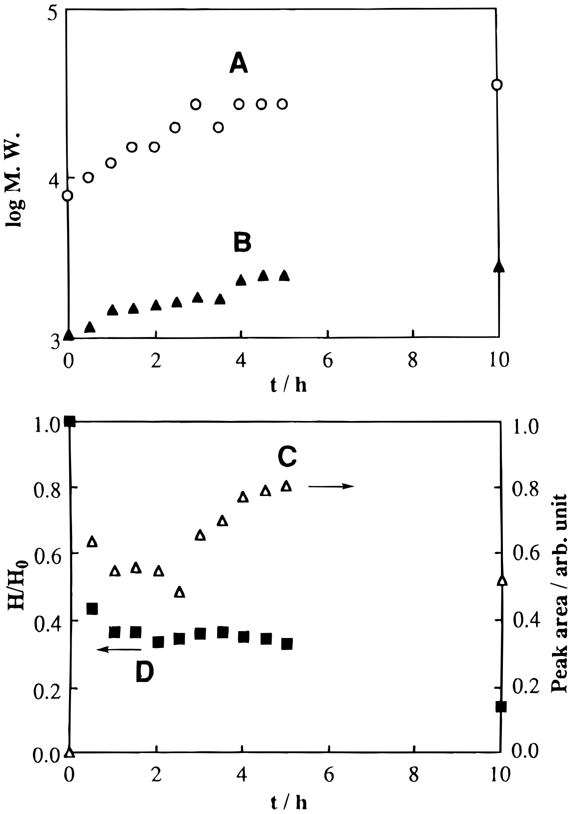

**Figure 1.** Plots of the highest (A) and most abundant (B) molecular weights and the peak area (C) of soluble polymeric components and the height ratio for the overlapped peak of *p*-diethynylbenzene and $CpCo(PPh_3)_2$ based on the peak height at $t = 0$ (D) detected with HPLC vs reaction time in the reaction of *p*-diethynylbenzene and $CpCo(PPh_3)_2$ in toluene at room temperature.

The infrared spectra of **1** and its structurally related monomeric complexes **7a** and **7b** exhibit a great similarity that is consistent with the polymer **1** consisting of repeating units of phenyl-substituted cobaltacyclopentadiene, Cp and $PPh_3$. A peak at 810 $cm^{-1}$, assignable to the CH out-of-plane deformation for para-substituted phenylene groups in the polymer, is stronger than the corresponding peaks for monomers **7a** and **7b** as expected. Whether the polymer has the 2,5-substituted or the 2,4-substituted structure cannot be determined because there are no characteristic differences between the infrared spectra of **7a** and **7b**.

Infrared spectra of **2**−**4** also indicate the formation of cobaltacyclopentadiene polymers. In the infrared spectra of fluorinated polymers, **2** and **3**, characteristic peaks for the C−F stretching mode appear at 1184 and 1159 $cm^{-1}$, respectively.[30] The spectra of polymer **4** exhibit characteristic bands for biphenylene moieties both at 808 $cm^{-1}$ (CH out-of-plane deformation vibra-

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(27) Wakatsuki, Y.; Nomura, O.; Kitaura, K.; Morokuma, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1983**, *105*, 1907.

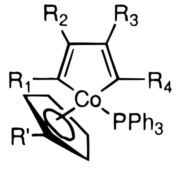
(28) Our attempts of MCP using α,β-diynes, $RC\equiv C-C\equiv CR$ (R = $SiMe_3$, Me, Ph) have failed in the preparation of significant amounts of polymers (see ref 24).

(29) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1977**, *139*, 157.

**Table 1. Yields and Diffuse-Reflection Vis Spectral Data for Cobaltacyclopentadiene Polymers**

| polymer | synthetic conditions[a] | $x$ | yield/% | $\lambda_{max}$/nm | |
|---|---|---|---|---|---|
| **1** | toluene, r.t., 24 h | 1.0 | 65 | 260 | 540 |
| **2** | toluene, r.t., 7 d | 1.0 | 66 | 260 | 476 |
| **3** | toluene, r.t., 11 d | 1.0 | 79 | 264 | 520 |
| **4** | benzene, r.t., 24 h | 2.0 | 63 | 265 | 440 |
| **4** | benzene, r.t., 24 h | 1.5 | 70 | 268 | 454 |
| **4** | benzene, r.t., 24 h | 1.2 | 92 | 285 | 488 |
| **4** | benzene, r.t., 24 h | 1.0 | 80 | 272 | 480 |
| **4** | benzene, r.t., 24 h | 0.8 | 73 | 272 | 508 |
| **4** | benzene, r.t., 24 h | 0.5 | 5 | 292 | 512 |
| **4** | toluene, 4 °C, 3 days | 2.0 | 48 | 268 | 484 |
| **4** | toluene, 4 °C, 3 days | 1.5 | 52 | 292 | 498 |
| **4** | toluene, 4 °C, 3 days | 1.2 | 72 | 295 | 508 |
| **4** | toluene, 4 °C, 3 days | 1.0 | 61 | 297 | 524 |
| **4** | toluene, 4 °C, 3 days | 0.8 | 57 | 300 | 533 |
| **4** | toluene, 4 °C, 3 days | 0.5 | 41 | 302 | 537 |

[a] r.t. = room temperature.



**7a**: $R_1 = R_4 = Ph, R_2 = R_3 = R' = H$
**7b**: $R_1 = R_3 = Ph, R_2 = R_4 = R' = H$
**8**: $R_1 = R_4 = p\text{-}C_6H_4\text{-}C_6H_5, R_2 = R_3 = R' = H$
**9a**: $R_1 = R_4 = Ph, R_2 = R_3 = H, R' = C_6H_{13}{}^n$
**9b**: $R_1 = R_3 = Ph, R_2 = R_4 = H, R' = C_6H_{13}{}^n$
**10a**: $R_1 = R_4 = Ph, R_2 = R_3 = Me, R' = C_6H_{13}{}^n$
**10b**: $R_1 = R_3 = Ph, R_2 = R_4 = Me, R' = C_6H_{13}{}^n$
**10c**: $R_1 = R_4 = Me, R_2 = R_3 = Ph, R' = C_6H_{13}{}^n$

tions) and at 1003 cm$^{-1}$ (CH in-plane deformation vibrations). It should be noted that no $\nu(C_{acetylene}-H)$ and $\delta$(CH) bands are detectable in the spectra of **4** when the synthetic mole ratio, $x$, is less than 1.5. When $x = 2.0$, a weak peak at 3300 cm$^{-1}$ due to $\nu(C_{acetylene}-H)$ appears, and the absorbance ratio of this peak to the 1003 cm$^{-1}$ peak characteristic of the biphenylene group indicates that $n$ = ca. 20 (accordingly M.W. = ca. 11 000) with reference to the data of **8** ($\nu(C_{acetylene}-H)$, 3274; $\delta$(CH), 1004 cm$^{-1}$). Polymers **1**–**4** do not show any $\nu(C_{acetylene}-H)$ bands when $x = 1$.

