Macromol. Symp. **2004**, *209,* 141-162

Synthesis and Physical Properties of π-Conjugated Metallacycle Polymers of Cobalt and Ruthenium

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Summary: Recent studies on two types of π-conjugated metallacylce polymers are reviewed. Reaction of $CpCo(PPh_3)_2$ with conjugated diacetylenes afford poly(arylene cobaltacyclopentadienylene) and that of CpRuBr(cod) does poly(arylene ruthenacyclopentrienylene)s in ambient conditions. Regioselectivity of the former metallacycling reacion is not perfect (at most 80% of the 2,5-diaryl selectivity) but that of the latter is satisfactory (~100% of the 2,5-diaryl selectivity) for the formation of π-conjugated structure. Electrochemical oxidation of the cobaltacyclopentadiene polymer and reduction of the ruthenacycle polymer occur facilely and quasi-reversibly by the contribution of metal *d*-orbitals. Physical properties in undoped (neutral) and doped (charged) sates show the behavior of electronic band structure derived from the organic π-conjugated main chain strongly coupled with the metal *d*-orbitals. This affords, for example, photoconductivity in the neutral form of the cobaltacylopentadiene polymer and ferromagnetic interaction in the reduced form of the ruthenacyclopentatriene polymer.

Keywords: cobalt; conducting polymers; metallacycle; organometallic polymers; polymer; redox properties; ruthenium

Introduction

"Organometallic conducting polymers"[1] are derived from the combination of transition metal complexes with π-conjugated organic polymer chains, so-called "conducting polymers", which exhibit various curious physical and chemical characteristics such as facile oxidation and reduction leading to charge storage, high electronic conductivity in the doped states, electrochromism, photo- and electro-luminescence.[2] Various kinds of organometallic conducting polymers and oligomers such as polymetallocenylene,[3,4] poly(metalyne),[5-9] poly(metallo-phthalocyanine),[10,11] polydecker sandwich compounds,[12] thiolate complex polymers,[13-15] cyclobutadienecobalt complex polymers,[16] and others have been synthesized.[17]

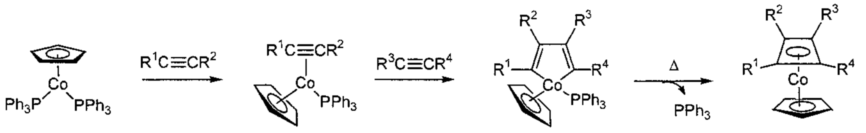
DOI: 10.1002/masy.200450510

Another category of such polymers is poly(arylene metallacyclopentadienylene), wherein the framework of the polymer is π-conjugated and in part composed of metallacyclopentadienes. In this polymer, the metallacyclopentadiene ring with its *d*-block heteroatom is structurally analogous to the rings found in other representative π-conjugated polymers, such as poly(pyrrole) and poly(thiophene), which contain *p*-block heteroatoms. Our synthesis of the first metallacyclopentadine polymers, poly(arylene cobaltacyclopentadiene)s, has been accomplished by a new type of polymerization scheme, MetallaCycling Polymerization (MCP), that is based on successive metallacyclization of conjugated diacetylenes.[18] Zirconacyclopentadiene polymers using MCP reactions have been reported by Tilley *et al.*[19] We have recently succeeded in the preparation of ruthenacyclopentatriene-based organometallic polymers using the similar MCP reactions.[20] This is the first example of the organometallic polymers involving metallacyclopentatriene and thus interesting to compare the properties with metallacyclopentadiene polymers. Our studies on the synthesis and physical properties of cobaltacyclopentadiene polymers have been overviewed in a separate paper,[21] and here we describe mainly the comparison of the synthesis and physical properties between the cobaltacyclopentadiene and ruthenacyclopentatriene polymers.

Synthesis

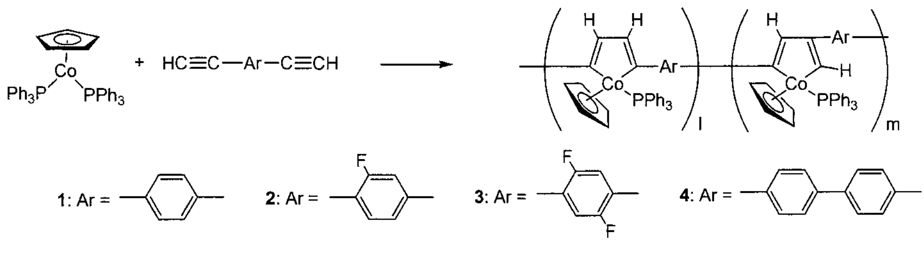
1. Poly(arylene cobaltacylopentadienylene)s

It is well established that the addition of two acetylenes to the metal center affords metallacyclopentadiene, which is the precursor of the formation of six-membered aromatic rings.[22-25] In the case of cobaltacyclopentadiene, the most common starting compound is $CpCo(PPh_3)_2$ (Cp = η^5-C_5H_5), which reacts with two acetylenes, $CR^1{\equiv}CR^2$ and $CR^3{\equiv}CR^4$ stepwise, affording $CpCo(CR^1{\equiv}CR^2)(PPh_3)$ and then $CpCo(CR^1{=}CR^2{-}CR^3{=}CR^4)(PPh_3)$ (Equation (1)). A further addition reaction with unsaturated compounds such as acetylene and nitrile gives aromatic six-membered rings. It is also known that the thermal reaction of cobaltacyclopentadiene $CpCo(CR^1{=}CR^2{-}CR^3{=}CR^4)(PPh_3)$ affords a cyclobutadiene complex, $CpCo(\eta^4$-$C_4R^1R^2R^3R^4)$ (Equation (1)).[26] This kind of unique chemical reactivity of metallacyclopentadiene units can be utilized to obtain interesting polymeric substances from metallayclopentadiene polymers. The regioselectivity of the metallacyclization is important to obtain highly π-conjugated polymers by MCP. When the cobaltacyclopentadiene unit is formed from two CR≡CR' molecules, there are three possible isomers, 2,4-R_2-3,5-R'_2, 2,5-R_2-3,4-R'_2 and 3,4-R_2-2,5-R'_2 forms. Wakatsuki *et al.* have shown the rule that the acetylenic carbon bearing a bulky group becomes the α-carbon of the metallacyclopentadiene.[27]

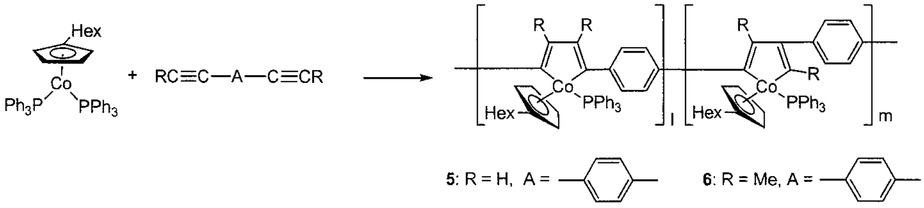


(1)

