Bull. Chem. Soc. Jpn., ***71***, *2351—2358 (1998)* 2351

Structure and Electrochemical Properties of Directly Bound Dinuclear Cobaltadithiolene Complexes. Substituent Effect on Reduction Potentials and Mixed-Valence States

Takeo Akiyama,* Masaki Amino, Tsutomu Saitou, Koutoku Utsunomiya, Ken-ichi Seki, Yoshiharu Ikoma, Masatsugu Kajitani, Toru Sugiyama, Kunio Shimizu, and Akira Sugimori*

Department of Chemistry, Faculty of Science and Technology, Sophia University,
Kioi-cho 7-1, Chiyoda-ku, Tokyo 102-8554

Engineering Research and Development Department, Yuki Gosei Kogyo Co., Ltd.,
Ochiai, Nishigo-machi, Iwaki, Fukushima 972-8316

(Received April 28, 1998)

The X-ray structures and electrochemical properties of the dinuclear cobaltadithiolene complexes, μ-(1,4-disubstituted 1,3-butadiene-1,2,3,4-tetrathiolato)-bis[(η^5-cyclopentadienyl)cobalt(III)], have been investigated. In the diphenyl derivative, two benzene rings in the same molecule are located face to face with the distance of 3.5 Å, while in the dimethyl derivative, two methyl groups are in remote positions. However, in the electrically neutral dinuclear complexes, there is no evidence for the intramolecular interaction between two aryl groups in solutions. Electrochemical and spectrochemical investigations revealed that in electrically neutral state, the interaction between two cobaltadithiolene moieties is small, while in monoanioic state it becomes greater. The Hammett's plot for $\Delta E^{\mathrm{r}}_{1/2}$ ($\Delta E^{\mathrm{r}}_{1/2} = E^{\mathrm{r}}_{1/2}(\mathrm{red.1}) - E^{\mathrm{r}}_{1/2}(\mathrm{red.2})$) shows that the electron-attracting substituents can stabilize the mixed-valence state, [Co(II)–Co(III)]$^-$. The smaller $\Delta E^{\mathrm{r}}_{1/2}$ values for the complexes having aryl substituents are due to the smaller interactions between the anioic and neutral moieties, because of the steric hindrance of aryl groups which inhibit the conjugation of the two cobaltadithiolene rings.

Recently, mixed-valence states derived from the interaction between two metal complex moieties attract much attention in relation to the increasing interest in the attempts to produce high temperature superconducting organometallic materials[1] and cooperative behavior of the metals in organometallic catalysts.[2] Such interactions have been studied in many systems including ferrocene derivatives,[3] bis(fulvalene)dimetal complexes,[4] heterodimetal fulvalene complexes,[5] bis(η^5-cyclopentadienyl)-metal(μ-cyclooctatetraene) complexes (metal = V, Cr),[6] bis(arene)chromium complexes,[7] triple-decker complexes,[8] butadiyne-bridged cyclopentadienyl-cyclobutadiene cobalt complexes[9] etc. by electrochemical methods.

However, most metal complexes studied have carbonyl, phosphine, or carbocyclic ligands, and no report has appeared concerning 1,2-ethenedithiolatometal complexes in which electrons are delocalized in the rings.

The metal–metal interactions have been discussed mainly in terms of the distances between metal centers[7] and in terms of the effects of spacer.[3c,3e] As our contribution to this area, we have preliminarily reported the intramolecular interaction of the two metal-complex-moieties in hetero bimetallic cobaltadithiolene complexes,[10] and the electrochemical behavior of mononuclear (η^5-cyclopentadienyl)(1,2-disubstituted 1,2-ethenedithiolato)cobalt(III) complexes by means of cyclic voltammetry.[11] Nishihara et al. studied the electrochemical behavior of a conjugated trinuclear cobaltadithiolene fused with a benzene ring and discussed the intramolecular interactions.[12]

We wish to report here that the electronic interaction between two cobaltadithiolene moieties bound directly is affected by both electronic and steric effects of the substituents in the metalladithiolene rings, on the basis of the first and the second reduction potentials and the difference of these two potentials ($\Delta E^{\mathrm{r}}_{1/2}$).