Elemental analysis data for the polymers coincided with the expected cobaltacyclopentadiene structure. A small discrepancy (within 1.6%) was seen in the results for polymers **2** and **4**, but this was most likely due to insufficient purification. Because of this discrepancy, clear dependency of the analysis data of the insoluble product on $x$ was not included for **4**.

UV–vis absorption spectra for thin films of **1**–**4** coated on quartz glass exhibit strong bands which have an edge at 500–600 nm as shown in Figure 2. In the diffuse-reflection spectra of **1**–**4**, an intense and broad band appeared near 500 nm in addition to the $\pi$–$\pi$* transition band for the aromatic rings at 260–270 nm (Table 1). These long-wavelength bands, which are not seen in the spectra of the monomeric cobaltacyclopentadiene complexes (**7a** and **7b** in Figure 2), indicate the formation of conjugated $\pi$-systems as a result of polymerization. Consequently, it can be concluded that the polymerization proceeds *significantly* at the 2,5 positions, and the resulting polymers involve the $\pi$-conjugated structures, **1**–**4**, as expected. However, the possibility of imperfect regioselectivity during the polymerization, which would yield a polymer with less extensive $\pi$-conjugation, cannot be ruled out completely, because when **1** was reacted with ethynylbenzene, both the 2,4- and 2,5-diphenylcobaltacyclopentadienes were formed in competitive yields. At present there is little information available regarding the extent of conjugation in polymers **1**–**4** because of their insolubility.

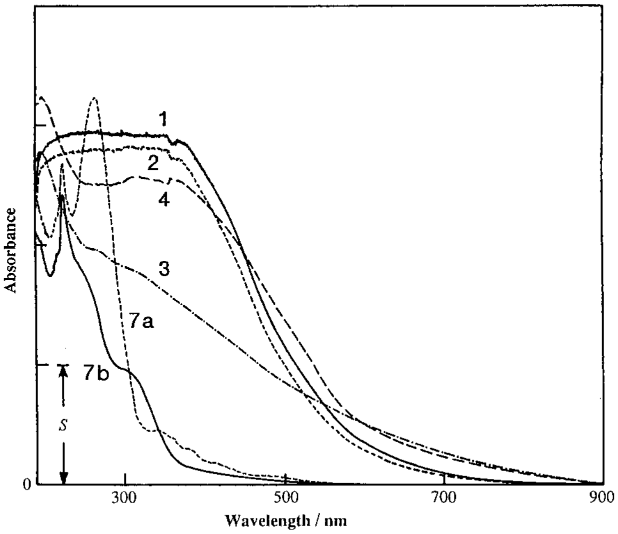


**Figure 2.** UV–vis absorption spectra of thin films of **1**, **2**, **3**, and **4** on quartz and mononuclear complexes, **7a** and **7b** (20 $\mu$M in $CH_2Cl_2$). Film thickness was 1.4, 0.93, 0.29, and 1.6 $\mu$m for **1**, **2**, **3**, and **4**, respectively. $S$ = 1.0 for **1** and **2**, 0.375 for **3**, 0.5 for **4**, and 0.25 for **7a** and **7b**.

The $\lambda_{max}$ values observed in the UV–vis spectra of various samples of polymer **4**, each synthesized under different conditions, are tabulated in Table 1. The $\lambda_{max}$ values for samples prepared in toluene at 4 °C are greater than those of samples prepared in benzene at room temperature. This indicates that the regularity in the polymerization at 2,5 positions and/or the average molecular weight of the insoluble product change with the reaction conditions (the former would be dominant in milder reaction conditions), because the shift of $\lambda_{max}$ to the longer wavelength should be due to a greater degree of $\pi$-conjugation. The $\lambda_{max}$ is also dependent on the synthetic mole ratio, $x$. This trend could be interpreted by the decrease in the polymerization degree with increasing $x$ when $x \geq 1$. However, the increase in $\lambda_{max}$ with decreasing $x$ when $x \leq 1$ is contradictory to the

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(30) Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*; Chapman and Hall: London, 1975.

**Table 2. Yields of Cobaltacyclopentadiene Isomers**

(a) From $\mathrm{PhC{\equiv}CH}$

| reaction temp/°C | yield/% | | | yield ratio **9a**/(**9a** + **9b** + **9c**) |
|---|---|---|---|---|
| | **9a** | **9b** | **9c** | |
| 90 | ∼0 | 17 | ∼0 | ∼0 |
| r.t. | 10 | 35 | ∼0 | 0.22 |
| 4 | 18 | 30 | ∼0 | 0.38 |
| −40 | 9 | 22 | ∼0 | 0.29 |

From $\mathrm{PhC{\equiv}CMe}$

| reaction temp/°C | yield[a]/% | | yield ratio **10a**/(**10a** + **10b** + **10c**) |
|---|---|---|---|
| | **10a** | **10b** + **10c** | |
| 40 | 29 | 16 | 0.64 |
| r.t. | 40 | 21 | 0.65 |

[a] The yield of **10b** plus **10c** was estimated from the GPC spectrum and the amount of **10a** isolated.

change in the polymerization degree as expected from the equation of the MCP process; i.e., the polymerization degree should be maximum when $x = 1$. We postulate at present two possibilities for this rationale. One is that the reactivity of intermediate complexes with both terminal acetylenes coordinating to cobalt (Scheme 1, **A**) is higher than those with one coordinating and one free terminal acetylenes (Scheme 1, **B**); the former intermediates are more dominant at lower $x$. The other possibility is a different reactivity between the three geometric isomers of disubstituted cobaltacyclopentadienes, and with smaller $x$, this results in achieving a higher regularity in the polymerization at 2,5 positions and more π-conjugation.