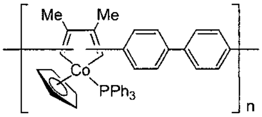
Application of the metallacyclization to the polymer synthesis has been successfully made using conjugated diacetylene with the formula, HC≡C-Ar-C≡CH (Ar = 1,4-phenylene, 2-fluoro-1,4-phenylene, 2,5-difluoro-1,4-phenylene, and 4,4'-biphenylene). The diacetylenes HC≡C-Ar-C≡CH of the first attempt have been chosen because the insertion of the arylene moieties in the diacetylene is because the diacetylene without a spacer, RC≡C-C≡CR, could not yield polymers because of the high steric hindrance due to Cp and PPh_3 groups around the cobalt center,[28,29] and because they would give 2,5-Ar_2 structures according to the stereochemical rule of metallacyclization as noted above. The respective polymers, **1** – **4** were obtained as insoluble powders,[30] and also as films when the glass plates were immersed in the solution of the MCP synthesis. It should be noted that the results on the soluble polymers suggest incomplete π-conjugation by the involvement of 2,4-Ar_2 units (*vide infra*), while the extension of π-conjugation by the involvement of 2,5-Ar_2 structures in the polymers was supported by the electronic spectra of the polymers showing the red shift of the absorption edge compared with the monomeric complex.



Improvement of the solubility was carried out using hexylcyclopentadienyl (HexCp) ligand instead of Cp in the starting cobalt complex[31,32] and/or using alkyl-terminated diacetylenes, $RC{\equiv}C\text{-}Ar\text{-}C{\equiv}CR$ (R = Me, Bu).[33,34] An MCP reaction between $(HexCp)Co(PPh_3)_2$ and *p*-diethynylbenzene at 4 °C for 4 days gave no insoluble product, and the GPC spectrum of the reaction product indicated several oligomeric and polymeric components, **5**, the highest molecular weight of which is more than 7×10^4 based on the polystyrene standard.[32] The oligomeric components $HC{\equiv}C\text{-}C_6H_4[C_4H_2\{Co(HexCp)(PPh_3)\}\text{-}C_6H_4]_nC{\equiv}CH$ were separated from dimer (n = 2) to nonamer (n = 9). The ^{1}H NMR analysis indicated that the products were mixtures of these two isomeric structures, 2,5- *vs*. 2,4-substituted cobaltacyclopentadienes with the ratio of 4 : 6. As mentioned above, the regioselectivity is principally dominated by the steric effect of the substituents on the acetylenic carbon. However, this result indicates another factor, probably the dipole-dipole interaction of two acetylenes ligated to cobalt, is concerted in determining the conformation at the intermediate state. Our reinvestigation of the stereochemistry of the metallacyclization for monomeric complexes actually supports this consideration; a reaction of $(HexCp)Co(PPh)_2$ with ethynylbenzene afforded 2,5- and 2,4-diphenylcobaltacyclopentadienes with the ratio of 4 : 6. The yield of 2,5-diarylcobaltacyclopentadiene was increased by using 1-propynylbenzene instead of ethynylbenzene. This acetylene can generate the large steric repulsion between phenyl and methyl groups in the 2,4-diphenyl-3,5-dimethylcobaltacyclopentadiene, and actually afforded the desirable isomer in the yield of 80%.[32] Based on this regioselectivity result, MCP reactions between $(HexCp)Co(PPh_3)_2$ and *p*-di-1-propynylbenzene were performed at room temperature and 40 °C, affording a soluble product, **6**, of which GPC spectra shows a drastic enhancement of polymerization by the temperature increase.



The reaction of $CpCo(PPh_3)_2$ with MeC≡C-*p*-C_6H_4-C_6H_4-*p*-C≡CMe,[33] with MeOCC≡C-*p*-C_6H_4-C_6H_4-*p*-C≡CCOMe,[33] with $BuC≡CC_6H_4C_6H_4C≡CBu$,[34] with MeC≡C-*p*-C_6H_4-C≡CMe,[35] and with MeC≡C-2,5-C_4H_2S-C≡CMe[35] afforded soluble polymers, **7** with M_w/M_n = 4.0 × 10^5 (M_w/M_n = 4.5), **8** with 3.0 × 10^4 (M_w/M_n = 3.7), **9** with M_n = 2.7 × 10^5 (M_w/M_n = 5.2), **10** with M_n= 3.8 × 10^5 (M_w/M_n = 4.5), and **11** with M_n = 4.4 × 10^3 (M_w/M_n = 1.3), respectively.



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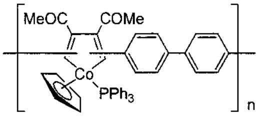

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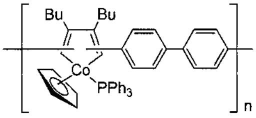

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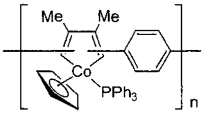

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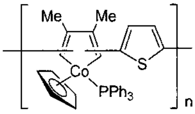

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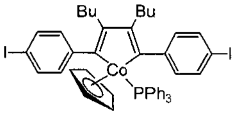
It should be mentioned that another method utilizing a polycondensation of a dihalogenated cobaltacyclopentadiene complex, $Cp(PPh_3)[Co\text{-}C(4\text{-}C_6H_4I)=CBu\text{-}CBu=C(4\text{-}C_6H_4I)]$ (**12**), with $Ni(cod)_2$ (cod = cycloocta-1,5-diene), was applied for the synthesis of perfectly π-conjugated polymer, **13**.[34] When the reaction of **12** was carried out with an excess amount of $Ni(cod)_2$ (2.0 eq) at 50 °C, the molecular weight, M_n, reached to 2.0 × 10^5 (M_w/M_n = 2.8) after 12 h. When the reaction of **12** was carried out with an equimolar of $Ni(cod)_2$ at a room temperature, the oligomers up to a hexamer were obtained. The polymer and oligomer could be purified with a recycling preparative GPC method. Especially, a dimer **13_2** and a trimer **13_3** were isolated and used as samples for investigating physical properties in detail.