**Synthesis of Soluble Polymers from $\mathrm{(hexCp)Co(PPh_3)_2}$.** We next attempted to synthesize soluble cobaltacyclopentadiene polymers using $\mathrm{(hexCp)Co(PPh_3)_2}$ in order to characterize the polymers in detail including the regioselectivity in MCP reactions and to increase the polymerization degree. Before carrying out the MCP reactions, reactions of $\mathrm{(hexCp)Co(PPh_3)_2}$ with ethynylbenzene and 1-phenyl-1-propyne were investigated at various temperatures to optimize reaction conditions. Yield distribution of three geometric isomers of monomeric cobaltacyclopentadienes are shown in Table 2. The yield of 2,5-diphenylcobaltacyclopentadiene compared to 2,4- and 3,4-diphenyl isomers is much higher for 1-phenyl-1-propyne; this is similar to the result of a reaction of $\mathrm{CpCo(PPh_3)_2}$ with 1-phenyl-1-propyne.[29] However, the yield of the 2,4-diphenyl isomer surpasses that of the 2,5-diphenyl isomer for ethynylbenzene. This seems inconsistent with the rule that the acetylenic carbon with a bulky group becomes the α-carbon of the cobaltacyclopentadiene due to the steric repulsion in the transition state of metallacyclization in the reaction of $\mathrm{CpCo(PPh_3)_2}$ with acetylenes.[27] We suppose that the steric repulsion between Ph and H is not significant as well as the one between two H's because of smallness of H in the metallacyclization process of $\mathrm{Cp'Co(PPh_3)_2}$ with $\mathrm{PhC{\equiv}CH}$, and further, an electronic factor based on dipole interaction may favor a formation of the 2,4-diphenyl isomer compared to 2,5-diphenyl isomer, resulted in a higher yield of the 2,4-diphenyl isomer than the 2,5-diphenyl one.

An MCP reaction between $\mathrm{(hexCp)Co(PPh_3)_2}$ and *p*-diethynylbenzene was carried out at 4 °C, the most effective temperature given in Table 2 for a formation of the 2,5-diphenyl isomer from ethynylbenzene. Contrary to the reaction of $\mathrm{CpCo(PPh_3)_2}$, no precipitates were formed even after a reaction for 4 days. Figure 3 shows a GPC spectrum of the reaction product. Several polymeric and oligomeric components are involved, and the $M_w$ and $M_n$ values of the whole product are $7 \times 10^3$ and $2 \times 10^3$, respectively, based on the polystyrene standard. The product was separated into nine components, **5a**−**i**, according to the increase in molecular weight as noted in Figure 3. The lower molecular weight products, **5a**−**e**, giving peaks in the chromatogram, can be assigned as monomeric and oligomeric products, $\mathrm{HC{\equiv}C{-}C_6H_4[{-}C_4H_2\{Co(hexCp)(PPh_3)\}{-}C_6H_4{-}]_{\mathit{n}}C{\equiv}CH}$ with $n = 1-5$, respectively, from the intensity ratio of acetylenic proton at δ 3 ppm to hexCp protons at 5 ppm in the $^1$H NMR spectra. Both signals derived from the 2,5-substituted isomer with a characteristic peak at 6.6 ppm due to protons at the 3,4 positions and from 2,4-substituted one with a peak at 8.8 ppm due to a proton at the 5 position exist in the spectra of **5a**−**d**, indicating that the products are mixtures of these two isomeric structures. The ratio of the 2,5- vs 2,4-substituted cobaltacyclopentadienes in **5a** is 0.6, similar to the ratio of the 2,5 vs 2,4-substituted complexes in the reaction of *p*-diethynylbenzene given in Table 2.

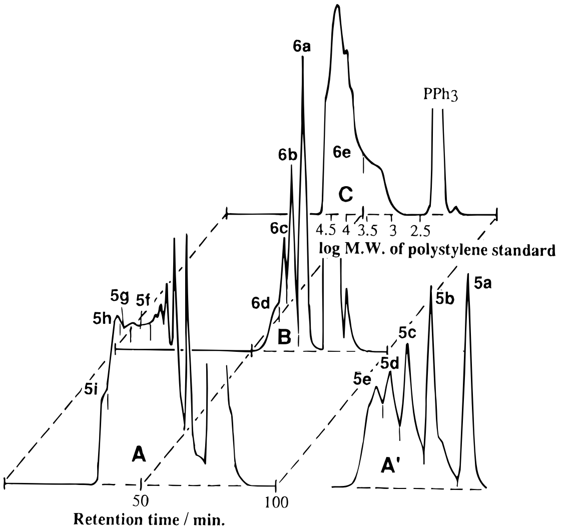

**Figure 3.** GPC spectra of **5** prepared at 4 °C (A) and **6** prepared at room temperature (B) and 40 °C (C). The spectrum of **5** in the third cycle of the recycling GPC is given as A′.

MCP reactions between $\mathrm{(hexCp)Co(PPh_3)_2}$ and *p*-di-1-propynylbenzene were performed at room temperature and 40 °C. No precipitates formed also in these cases and GPC spectra of the products are displayed in Figure 3, showing a drastic enhancement of polymerization by the temperature increase. The $M_w$ and $M_n$ values of the product at 40 °C are $1.5 \times 10^4$ and $6 \times 10^3$, respectively. Judging from the result for 1-phenyl-1-propyne (see Table 2), we postulate that the polymer **6e** is mainly composed of 3,4-dimethyl-2,5-diphenylenecobaltacyclopentadienyl units, although it is difficult to estimate the ratio of the three geometrically isomeric units from the $^1$H NMR spectrum because of broadness of the signal due to methyl groups on the metallacycle. The solubility of **6e** in toluene decreases with repeating dissolution and evaporation processes probably due to

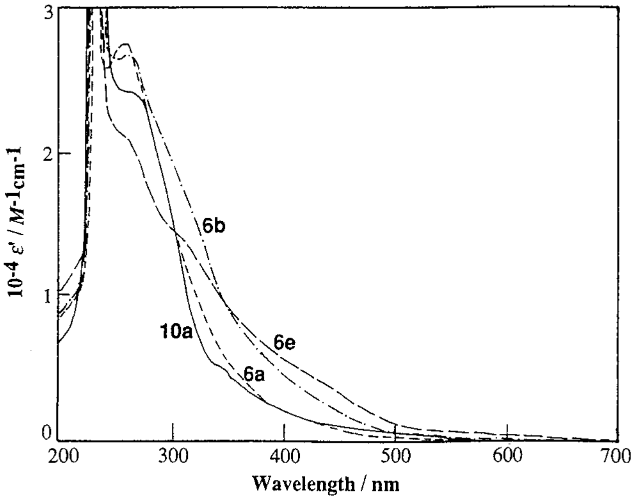

**Figure 4.** UV−vis absorption spectra of **6a**, **6b**, **6e**, and **10a** in $CH_2Cl_2$. The absorption coefficient, $\epsilon'$, was estimated based on molar concentration of cobaltacyclopentadiene units.