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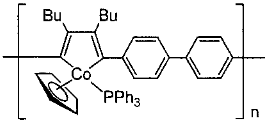

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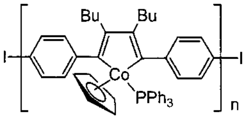
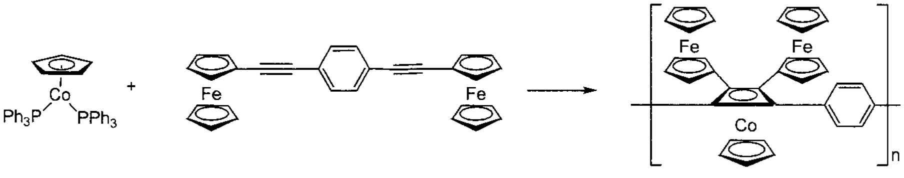


13_2: n = 2, **13_3**: n = 3

As mentioned above, it has been reported that thermal tranformation of cobaltacyclopentadienes into cyclobutadienecobalt complexes occures facilely.[26] This implies that polymers composed of cyclobutadienecobalt complex units can be formed in the MCP reactions. Actually, the reaction of $CpCo(PPh_3)_2$ with FcC≡C-*p*-C_6H_4-C≡CFc affords a cyclobutadienecobalt complex polymer.[36] The reaction at 50 °C for 22 h, followed by reprecipitation from toluene-hexane afforded an orange powdery solid of $[p\text{-}C_6H_4\{(\eta^4\text{-}C_4Fc_2)CoCp\}]_n$ (**14**). GPC analysis of **14** showed that M_n = 5 500 and M_w = 9 600, based on the polystyrene standard. The molecular weight of 5 500 indicates that the degree of polymerization is ca. 9.



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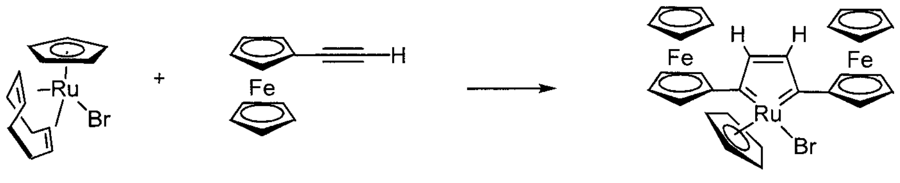
2. Poly(arylene ruthenacylopentatrienylene)s

It has been reported that ruthenacyclopentatriene is formed by the metallacycling reaction of two RC≡CH molecules with CpRuBr(cod) or $(\eta^5\text{-}C_5Me_5)$RuCl(cod).[37,38] The difference in the cyclization reaction compared with the cobalt system described above might be the regioselectivity of this reaction, because it was reported that only 2,5-R_2 isomer is formed in the case R = Ph in the literature.[37,38] Our study for the reaction using ethynylferrocene also afforded one isomer, 2,5-bis(ferrocenyl)ruthenacyclopentatriene, **15**.[39]



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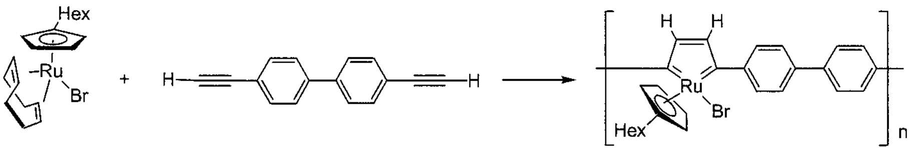
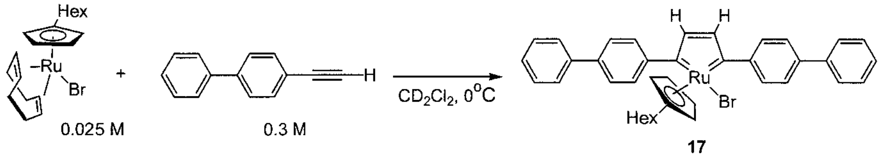
The ruthenacyclopentatriene polymer was synthesized as follows.[20] Reaction of (HexCp)RuBr(cod) with 4,4′-diethynylbiphenyl in dichloromethane at 0 °C yielded a reddish-brown polymeric product. This product was purified by washing with ether to remove residual starting materials, and then the residue was extracted with dichloromethane to remove any insoluble components. Evaporation of the solvent under vacuum resulted in a pure product that was a lustrous black film. The product was characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, IR, and UV-vis spectra, and electrochemical measurements, which together indicated the structure of poly(biphenylene ruthenacyclopentatrienylene), **16.** Polymer **16** is air-sensitive and its thermal stability is low. Its solution turned into an insoluble gel after standing for a few days at room temperature, even under nitrogen.



16

The composition of geometric isomers for ruthenacyclopentatriene units in **16** was examined by ^{1}H NMR spectra. In the spectra of **16** in CD_2Cl_2, a signal appeared at δ 7.86, assignable to β-protons of ruthenacyclopentatriene,[40] and no signals due to metallacycle α-protons were detected. Two peaks, one at δ 5.12 and the other at 5.05, both attributed to a cyclopentadienyl ligand, indicate the existence of only one kind of geometric isomers. It is thus concluded that only a 2,5-diaryl derivative of ruthenacyclopentatriene exists in **16**. The result that no geometrical isomer was formed in the polymerization indicates the formation of a fully π-conjugated main chain structure as noted above, which has not been accomplished by the MCP-formed cobaltacylopentadiene polymers.

Although ruthenacyclopentatriene is known as an intermediate that allows cyclotrimerization of acetylenes to yield a benzene derivative[40] as well as cobaltacycloopentadiene, there was no sign of cyclotrimerization during the polymerization in the conditions of this study. In a reaction of (η^5-C_5Me_5)RuCl(cod) with phenylacetylene, the reaction initially affords ruthenacyclopentatriene, which further reacts with excess acetylene to form (η^5-C_5Me_5)Ru(1,2,4-triphenylbenzene).[38] Although ruthenacycles can react with acetylenes, we found that cyclotrimerization did not occur at 0 °C in the reaction of (HexCp)RuBr(cod) with 4-ethynylbiphenyl. In the reaction of (HexCp)RuBr(cod) (0.025 M) with 4-ethynylbiphenyl (0.3 M) at 0 °C, which was monitored by ^{1}H NMR spectra, ruthenacycle **17** was formed in 100% yield, and the amount of **17** did not decrease. As a result, **17** did not react with excess acetylenes under these conditions (Figure 1).



17

The GPC of **16** in dichloromethane showed that the molecular weight was up to 2 × 10^4 (the number of units, n = 40). The high solubility of **16** can be attained by the attachment of a hexyl group on Cp. The average molecular weights of **16,** M_n and M_w were 3400 (n = 5.9) and 5 800, respectively. It was revealed that these values correspond primarily to the theoretical ones by time course GPC analysis of the molecular weight distribution under polymerization at 0 °C (*vide infra*). As the polymerization proceeded, M_n and M_w increased at first and became saturated around 90 h, when the M_w/M_n ratio approached the value of 2. In the polycondensation mechanism, the reaction of (HexCp)RuBr(cod) with 4,4′-diethynylbiphenyl is in equilibrium with the reaction of **16** with COD, which is eliminated from (HexCp)RuBr(cod), and both M_n and M_w are maximal when the initial concentrations of (HexCp)RuBr(cod) and 4,4′-diethynylbiphenyl are equal. The maximal M_n and M_w depend on the equilibrium constant of the polycondensation.

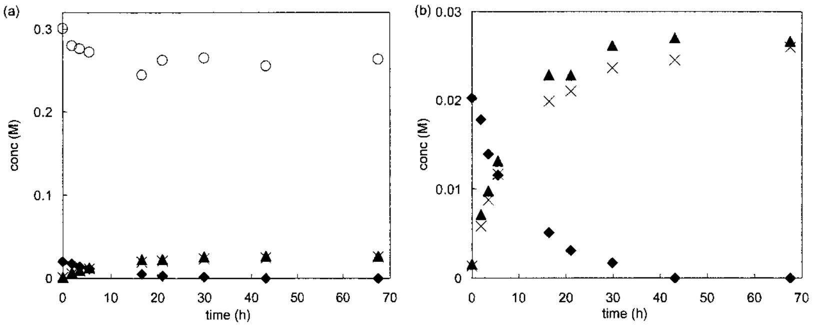


Figure 1. Time course change of concentration in reaction of (HexCp)RuBr(cod) with 4-ethynylbiphenyl (♦: (HexCp)RuBr(cod), ○: 4-ethynylbiphenyl, ▲: **17**, ×: COD). The reaction at 0 °C (a) and its enlarged view (b). (Reprinted with permission from ref. 20)

We assumed that the reaction of (HexCp)RuBr(cod) with 4,4′-diethynylbiphenyl is in equilibrium with the reaction of **16** with COD where k_1 and k_{-1} are the rate constants for forward and back polymerization. If the polymerization was polycondensation and initial concentration of (HexCp)RuBr(cod) and 4,4′-diethynylbiphenyl are the same ($[A]_0$), the number average polymerization degree, $\overline{P}_n$, and the weight average polymerization degree, $\overline{P}_w$, are given by Equation (2) and (3)[41]

$$\overline{P}_n = 1 + \sqrt{K}\,\frac{1-\exp\left(-2k_1[A]_0 t/\sqrt{K}\right)}{1+\exp\left(-2k_1[A]_0 t/\sqrt{K}\right)} \tag{2}$$

$$\overline{P}_w = 2\overline{P}_n - 1 \tag{3}$$

where K is the equilibrium constant (k_1 / k_{-1}) and t is the reaction time. For $[A]_0 = 0.025$ M, $K = 15$, and $k_1 = 4.4 \times 10^{-4}\ \mathrm{M^{-1}s^{-1}}$, Eqs (2) and (3) are in agreement with the time course change of M_n and M_w in polymerization. Calculated curves of M_n and M_w are plotted on Figure 2. At equilibrium (t → ∞), the maximum of the $\overline{P}_n$ is given by Equation (4).[37]

$$\overline{P}_n(t \rightarrow \infty) = 1 + \sqrt{K} \qquad (4)$$

The maximum values are calculated to M_n = 2 800 and M_w = 4 800 from Equation (4). These values are slightly smaller than those experimentally obtained as noted above. This could be because reprecipitation to purify polymer **16** removed the shorter polymer.

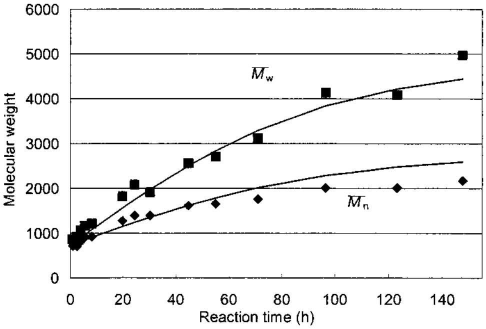


Figure 2. Time course change of M_n and M_w in reaction of (HexCp)RuBr(cod) with 4,4′-diethynylbiphenyl. (Reprinted with permission from ref. 20)

Physical properties

1. Poly(arylene cobaltacylopentadienylene)s

1-1. Electronic spectra

The color of all the cobaltacyclopentadiene polymers noted above is dark brown and the UV-Vis absorption spectra of the films of **1**-**4** coated on quartz glass show strong bands that have an edge at 500 to 600 nm.[32] As for the soluble polymer, the band edge shifts to the higher wavelength according to an increase in polymerization degree for **9** in CH_2Cl_2 solutions, indicating the formation of π-conjugated structure.[32] The perfectly π-conjugated polymer **13** prepared by polycondensation on dihalogenated complex exhibit a shift of the peak edge to the longer wavelength compared with the corresponding polymer, **9** prepared by metallacycling polymerization (Figure 3).[34]

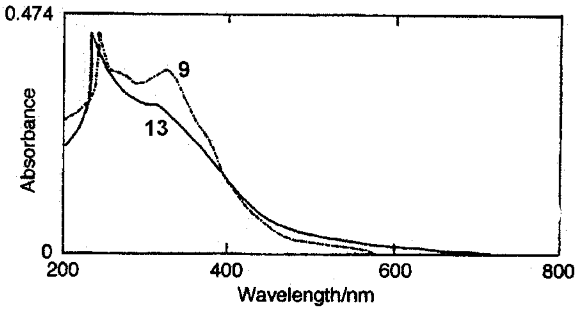


Figure 3. The UV/VIS spectra of compounds **9** and **13** in CH_2Cl_2. (Reprinted with permission from ref. 34)

Band gap energies, E_g, for the cobaltacyclopentadiene polymers were evaluated from the absorption edge based on the semiconductor theory.[36] The E_g values thus evaluated were 2.1 to 2.3 eV,[32] which correspond roughly to the value observed in poly(thiophene) (2.0 eV) and are relatively small when compared to the band gaps among previously known π-conjugated organic polymers.[2]

1-2. Redox properties

Cobaltacylopentadiene complexes undergo one-electron oxidation and their potential and chemical reversibility depend strongly on the substituents on the metallacycle.[42-45] This directly reflects the redox properties of the cobaltacylopentadiene polymers. The oxidation potential of the polymers becomes more positive when the electron-withdrawing substituents such as –COMe were bound to the metallacycle,[33] and the chemical reversibility increases in the order of the substituents, -COMe < -H < alkyl (-Me, Bu).[33] The polymers with alkyl groups as substituents show cyclic voltammograms indicating high chemical reversibility at a scan rate of 0.1 Vs^{-1} in NBu_4ClO_4-CH_2Cl_2. These results support our consideration that the HOMO based on the *d*-orbitals of the metal atoms in the polymer exists between the valence band (VB) and the conduction band (CB) derived from π-conjugation, and the oxidation occurs at metal sites.