**Table 3. Redox Properties[a] and Bandgap Energies Obtained from Vis Spectra for Cobaltacyclopentadiene Polymers**

| polymer | $E^{\circ\prime}_{ox}$ (V vs Ag/Ag$^+$) | $E_{p,red}$ (V vs Ag/Ag$^+$) | $E_g$ (eV) |
|---|---|---|---|
| **1** | 0.08[b] | −1.38 | 2.1 |
| **2** | 0.17[b] | −1.39 | 2.2 |
| **3** | 0.27[b] | −1.41 | 2.3 |
| **4** | 0.04[b] | −1.8 | 2.1 |
| **5a** | 0.08 | −2.2[c,d] | |
| **5f** | 0.06 | −2.2[d] | |
| **5g** | 0.11 | −1.8[d] | |
| **5h** | 0.11 | −1.8[d] | |
| **5i** | 0.11 | −1.6[d] | 2.3 |
| **6e** | −0.08 | −1.56 | 2.3 |

[a] Polymers were coated on ITO glasses except otherwise stated. [b] Measured in 0.1 M $Bu_4NClO_4$−$CH_2Cl_2$ at −60 °C. Others were measured in 0.1 M $Bu_4NClO_4$−MeCN at −20 °C. [c] Dissolved in solution and measured at GC. [d] No clear reduction peak was observed, and the potential at the positive edge of the reduction wave was noted.

gelation,[31] which prevents sufficient purification of **6e** and its elemental analysis has not been satisfactory.

UV−vis spectra of monomer **6a**, dimer **6b**, and polymer **6e** in $CH_2Cl_2$ solutions are displayed in Figure 4. The band edge shifts to the higher wavelength according to an increase in polymerization degree, indicating the formation of $\pi$-conjugated structure, as indicated in the spectra of films for insoluble polymers, **1**−**4** (Figure 2). Bandgap energies for polymers **1**−**6** were evaluated from the absorption edge based on the semiconductor theory[32] and the values thus obtained are given in Table 3 as $E_g$. The $E_g$ values, 2.1−2.3 eV, which corresponds roughly to the value observed in poly(thiophene) (2.0 eV), are relatively small when compared to the bandgaps among previously known $\pi$-conjugated organic polymers.[1]

**Redox Properties.** Cyclic voltammograms of **1** coated on ITO, **7a**, and **7b** dissolved in solution at glassy carbon (GC) electrodes are displayed in Figure 5. Monomeric complexes **7a** and **7b** undergo reversible one- or two-step 1e$^-$ oxidation and two-step irreversible reductions (Figure 5C−F), much like the previously reported cobaltacyclopentadienes.[33,34] On the other hand, the oxidation of polymer **1** is less reversible (Figure 5A), exhibiting a broad oxidation peak at $E_{p,a}$ = +0.60 V vs Ag/Ag$^+$ with the corresponding rereduction at $E_{p,c}$ = −0.43 V (scan rate 20 mV s$^{-1}$; 0.1 M $Bu_4NClO_4$ in $CH_2Cl_2$; −60 °C). This peak separation is greater for thicker films due to a larger ohmic drop across the film. At higher temperatures, the polymer's electrochemical behavior becomes less reversible until only the oxidation wave is seen at room temperature (even at scan rate 1 V s$^{-1}$). It is possible that an oxidative decomposition reaction involving an intramolecular cobaltacycle−phosphine reaction occurs.[34]

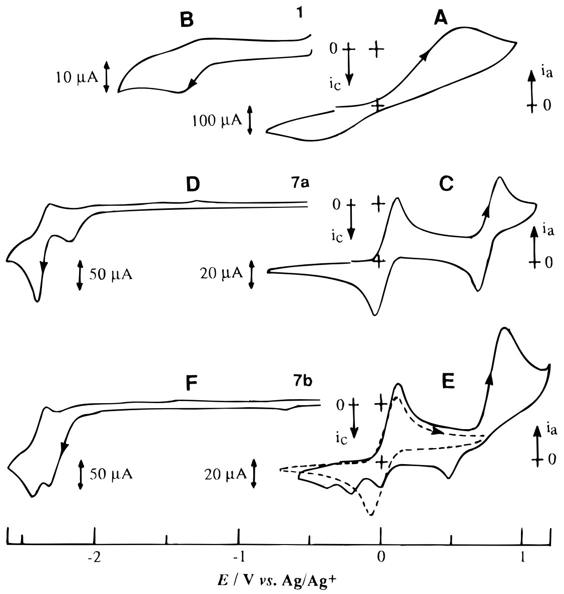

**Figure 5.** Cyclic voltammograms of a 1.4 $\mu$m film of **1** coated on ITO (A, B), 2 mM solution of **7a** (C, D) and **7b** (E, F) at GC, at a scan rate of 100 mV s$^{-1}$. A, C, E: in 0.1 M $Bu_4NClO_4$−$CH_2Cl_2$ at −60 °C; B, D, F: in 0.1 M $Bu_4NClO_4$−MeCN at −20 °C.

The electrochemical reduction of **1** occurs at $E_{p,c}$ = −1.38 V vs Ag/Ag$^+$, and only a small reoxidation peak is observed at −1.21 V (0.1 M $Bu_4NClO_4$ in MeCN, −20 °C) as shown in Figure 5B. While the oxidation potential of **1** falls near that of the monomeric species, **7a** and **7b**, the same cannot be said for the reduction potential, which is shifted significantly to a more positive potential (by ca. 0.8 V) compared to the monomeric species.

Cyclic voltammograms of monomeric and polymeric complexes obtained from (hexCp)Co($PPh_3$)$_2$ are shown in Figure 6. The polymers were insoluble in acetonitrile and thus their spin-coated films on ITO were used for the measurements. Results of the polymers are similar to those of **1**−**4**, i.e., they undergo quasi-reversible oxidation and irreversible reduction with significant shifts in only reduction potential compared with the monomers. The fact that the reduction potential of **6e** is more positive than **5i** may be related to the higher $\pi$-conjugation length in the former compared to the latter due to the difference in regioselectivity in the MCP process as noted above. Electrochemical data

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[32] Kudmar, I.; Seidel, T. *J. Appl. Phys.* **1962**, *33*, 771.

[33] (a) Kelly, R. S.; Geiger, W. E. *Organometallics* **1987**, *6*, 1432. (b) Donovan, B. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1988**, *110*, 2335. (c) Donovan, B. T.; Geiger, W. E. *Organometallics* **1990**, *9*, 865.

[34] Ohkubo, A.; Fujita, T.; Ohba, S.; Aramaki, K.; Nishihara, H. *J. Chem. Soc., Chem. Commun.* **1992**, 1553.