In the cyclic voltammograms of a dimer **13**$_2$ and a trimer **13**$_3$, the waves are broader compared with that of the monomer, although only a single oxidation peak is observed for the dimer and the trimer (Figure 4).[34] This discrepancy suggests that Co(III) and Co(IV) sites are weakly interacted and the mixed-valence states, [Co(III), Co(IV)], [Co(III), Co(IV), Co(III)] and [Co(IV), Co(III), Co(IV)], are generated within a narrow potential range. On the basis of computer simulation, the oxidation potentials are calculated to be $E^{0'}_1$ = -0.285 V and $E^{0'}_2$ = -0.212 V *vs.* ferrocenium/ferrocene (Fc$^+$/Fc) for the dimer, and $E^{0'}_1$ = -0.291 V, $E^{0'}_2$ = -0.248 V, and $E^{0'}_3$ = -0.189 V *vs.* Fc$^+$/Fc for the trimer. The $\Delta E^{0'}$ values indicate that the intereaction energy between ferrocene and ferrocenium sites, u_{OR} is estimated to be -2 kJ mol^{-1} based on the neighboring site intereaction model of Aoki and Chen,[46] and the value is about one-fifth compared with that for oligo(1,1'-dihexylferrocenylene)s.[47,48]

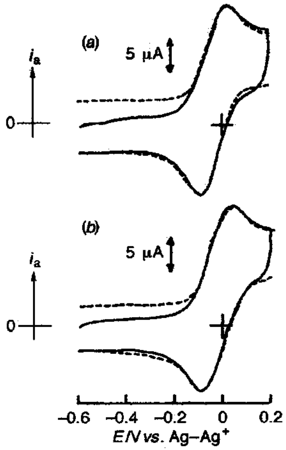


Figure 4. Cyclic voltammograms of compounds **13**$_2$(a) and **13**$_3$(b) at a glassy carbon electrode in 0.1 M NBu_4ClO_4-CH_2Cl_2 at a scan rate of 0.1 Vs^{-1}(full lines) and their simulation based on the open boundary finite-diffusion model(broken lines) . (Reprinted with permission from ref. 34)

The oxidation wave in the cyclic voltammograms of thenylene-bridged cobaltacyclopentadiene polymer, **11**, is fairly broader than that of the phenylene-bridged one.[35] This is because the energy level for the highest occupied π-orbital of thiophene is closer than that of phenylene to *d*-orbital level of the cobalt site, so that the internuclear electronic interaction through the thiophene ring is considered to be stronger. In the oxidation process, there are more than one oxidation wave due to the formation of mixed-valence states overlap, resulting in a broad wave in the cyclic voltammogram.

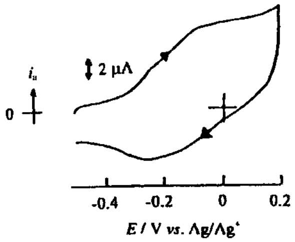


Figure 5. Cyclic voltammogram of a cobaltacyclopentadiene polymer complex, **11** at a glassy carbon electrode in 0.1 M NBu_4ClO_4-CH_2Cl_2 at a scan rate of 0.1 Vs^{-1}. (Reprinted with permission from ref. 35)

1-3. Electrical conductivity and photoconductivity

The cobaltacyclopentadiene polymers **4** and **7** show an electrical conductivity of 10^{-12} – 10^{-6} Scm^{-1} in the neutral form at room temperature.[33,49] When **7** was treated with I_2, the conductivity increased up to 10^{-4} Scm^{-1}.[33] This result could be interpreted by the consideration that I_2-doping generates Co(III)/Co(IV) mixed-valence states in the polymer chain; this state is stable to some extent as suggested by the electrochemical properties; and consequently, Co(III) and Co(IV) sites are interacted through a π-conjugated chain, causing the mixed-valence conductivity.

The intrinsic photoconductive property was found for a cobaltacyclopentadine polymer **6**.[32] Photo-response of i-V characteristics for ITO/**6**/ITO indicates that the polymer has a low conductivity in dark, and photocurrent is four 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.[50,51] 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 photo-activation of electrons from the valence band to the conduction band.

2. *Poly(arylene ruthenacylopentatrienylene)s*

2-1. Electronic spectra

UV-vis-NIR absorption spectra of the monomeric ruthenacyclopentatriene complex **17** and the ruthenacyclopentatriene polymer **16** in dichloromethane are displayed in Figure 6.[20] The bands of **17** at 256, 378, and 505 nm are shifted to 296, 400, and 525 nm, respectively, for **16**. These red shifts should be caused by the extension of the conjugated system for the polymer. However, the band at 694 nm remains unchanged between **16** and **17**. This can be ascribed to LMCT (carbene π → Ru *d*) at the ruthenacyclopentatriene unit.

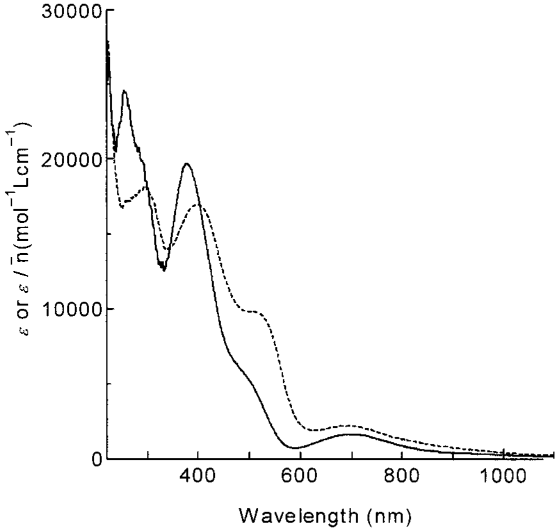


Figure 6. The UV-vis-NIR spectra of **17** (solid line) and **16** (dotted line). (Reprinted with permission from ref.[20])

2-2 Redox properties

Ruthenacyclopentadiene complexes undergo reversible 1e$^-$ reduction as shown in the cyclic voltammogram of **17**, indicating the role of ruthenacyclopentatriene as a good electron acceptor (Figure 7). This redox property is quite different from those of cobaltacyclopentadiene, for which the oxidation potential is 0–0.5 V vs. Fc$^+$/Fc, indicating that it functions as a fine electron donor.[32] The cyclic voltammogram of the polymer **16** in Figure 7 indicates that it also undergoes reversible 1e$^-$ reduction ascribed to the ruthenacyclopentatriene unit at $E^{0\prime}$ = –1.01 V for **16** and –1.03 V for **17** vs. Fc$^+$/Fc. The peak of **16** is broader than that of **17**, indicating an existence of electronic interaction between ruthenacycle units in **16**. The location of the modestly localized Ru-centered orbital between the π and π* orbitals of the conjugated chain is consistent with the electronic spectra as noted above.

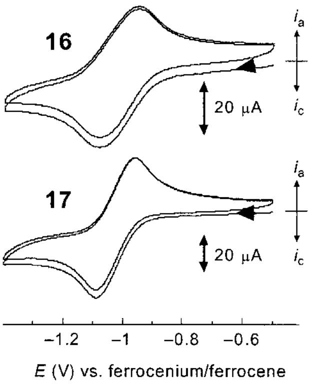


Figure 7. Cyclic voltammograms of **16** (top) and **17** (bottom) on a glassy carbon disk in 0.1 M Bu_4NClO_4-CH_2Cl_2 at a scan rate of 0.1 Vs^{-1}. (Reprinted with permission from ref.[20])

To evaluate the ability of the ruthenacycle to assist the interaction between the ferrocenyl moieties, cyclic voltammetry was carried out with the 2,5-diferrocenyl derivative, **15** in Bu_4NClO_4-dichloromethane, the result of which is shown in Figure 8.[39] A reversible reduction wave of the ruthenacycle was observed at -1.40 V vs. Fc$^+$/Fc (–1.18 V vs. Ag/Ag$^+$), and two quasi-reversible waves of the ferrocene moieties appear at -0.01 and 0.23 V vs. Fc$^+$/Fc. The separation of the oxidation waves by the ferrocenyl moieties in **15** indicates the existence of an interaction between the two ferrocene moieties. The difference in potential of the two waves, 0.24 V, is smaller than those for simple biferrocene (0.42 V) [52] and cobaltacyclopentadienyl-bridged complex **18** (0.47 V),[45] whereas the value is larger than those for most bis-ferrocenyl compounds with π-conjugated organic bridges, such as 1,2-diferrocenylethylene (0.17 V)[53] and 1,2-diferrocenylacetylene (0.13 V).[52]

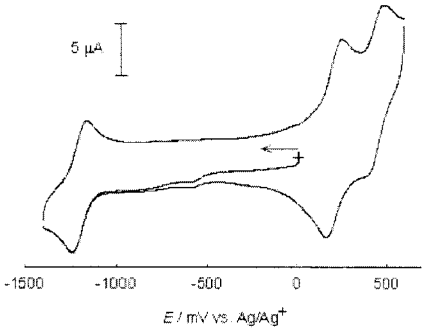


Figure 8. Cyclic voltammogram of **15** on a glassy carbon disk in 0.1 M Bu_4NClO_4-CH_2Cl_2 at a scan rate of 0.1 V s^{-1}. (Reprinted with permission from ref.[39])

To investigate the delocalization of electron in a mixed-valence state, **15** was oxidized with 1 eq of $[Fe(C_5H_4Cl)_2]PF_6$ [54] in dichloromethane, and the electronic spectrum was measured (Figure 9). In response to the oxidation, the absorption bands up to 800 nm were blue-shifted, and a new broad band, assignable to the intervalence-transfer between the Fe(II) and Fe(III) atoms, appeared in the near-IR region. Deconvolution of the spectrum into Gaussian functions revealed that the near-IR band was centered at 1180 nm (= 8484 cm^{-1}) with FWVH = 3840 cm^{-1}. Based on Marcus-Hush theory,[55] the mixing coefficient was calculated to be 0.06, which is smaller than or comparable to those for biferrocene (0.09),[52] 1,2-diferrocenylethylene (0.09),[53] and 1,2-diferrocenylacetylene (0.07).[52] From these measurements, the ruthenacyclopentatriene moiety of **15** is found to conduct significant electronic interaction between its 2- and 5-substituents like π-conjugated organic bridges, although the magnitude of this interaction appears to be smaller than that of the cobaltacyclopentadiene analogue **18**. One possible explanation for the larger internuclear interaction in **18** than in **15** is that the stronger donor ability of the cobaltacycle than the ruthenacycle enhances the hole transfer in the electron exchange between the ferrocenyl moieties. However, it may also be due to the difference in the π-conjugation on the carbon atoms.

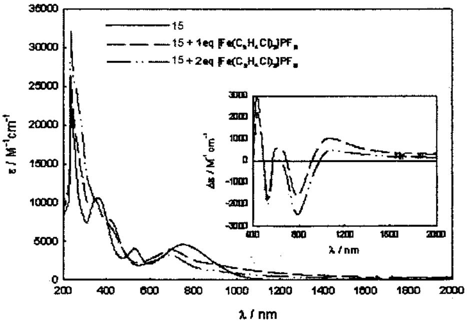
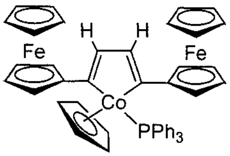


Figure 9. Electronic spectra of **15**. and its oxidized forms generated by addition of 1 eq and 2 eq. $[Fe(C_5H_4Cl)_2]PF_6$ in CH_2Cl_2. Inset: differences in the spectra of the oxidized forms from the spectrum of **15**. (Reprinted with permission from ref.[39])



18

2-3. Physical Properties in the Reduced State

It is interesting to see the magnetic interaction between Ru sites via π-conjugated linker in the reduced form of **16**. We investigated this interaction by comparing the EPR spectra between the reduced forms of **16** and **17**.[20] Reductions of **16** and **17** were carried out under vacuum by treatment with cobaltocene vapor. To confirm whether or not cobaltocene reduced **16** and **17** successfully, we measured the changes in the UV-vis-NIR spectra of **16** and **17** after adding cobaltocene. We found that the spectrum of **17** was recovered by using iodine vapor to reoxidize the reduced form of **17** (Figure 10). This indicates the reversibility of the chemical redox reaction. For the reduced form of **16**, 20% of spectrum **16** was recovered by oxidation with iodine at room temperature. The changes in the UV-vis-NIR spectra of **16** and **17** showed the same tendency; that is, the band at ca. 500 nm decreased, and the LMCT band at λ_{max} = 694 nm shifted to ca. 800 nm.

The EPR spectra of the reduced forms of **16** and **17** in frozen THF are displayed in Figure 11. The reduced form of **17** afforded axial symmetry with weak rhombic spectra ($g_{\perp}$ = 2.18, $g_{//}$ = 1.99). The spectra was similar to that of an S = 1/2 spin in a low-spin d^5 configuration of Ru(III).[56-58] Oxidation number of Ru in the reduced form of **17** is formally V because that in the ruthenacyclopentatriene is VI (carbene counted as dianion). Spin of the Ru in the reduced form of **17** in d^3 configuration is S = 1/2 because the strong ligand field and the low symmetry of the complex structure divides the d-orbitals into non-degenerated components. Instability of the reduced form of **17** as well as that of **16** makes difficult the measurement of magnetic susceptibility to confirm S. Hyperfine interaction with ^{99}Ru and ^{101}Ru isotopes (I = 5/2, 12.7% and 17%, respectively) was resolved in the spectra, especially for g_2 (a = 3 mT), indicating that the unpaired electron of the reduced form of **17** localizes in the ruthenacycle moiety and does not interact with other molecules. On the other hand, the EPR spectrum of the reduced form of **16** showed several peaks in a wide magnetic field and was completely different from that of **17**. If there is no interaction between Ru sites, the spectrum should be the same as that of **16**, and if there is antiferromagnetic interaction between Ru sites, the signals should diminish. However, neither occurred in this case. We attribute this inconsistency to the ferromagnetic interaction between Ru sites. The interaction was not inter-molecular but intra-molecular, because the concentration of the reduced form of **16** (0.03 mM, converted to ruthenacycle unit concentration) was much lower than that of **17** (0.27 mM). The signal at g = 2 was caused mainly by isolated spin in the ruthenacycle, but it should be the sum of this state and the triplet state, indicated by a signal at g = 4. Broad signals at 50, 205, 553, and 855 mT indicated interactions between more than two ruthenacyclopentatriene units.