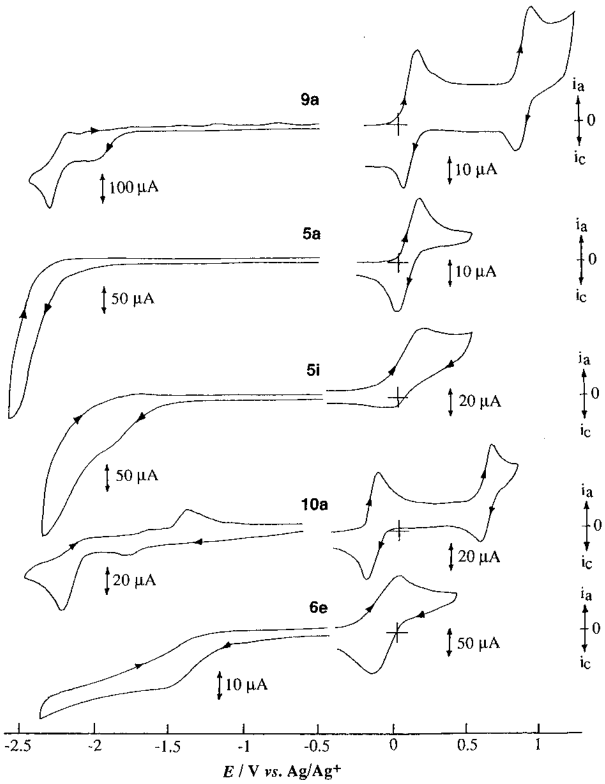

**Figure 6.** Cyclic voltammogram of **9a** at GC, **5a** at GC, **5i**/ITO, **10a** at GC and **6e**/ITO at a scan rate of 100 mV $s^{-1}$ in 0.1 M $Bu_4NClO_4$−MeCN at −20 °C.

obtained for the cobaltacyclopentadiene polymers are summarized in Table 3.

The possible explanation of the phenomena noted above involving large shifts in the reduction potential and a slight change in the oxidation potential is considered here based on the EHMO calculation for a model monomeric compound of cobaltacyclopentadiene, $Cp(PH_3)[\overline{CoCH{=}CHCH{=}CH}]$ by Thorn and Hoffman.[19] Their calculations indicate the following: (1) there are no immediately obvious strong interactions involving the $C_4H_4$ π-type orbitals, (2) the HOMO and LUMO are ascribed to σ-bonding between $CpCo(PH_3)^{2+}$ and $C_4H_4{}^{2-}$ fragments, and (3) it is the next HOMO and LUMO that are ascribed to the π-system. The situation for the highly conjugated polymers is expected to be quite different, because orbitals from the π-system would form band structures and their energy levels should change significantly. Thus, it is likely that the HOMO in the polymers can be ascribed to σ-bonding just as it is for the model monomeric complex, but the LUMO in the polymers is derived from π* orbitals. This would mean that $E_g$ would correspond to π−π* transition while the difference in redox potentials would be related to the energy difference between σ and π* orbitals, but a better understanding of the energy levels in the polymers is required to elaborate any further.

**Photoconductivity.** Photoresponse of $i-V$ characteristics for ITO/**6e**/ITO is given in Figure 7. The polymer has a low conductivity, $10^{-12}$ S $cm^{-1}$ in the dark, and photocurrent is 4 times larger than the dark current. This kind of remarkable photoconductivity does not appear for common π-conjugated organic polymers in the *undoped* state but is caused by forming charge-transfer complexes with donor or acceptor molecules such as fullerene.[35] It should be noted that the photoconductivity of undoped poly(vinylcarbazole) was much smaller than that of **6e** when similar equipments were used. We propose that the metal d-character orbitals localized at cobalt sites and their energy level lying between valence and conduction bands act as the trapping sites of holes generated by photoactivation of electrons from the valence band to the conduction band. Details of photoconductivity parameters and mechanisms are currently under investigation.

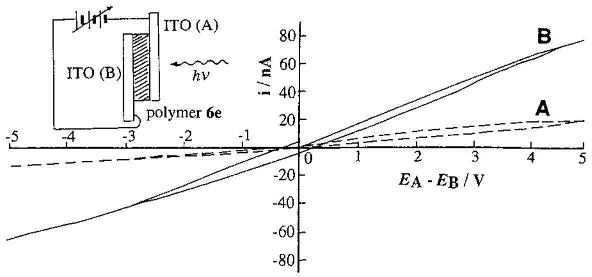

**Figure 7.** Current vs voltage characteristics of ITO/**6e**/ITO at 0.1 V $s^{-1}$ in dark (A) and under white light irradiation (B).

## Experimental Section

The cobalt complex $CpCo(PPh_3)_2$ was prepared according to the method in the literature.[36] The hexyl complex (hexCp)-$Co(PPh_3)_2$ was prepared as described in a communication.[23] Acetylenes, *p*-diethynylfluorobenzene, 1,4-diethynyl-2,5-difluorobenzene, 4,4′-diethynylbiphenyl, 4-ethynylbiphenyl, and *p*-di-1-propynylbenzene were prepared according to the procedure in the literature.[37] Other acetylenes, *p*-diethynylbenzene, ethynylbenzene, and 1-phenyl-1-propyne were purchased from Tokyo Kasei Kogyo and purified by silica gel column chromatography. Anhydrous solvents were purchased from Kanto Chemical. An electrolyte, $Bu_4NClO_4$ was obtained as lithium battery grade from Tomiyama Chemical. ITO-coated glasses (resistance < 30 Ω/square) used for electrodes were purchased from Nippon Sheet Glass Co. LTD and were cleaned by sonicating in 1 M $HClO_4$, in distilled water and in acetone and dried just before use. FT-IR, UV−vis, and NMR spectra were recorded with Shimadzu FTIR-8100M, Shimadzu MPS-2000, and JEOL GX400 spectrometers, respectively. Film thickness was measured with a Tokyo Seimitsu Surfcom surface profilometer. Separation of isomers and soluble polymers was carried out with a JAI LC-908 recycling preparative HPLC apparatus with a JAI UV-254H and/or a JAI RI-5 detectors.

**GPC Analysis of Polymerization Process.** Over 8 min, a 0.7 mL toluene solution of *p*-diethynylbenzene (53.9 mg, 0.427 mmol) was added dropwise to a 4.3 mL solution of CpCo-$(PPh_3)_2\cdot{}^1/_2$hexane (295 mg, 0.427 mmol). Then, the mixture was stirred at room temperature under argon. A part of the solution (10 or 20 μL) was sampled at intervals of 30 min, diluted in 2 mL of THF, and the components in the solution were analyzed with a Shimadzu LC-4A HPLC apparatus (column: Tosoh TSKgel 45000HGX, detector: Shimadzu SPD2A UV spectrometer monitoring at the wavelength of 254 nm). Highest and maximum molecular weights of the soluble polymeric components and the height of an overlapped peak for $CpCo(PPh_3)_2\cdot{}^1/_2$hexane and *p*-diethynylbenzene were monitored. Molecular weights were evaluated based on polystyrene standards.