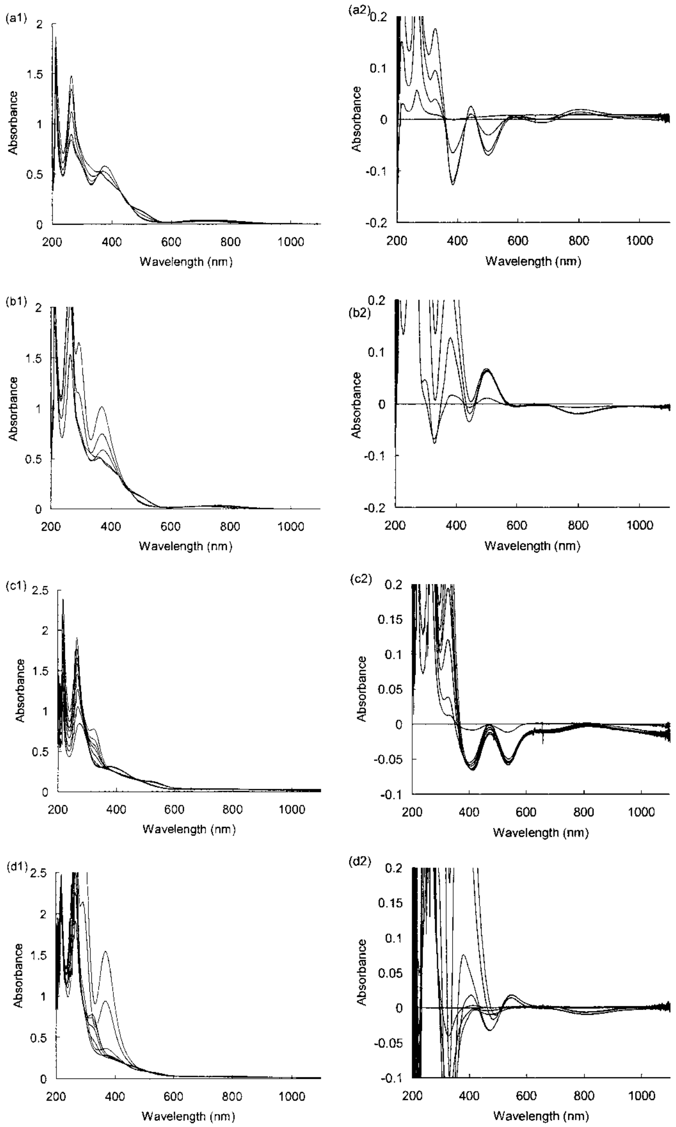


Figure 10. Changes of the UV-vis-NIR spectra with reduction and oxidation of **16** and **17**. Reduction of **17** and their oxidation, and reduction of **16** and their oxidation are displayed in (a1)-(d1) respectively. Differences in spectra of (a1)-(d1) from that of each initial state are displayed in (a2)-(d2) respectively. (Reprinted with permission from ref. 20)

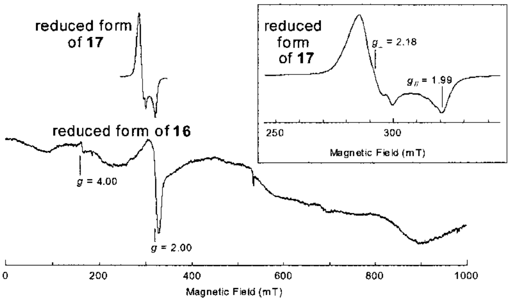


Figure 11. The EPR spectra of reduced forms of **17** (top) and **16** (bottom) at 4 K. Inset: enlarged view of EPR spectrum of reduced form of **17**. (Reprinted with permission from ref.[20])

Conclusion

The metallacyclization reaction using conjugated diacetylenes affords π-conjugated conducting organometallic polymers. Regioselectivity of the metallacyclization is important for the π-conjugation, and up to present, 80% of the regioselectivity has been achieved for the cobaltacylopentadiene polymers and 100% for the ruthenacyclopentatriene polymer. The oxidation of the cobalt center in the cobaltacyclopentadiene polymer occurs facilely and the location of the Co *d*-orbital between the conduction and valence bands brings intrinsic photoconductivity. The reduction of the ruthenium center in the ruthenacyclopentatriene polymer occurs facilely, and the ferromagnetic interaction between the ruthenium centers are observed in the reduced form. These results indicate the dominant role of metal centers in the synthesis and physical properties of π-conjugated metallacycle polymers. In other words, new properties and fuctions are expected by the development of new metallacycle polymers.

Acknowledgments

This work was supported in part by Grants-in-Aid for Scientific Research (Nos. 14044021 (area 412), 14204066) from the Ministry of Culture, Education, Science, Sports, and Technology, Japan, and by The 21st Century COE Program for Frontiers in Fundamental Chemistry.