**Cobaltacyclopentadiene Polymers from $CpCo(PPh_3)_2$.** The starting material, $CpCo(PPh_3)_2\cdot{}^1/_2$hexane was recrystal-

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(35) (a) Yoshino, K.; Morita, S.; Kawai, T.; Araki, H.; Yin, X. H.; Zakhidov, A. A. *Synth. Met.* **1993**, *56*, 2991. (b) Sariciftci, N. S.; Smilowitz, L.; Braun, D.; Srdaniov, G.; Srdanov, V.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1993**, *56*, 3125.

(36) Rinze, P. V.; Lorberth, J.; Nöth, H.; Stutte, B. *J. Organomet. Chem.* **1969**, *19*, 399.

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lized several times and then dissolved in either benzene or toluene. The resulting solution was thrice filtered since its purity affected both the polymerization rate and the purity of insoluble product.

As a typical example of the synthesis of insoluble polymers, preparation of **1** is described in the following. A 1.2 mL toluene solution of *p*-diethynylbenzene (182 mg, 1.45 mmol) was added slowly to a 14.5 mL toluene solution of $\mathrm{CpCo(PPh_3)_2\cdot{}^1/_2}$hexane (1.00 g, 1.45 mmol) with stirring. Further stirring at room temperature in an Ar-filled drybox saw the color of the mixture gradually change from dark red to greenish brown and then to dark brown, and precipitates formed within a few hours. The reaction was stopped after 24 h of stirring and the precipitates were collected by filtration and rinsed thoroughly with toluene. After drying, a dark brown powder was obtained in a yield of 481 mg (65%). IR (KBr) $\nu_{\max}$ 3040(w), 2938(w), 2915(w), 2845(w), 1586(w), 1478(m), 1431(m), 1181(m), 1117(m), 1088(m), 810(s), 749(s), 730(w), 693(s), 540(m), 529(m), 509(m), 494(w) $\mathrm{cm^{-1}}$. Anal. Calcd for $\mathrm{(C_{33}H_{26}CoP)}_n$: C, 77.34; H, 5.11. Found: C, 77.61; H, 5.40.

Polymers **2**−**4** were prepared and collected in a manner similar to that described above. Reaction of $\mathrm{CpCo(PPh_3)_2\cdot{}^1/_2}$hexane (243 mg, 0.351 mmol) with *p*-diethynylfluorobenzene (42.4 mg, 0.294 mmol) at room temperature in benzene for 7 days gave precipitates of **2** as a black powder in a yield of 104 mg (66%). IR (KBr) $\nu_{\max}$ 3052(w), 2959(w), 2924(w), 2855(w), 1478(m), 1433(m), 1184(m), 1117(m), 1090(s), 808(m), 743(s), 693(s), 612(m), 527(m) $\mathrm{cm^{-1}}$. Anal. Calcd for $\mathrm{(C_{33}H_{25}CoFP)}_n$: C, 74.72; H, 4.75. Found: C, 73.10; H, 4.84.

Reaction of $\mathrm{CpCo(PPh_3)_2\cdot{}^1/_2}$hexane (180 mg, 0.260 mmol) with 1,4-diethynyl-2,5-difluorobenzene (33.7 mg, 0.208 mmol) at room temperature in benzene for 11 days gave precipitates of **3** as a black powder in a yield of 90.0 mg (79%). IR (KBr) $\nu_{\max}$ 3058(w), 2955(w), 2924(w), 2855(w), 1478(s), 1433(m), 1264(m), 1159(s), 1090(m), 882(m), 814(m), 743(m), 693(s), 675(m), 529(m), 509 (m) $\mathrm{cm^{-1}}$. Anal. Calcd for $\mathrm{(C_{33}H_{24}CoF_2P)}_n$: C, 72.27; H, 4.41. Found: C, 71.77; H, 4.07.

Reaction of $\mathrm{CpCo(PPh_3)_2\cdot{}^1/_2}$hexane (55.9 mg, 0.276 mmol) with 4,4′-diethynylbiphenyl (191 mg, 0.276 mmol) at 4 °C in toluene for 3 days gave precipitates of **4** as a dark brown (with a violet tint) powder in a yield of 118 mg (61%). IR (KBr) $\nu_{\max}$ 3050(w), 3015(w), 2950(w), 2929(w), 2855(w), 1597(w), 1478(s), 1433(m), 1182(m), 1116(w), 1090(m), 1001(m), 810(s), 745(s), 693(s), 669(w), 529(s), 511(m), 484(w) $\mathrm{cm^{-1}}$. Anal. Calcd for $\mathrm{(C_{39}H_{30}CoP)}_n$: C, 79.59; H, 5.14. Found: C, 78.22; H, 5.20.

Thin films of **1**−**4** were prepared on quartz glass by immersing the bare glass in the toluene polymerization solution for 24 h and washing the resulting film thoroughly with toluene, followed by drying under vacuum.

**Cobaltacyclopentadiene Polymers from (hexCp)Co(PPh$_3$)$_2$.** A mixture of $\mathrm{(hexCp)Co(PPh_3)_2\cdot{}^1/_3}$hexane (1.01 g, 1.30 mmol) and *p*-diethynylbenzene (164 mg, 1.31 mmol) in toluene (13 mL) was stirred for 4 days at 4 °C. The color of the mixture was turned from reddish brown to greenish brown, then dark brown. The product was separated into 9 portions (**5a**−**i**) according to the molecular weight using recycling preparative HPLC apparatus (column: JAIGEL-2H + 3H, eluent: toluene). Yields of **5a**−**h** were 32, 57, 27, 19, 13, 116, 27, and 11 mg, respectively, and the yield of **5i** was less than 1 mg. **5a**: $^1$H NMR ($\mathrm{C_6D_6}$) $\delta$ 8.85 (t, $J_{\mathrm{PH}}$ = 3.42 Hz, $J_{\mathrm{HH}}$ = 0.63 Hz, 0.63H, CoC*H*=), 7.75−7.05 (m, 23H, $-\mathrm{C_6}H_4-$, P*Ph*$_3$), 6.81 (d, $J_{\mathrm{PH}}$ = 6.84 Hz, 0.75H, CoC=C*H*C*H*=C−), 5.10−4.75 (m, 4H, hex*Cp*), 3.09 (s, 1.5H, −C≡C*H*), 2.23−2.10 (m, 2H, $-\mathrm{C}H_2\mathrm{C_5H_{11}}$), 1.51−1.36 (m, 8H, $-\mathrm{CH_2C_4}H_8\mathrm{CH_3}$), 1.07 (t, $J_{\mathrm{HH}}$ = 6.84 Hz, 3H, $-\mathrm{C}H_3$). **5g**−**i**: $^1$H NMR ($\mathrm{C_6D_6}$) $\delta$ 7.8−6.8 (m, 21H, $-\mathrm{C_6}H_4-$, P*Ph*$_3$, CoC=C*H*C*H*=C−), 4.95−4.69 (m, 4H, hex*Cp*), 2.11 (m, 2H, $-\mathrm{C}H_2\mathrm{C_5H_{11}}$), 1.5−1.1 (m, 8H, $-\mathrm{CH_2C_4}H_8\mathrm{CH_3}$), 0.89 (br, s, 3H, $-\mathrm{C}H_3$); $^{13}$C NMR ($\mathrm{C_6D_6}$) 134.28, 132.36, 131.55, 129.63, 129.30, 128.53, 128.26, 128.15, 128.02, 127.90, 127.79, 125.67, 88.10, 85.61, 32.07, 31.94, 30.19, 29.62, 27.56, 23.03, 21.40, 14.33; $^{31}$P NMR ($\mathrm{C_6D_6}$) 59.90 (s, *P*Ph$_3$), 53.51 (s, *P*Ph$_3$).