[1] H. Nishihara, in *"Handbook of Organic Conductive Molecules and Polymers"*, H. S. Nalwa, Ed., Wiley, Weinheim 1997, Vol. 2, Chapter 19, pp. 799-832.
[2] H. S. Nalwa (Ed.), *"Handbook of Organic Conductive Molecules and Polymers"*, Wiley-VCH, Weinheim 1997.
[3] E. W. Neuse, *J. Macromol. Sci.-Chem.* **1981**, *A16*, 3.
[4] T. Yamamoto, K. Sanechika, A. Yamamoto, *Inorg. Chim. Acta* **1983**, *73*, 75.
[5] Y. Okamoto, M. C. Wang, *J. Polym. Sci., Polym. Let. Ed.* **1980**, *18*, 249.
[6] K. Krikor, M. Rotti, P. Nagles, *Synth. Met.* **1987**, *21*, 353.
[7] H. Matsuda, H. Nakanishi, M. Kato, *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 107.
[8] N. Hagihara, K. Sonogashira, S. Takahashi, *Adv. Polym. Sci.* **1980**, *41*, 159.
[9] M. S. Khan, S. J. Davies, A. K. Kakkar, D. Schwartz, B. Lin, B. F. D. Johnson, J. Lewis, *J. Organomet. Chem.* **1992**, *87*, 424.
[10] J. W. P. Lin, L. P. Dudek, *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1579.
[11] S. Venkatachalam, K. V. C. Rao, P. T. Manoharan, *Synth. Met.* **1988**, *26*, 237.
[12] T. Kuhlmann, S. Roth, J. Rozière, W. Siebert, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 105.
[13] R. A. Clark, K. S. Varma, A. E. Underhil, J. Becher, H. Toftlund, *Synth. Met.* **1988**, *25*, 227.
[14] J. R. Reynolds, F. E. Karasz, C. P. Lillya, J. C. W. Chien, *J. Chem. Soc., Chem. Commun.* **1985**, 268.
[15] R. Vincete, J. Ribas, P. Cassoux, L. Valade, *Synth. Met.* **1986**, *13*, 265.
[16] M. Altmann, U. H. F. Bunz, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 569.
[17] H. S. Nalwa, *Appl. Organometal. Chem.* **1990**, *4*, 91.
[18] A. Ohkubo, K. Aramaki, H. Nishihara, *Chem. Lett.* **1993**, 271.
[19] J. R. Nitschke, S. Zurcher S, T. D. Tilley, *J. Am. Chem. Soc.*, **2000**, *122*, 10345.
[20] M. Kurashina, M. Murata, T. Watanabe, and H. Nishihara, *J. Am. Chem. Soc.*, **2003**, *125*, 12420.
[21] H. Nishihara, M. Kurashina, M. Murata, *Macromolecular Symposia*, **2003**, *196*, 27.
[22] H. Yamazaki, N. Hagihara, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2260.
[23] Y. Wakatsuki, H.Yamazaki, *J. Chem. Soc., Chem. Commun.* **1973**, 280.
[24] Y. Wakatsuki, T. Kuramitsu, H. Yamazaki, *Tetrahedron Lett.* **1974**, 4549.
[25] H. Bönnenman, *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248.
[26] K. M. Nicholas, M. O. Nestle, D. Seyferth, in *"Transition Metal Organometallics in Organic Synthess"*, H. Alper Ed., Academic Press, New York, 1978, Vol. 2.
[27] Y. Wakatsuki, O. Nomura, K. Kitaura, K. Morokuma, H. Yamazaki, *J. Am. Chem. Soc.* **1983**, *105*, 1907.
[28] T. Shimura, A. Ohkubo, K. Aramaki, H. Uekusa, T. Fujita, S. Ohba, H. Nishihara, *Inorg. Chim. Acta* **1995**, *230*, 215.
[29] T. Fujita, H. Uekusa, A. Ohkubo, T. Shimura, K. Aramaki, H. Nishihara, S. Ohba, *Acta Cryst.* **1995**, *C51*, 2265.
[30] H. Nishihara, T. Shimura, A. Ohkubo, N. Matsuda, K. Aramaki, *Adv. Mater.* **1993**, *5*, 752.
[31] N. Matsuda, T. Shimura, K. Aramaki, H. Nishihara, *Synth. Metals* **1995**, *69*, 559.
[32] T. Shimura, A. Ohkubo, N. Matsuda, I. Matsuoka, K. Aramaki, H. Nishihara, *Chem. Mater.* **1996**, *8*, 1307.
[33] I. Matsuoka, K. Aramaki, H. Nishihara, *Mol. Cryst. Liq. Cryst.*, **1996**, *285*, 199.
[34] I. Matsuoka, K. Aramaki, H. Nishihara, *J. Chem. Soc., Dalton Trans.*, **1998**, 147.
[35] I. Matsuoka, H. Yoshikawa, M. Kurihara, H. Nishihara, *Synth. Metals* 1999, **102**, 1519.
[36] M. Murata, T. Hoshi, I. Matsuoka, T. Nankawa, M. Kurihara, H. Nishihara, *J. Inorg. Organomet. Polym.* **2000**, *10*, 209.
[37] M. O. Albers, D. J. A. deWaal, D. C. Lies, D. J. Robinson, E. Singleton, M. B. Wiege, *J. Chem. Soc., Chem. Commun.* **1986**, 1681.
[38] C. Ernst, O. Walter, E. Dinjus, S. Arzberger, H. Görls, *J. Pract. Chem.* **1999**, *8*, 341.
[39] Y. Yamada, J. Mizutani, M. Kurihara, H. Nishihara, *J. Organomet. Chem.* **2001**, *80-83*, 637.
[40] T. Naota, H. Takaya, S. Murahashi, *Chem. Rev.* **1998**, *98*, 2599.
[41] S. Nakahama, T. Nose, S. Akiyama, K. Sanui, Y. Tsujita, M. Doi, K. Horie, K. *Essential Koubunshi Kagaku*; Koudan-Sha: Tokyo, 2000; Chapter 3, 27.
[42] R. S. Kelly, W. E. Geiger, *Organometallics* **1987**, *6*, 1432.
[43] B. T. Donovan, W. E. Geiger, *J. Am. Chem. Soc.* **1988**, *110*, 2335.

[44] B. T. Donovan, W. E. Geiger, *Organometallics* **1990**, *9*, 865.
[45] A. Ohkubo, T. Fujita, S. Ohba, K. Aramaki, H. Nishihara, *J. Chem. Soc., Chem. Commun.* **1992**, 1553.
[46] K. Aoki, J. Chen, *J. Electroanal. Chem.*, **1995**, *380*, 35.
[47] T. Hirao, M. Kurashina, K. Aramaki, H. Nishihara, *J. Chem. Soc., Dalton Trans.*, **1996**, 2929.
[48] H. Nishihara, T. Hirao, K. Aramaki, K. Aoki, *Synth. Metals*, **1997**, *84*, 935.
[49] H. Nishihara, A. Ohkubo, K. Aramaki, *Synth. Metals*, **1993**, *55*, 821.
[50] K. Yoshino, S. Morita, T. Kawai, H. Araki, X. H. Yin, A. A. Zakhidov, *Synth. Met.* **1993**, *56*, 2991.
[51] N. S. Sariciftci, L. Smilowitz, D. Braun, G. Srdaniov, V. Srdanov, F. Wudl, A. J. Heeger, *Synth. Met.* **1993**, *56*, 3125.
[52] C. Lavenda, K. Bechgaard, D. O. Cowan, *J. Org. Chem.*, **1970**, *41*, 2700.
[53] A. C. Ribou, J. P. Launay, M. L. Sachtleben, H. Li, C. W. Spangler, *Inorg. Chem.*, **1996**, *35*, 3735.
[54] T. Hirao, K. Aramaki, H. Nishihara, *Bull. Chem. Soc. Jpn.*, **1998**, *71*, 1817.
[55] N. S. Hush, *Coord. Chem. Rev.*, **1985**, *64*, 135.
[56] A. Pramanik, N. Bag, G. K. Lahiri, A. Chakravorty, *J. Chem. Soc., Dalton Trans.* **1990**, 3823.
[57] A. Ceccanti, P. Diversi, G. Ingrosso, F. Laschi, A. Lucherini, S. Magagna, P. Zanello, *J. Organomet. Chem.* **1996**, *526*, 251.
[58] D. Bhattacharyya, S. Chkraborty, P. Munshi, G. K. Lahiri, *Polyhedron* **1999**, *18*, 2951.