A mixture of $\mathrm{(hexCp)Co(PPh_3)_2\cdot{}^1/_3}$hexane (175 mg, 0.23 mmol) and *p*-di-1-propynylbenzene (34 mg, 0.22 mmol) in toluene (2.3 mL) was stirred for 1 day at room temperature. The product was separated into 4 portions (**6a**−**d**) according to the molecular weight using recycling preparative HPLC apparatus (column: JAIGEL-2- + 3H, eluent: toluene). Yields of **6a**, **6b**, and **6c** were 28, 18, and 10 mg, respectively and the yield of **6d** was less than 1 mg.

A similar reaction was carried out at 40 °C and a higher molecular weight component (**6e**, M.W. > $10^{3.5}$ based on the polystyrene standard) was collected. **6e**: $^1$H NMR ($\mathrm{C_6D_6}$) $\delta$ 7.67−6.59 (m, 19H, $-\mathrm{C_6}H_4-$, P*Ph*$_3$), 5.20−4.43 (m, 4H, hex*Cp*), 2.4−1.8 (m, 8H, CoC=C*Me*C*Me*=C−, $-\mathrm{C}H_2\mathrm{C_5H_{11}}$), 1.7−1.1 (m, 8H, $-\mathrm{CH_2C_4}H_8\mathrm{CH_3}$), 0.83 (br, s, $-\mathrm{C_5H_{10}C}H_3$); $^{13}$C NMR ($\mathrm{C_6D_6}$) 151.23, 150.37, 149.37, 134.61, 134.23, 134.03, 132.42, 132.32, 131.80, 131.52, 130.88, 129.69, 129.27, 128.81, 128.72, 128.54, 128.48, 128.43, 128.23, 128.12, 127.87, 127.75, 126.60, 125.63, 106.10, 105.80, 90.59, 86.72, 32.22, 32.05, 31.90, 31.44, 31.28, 29.77, 29.60, 27.93, 23.04, 22.99, 22.95, 21.37, 19.48, 14.35, 14.30; $^{31}$P NMR ($\mathrm{C_6D_6}$) 57.67 (s, *P*Ph$_3$), 53.88 (s, *P*Ph$_3$). Anal. Calcd for $\mathrm{(C_{41}H_{42}CoP)}_n$: C, 78.83; H, 6.78. Found: C, 75.33; H, 6.70.

**Monomeric Cobaltacyclopentadienes.** Mononuclear cobaltacyclopentadiene complexes were prepared by the reaction of $\mathrm{CpCo(PPh_3)_2\cdot{}^1/_2}$hexane or $\mathrm{(hexCp)Co(PPh_3)_2\cdot{}^1/_3}$hexane with monoacetylenes in a manner similar to the methods in the literature[26,29] and the geometric isomers were separated using Japan Analytical Industry Model 908 recycling preparative HPLC apparatus (column: JAIGEL-1H + 2H, eluent: 1,2-dichloroethane). Physical data of the complexes are given below.

$\mathrm{Cp(PPh_3)}$[CoCPh=CHCH=CPh] (**7a**): $^1$H NMR ($\mathrm{CD_2Cl_2}$) $\delta$ 7.8−6.8 (m, 25H, CoC*Ph*=CHCH=C*Ph*, P*Ph*$_3$), 6.12 (d, $J_{\mathrm{PH}}$ = 6.84 Hz, 2H, CoCPh=C*H*C*H*=CPh), 4.77 (s, 5H, *Cp*). IR (KBr) $\nu_{\max}$ 3054(w), 2945(w), 2915(w), 2845(w), 1593(w), 1480(m), 1435(m), 1184(w), 1119(w), 1090(m), 812(s), 754(s), 722(m), 696(s), 565(m), 529(s), 511(m) $\mathrm{cm^{-1}}$. Anal. Calcd for $\mathrm{C_{39}H_{32}CoP}$: C, 79.32; H, 5.46. Found: C, 78.63; H, 5.53. $\mathrm{Cp(PPh_3)}$[CoCPh=CHCPh=CH] (**7b**): $^1$H NMR ($\mathrm{CD_2Cl_2}$) $\delta$ 8.20 (t, $J_{\mathrm{PH}}$ = 3.42 Hz, $J_{\mathrm{HH}}$ = 3.42 Hz, 1H, CoCPh=CHCPh=C*H*), 7.6−6.9 (m, 25H, CoC*Ph*=CHC*Ph*=CH, P*Ph*$_3$), 6.48 (dd, $J_{\mathrm{PH}}$ = 6.35 Hz, 1H, CoCPh=C*H*CPh=CH), 4.77 (s, 5H, *Cp*). IR (KBr) $\nu_{\max}$ 3052(w), 2940(w), 2910(w), 2840(w), 1595(w), 1482(m), 1435(m), 1184(m), 1119(w), 1090(m), 812(s), 749(s), 722(w), 695(s), 542(m), 531(m), 511(m) $\mathrm{cm^{-1}}$. Anal. Calcd for $\mathrm{C_{39}H_{32}CoP}$: C, 79.32; H, 5.46. Found: C, 78.92; H, 5.75. $\mathrm{Cp(PPh_3)[CoC(C_{12}H_9){=}CHCH{=}C(C_{12}H_9)]}$ (**8**): UV−vis $\lambda_{\max}$ ($\epsilon$) in $\mathrm{CH_2Cl_2}$ 228 (28 200), 296 (25 500), 414 nm (5800). IR (KBr) 3058(m), 3025(m), 2946(m), 1597(m), 1480(s), 1433(m), 1264(m), 1088(m), 816(m), 806(m), 764(s), 737(s), 696(s), 527(m), 513(m), 496(m), 484(m) $\mathrm{cm^{-1}}$. $^1$H NMR ($\mathrm{CD_2Cl_2}$) $\delta$ 7.6−6.9 (m, 33H, $\mathrm{CoC(C_{12}}H_9\mathrm{){=}CHCH{=}C(C_{12}}H_9\mathrm{)}$, P*Ph*$_3$), 6.22 (d, $J_{\mathrm{PH}}$ = 6.35 Hz, 2H, $\mathrm{CoC(C_{12}H_9){=}C}H\mathrm{C}H\mathrm{{=}C(C_{12}H_9)}$), 4.82 (s, 5H, *Cp*). Anal. Calcd for $\mathrm{C_{51}H_{40}CoP}$: C, 82.47; H, 5.43. Found: C, 82.67; H, 5.59. $\mathrm{(hexCp)(PPh_3)}$[CoCPh=CHCH=CPh] (**9a**): $^1$H NMR ($\mathrm{C_6D_6}$) $\delta$ 7.85−7.01 (m, 25H, CoC*Ph*=CHCH=C*Ph*, P*Ph*$_3$), 6.76 (d, $J_{\mathrm{PH}}$ = 6.84 Hz, 2H, CoCPh=C*H*C*H*=CPh), 4.91 (s, 4H, hex*Cp*), 2.12 (m, 2H, $-\mathrm{C}H_2\mathrm{C_5H_{11}}$), 1.51−1.23 (m, 8H, $-\mathrm{CH_2C_4}H_8\mathrm{CH_3}$), 0.92 (t, $J_{\mathrm{HH}}$ = 6.84 Hz, 3H, $-\mathrm{C}H_3$). Anal. Calcd for $\mathrm{C_{45}H_{44}CoP}$: C, 80.10; H, 6.57. Found: C, 80.19; H, 6.79. $\mathrm{(hexCp)(PPh_3)}$[CoCPh=CHCPh=CH] (**9b**): $^1$H NMR ($\mathrm{C_6D_6}$) $\delta$ 8.53 (t, $J_{\mathrm{PH}}$ = 3.42 Hz, $J_{\mathrm{HH}}$ = 3.42 Hz, 1H, CoCPh=CHCPh=C*H*), 7.61−7.02 (m, 26H, CoC*Ph*=C*H*C*Ph*=CH, P*Ph*$_3$), 5.00 (s, 1H, hex*Cp*), 4.79 (s, 1H, hex*Cp*), 4.76 (s, 1H, hex*Cp*), 4.69 (s, 1H, hex*Cp*), 2.16 (m, 2H, $-\mathrm{C}H_2\mathrm{C_5H_{11}}$), 1.50 (m, 2H, $-\mathrm{CH_2C}H_2\mathrm{C_4H_9}$), 1.34−1.25 (m, 6H, $-\mathrm{C_4H_4C_3}H_6\mathrm{CH_3}$), 0.92 (t, $J_{\mathrm{HH}}$ = 6.84 Hz, 3H, $-\mathrm{C}H_3$). Anal. Calcd for $\mathrm{C_{45}H_{44}CoP}$: C, 80.10; H, 6.57. Found: C, 79.87; H, 6.76. $\mathrm{(hexCp)(PPh_3)}$[CoCPh=CMeCMe=CPh] (**10a**): $^1$H NMR ($\mathrm{C_6D_6}$) $\delta$ 7.77−

6.89 (m, 25H, CoC*Ph*═CMeCMe═C*Ph*, P*Ph*$_3$), 4.74 (d, $J_{\mathrm{HH}}$ = 1.98 Hz, 2H, hex*Cp*), 4.62 (d, $J_{\mathrm{HH}}$ = 1.98 Hz, 2H, hex*Cp*), 1.89 (s, 6H, CoCPh═C*Me*C*Me*═CPh), 1.78 (t, $J_{\mathrm{HH}}$ = 7.26 Hz, 2H, −C*H*$_2$C$_5$H$_{11}$), 1.42−1.14 (m, 8H, −CH$_2$C$_4$*H*$_8$CH$_3$), 0.92 (t, $J_{\mathrm{HH}}$ = 6.27 Hz, 3H, −C*H*$_3$). $^{13}$C NMR ($C_6D_6$) 153.99, 151.00 (Co*C*Ph═CMeCMe═*C*Ph), 134.58, 134.48, 134.23, 134.03, 132.42, 132.32, 131.50, 129.59, 129.25, 128.81, 128.54, 128.43, 128.23, 128.12, 127.98, 127.87, 127.75, 127.66, 127.54, 123.83 (*Ph*) 105.68, 105.64 (CoCPh═*C*Me*C*Me═CPh), 90.70, 86.59 (hex*Cp*), 31.89 (CoCPh═C*Me*C*Me*═CPh), 31.20, 29.54, 27.83, 22.93, 19.12, 14.27 (*hex*Cp); $^{31}$P NMR ($C_6D_6$) 54.11 (s, *P*Ph$_3$). Anal. Calcd for $C_{47}H_{48}CoP$: C, 80.32; H, 6.88. Found: C, 80.10; H, 7.09.

**Cyclic Voltammetry.** Polymers **1**−**4** were deposited as films on ITO-coated glass by immersing the ITO in the toluene polymerization solution for 24 h, washing thoroughly with benzene or toluene, and drying under vacuum prior to use in cyclic voltammetry experiments. Whenever inhomogeneous thick films formed, the film-coated ITO glasses were sonicated in toluene or benzene under nitrogen or argon and dried under vacuum, which resulted in uniform and thin films of the polymers. Films of polymers **5i** and **6e** were deposited on ITO glasses from $CH_2Cl_2$ solutions by the spin-coating method.

Cyclic voltammetry was carried out in a standard one-compartment cell equipped with a Pt wire counter electrode and an Ag/Ag$^+$ (10 mM $AgClO_4$ in 0.1 M $Bu_4NClO_4$/MeCN, $E^{\circ\prime}$-(ferrocenium/ferrocene) = 0.09 V vs Ag/Ag$^+$ with a Toho Technical Research 2001 potentiostat/galvanostat, 2230 function generator, and a Riken Denshi Model F-35 $X-Y$ recorder.

**Photoconductivity Measurements.** An ITO/**6e**/ITO structure was made by drop-coating a film of **6e** with a thickness of 30 $\mu$m and an area of 0.25 cm$^2$ on a ITO glass from a condensed $CH_2Cl_2$ solution, followed by covering another ITO glass. Current vs voltage characteristics were measured without and with white light irradiation using 500 W Xe lamp with an IR-cut filter. Photocurrent response was measured with applying 5 V.

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**Supporting Information Available:** Infrared spectra of **1**, **7a**, **7b**, 4,4′-diethynylbiphenyl, and **4** prepared in benzene at room temperature at $x = 2.0$ and at $x = 0.8$ and $^1$H NMR spectra of **5a**, **5b**, **5c**, **5d**, and **5f** (4 pages). Ordering information is given on any current masthead page.

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