Experimental

General Procedures. All preparation procedures were performed under the atmosphere of argon. Solvents were purified by initial distillation from an appropriate drying agent. The separations and purifications of the complexes were carried out either by column chromatography on silica gel, followed by a recycle type-preparative gel permiation liquid chromatography (GPLC) (apparatus: Japan Analytical Industry Co., Ltd., LC-08 or LC-908; column: JAIGEL 1H+2H, connected type; solvent: chloroform) or by centrifugal chromatography (apparatus, Harrison Research Inc., Model 7924T) followed by a recycle preparative GPLC. The ^{1}H NMR spectra were measured in $CDCl_3$ with a JEOL JNM GX-270 (270 MHz) spectrometer using tetramethylsilane (TMS) as an internal standard. Mass spectra were obtained on a JEOL JMD-300 or on a JEOL SX-102A spectrometer. UV-vis spectra were recorded on a Hitachi U-3210 spectrophotometer. Elemental analyses were conducted on a Perkin–Elmer 240C, or 2400 elemental analyzers. All melting points were determined on a Yanaco melting point apparatus and were uncorrected.

Cyclic voltammograms were recorded on a Huso polarograph Model 312 equipped with a Riken Denshi X–Y recorder Model F-42 DG and a Huso potential scanning unit Model 321. All electrochemical measurements were carried out in dichloromethane solutions containing 0.1 mol dm^{-3} $(C_4H_9)_4NClO_4$ (Fulka) at 25 °C under a stream of argon by using three electrode system {platinum disk electrode embedded in glass (2 mm diameter) as a working electrode, a coiled Pt wire as a counter electrode, and Ag | 0.1 mol dm^{-3} $AgClO_4$ in acetonitrile as a reference electrode}.

X-Ray Structure. Crystals for X-ray analyses were obtained as described in the preparations. All measurements were made on a Rigaku AFC5S diffractometer with graphite monochromated Mo $K\alpha$ radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the ranges $20.29 < 2\theta < 24.92°$ (**1b**) and $20.67 < 2\theta < 24.97°$ (**1d**) corresponded to C-centered monoclinic cells with dimensions as given in Table 1. The final atomic positions and thermal parameters are given in Table 2.

The data were collected at a temperature of 23±1 °C using the ω–2θ scan technique to a maximum 2θ value of 55.0°.

Of the 2998 reflections which were collected, 2893 were unique (R_{int} = 0,056) (**1d**). Of the 2297 reflections which were collected, 2223 were unique (R_{int} = 0,019) (**1b**). The intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied.

The structures were solved by direct method (**1b**) or heavy-atom Patterson method (**1d**), and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included, but their positions were not refined; B values were refined. The final cycle of full-matrix-least-squares refinement was based on 1575 (**1b**) and 1167 (**1d**) observed reflections ($I > 3.00\sigma(I)$).

All of the calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.

The selected bond lengths and angles are listed in Table 3. Figure 1 shows ORTEP drawings of **1b** and **1d**. Full crystal data, H-atom coordinates, thermal parameters, $F_o - F_c$ tables, and remaining bond lengths and angles are deposited as Document No. 71049 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Preparation and Identification of Complexes. Most bis(cobaltadithiolene) complexes were prepared in one-pot reactions among 1,4-disubstituted 1,3-butadiynes, (η^5-cyclopentadienyl)dicarbonylcobalt(I) (abbreviated as $[(Cp)Co(CO)_2]$), and elemental sulfur. 1,4-Disubstituted butadiynes were synthesized by coupling reactions of appropriate monosubstituted acetylenes using copper(II) acetate as a catalyst, carried out in pyridine–methanol solutions unless otherwise noted.

μ-(1,3-Butadiene-1,2,3,4-tetrathiolato)-bis[(η^5-cyclopentadienyl)cobalt(III)] (1a). The compound was prepared from complex **1c** (described below) by the conversion of trimethylsilyl group to H by the reaction with tetrabutylammonium fluoride in a THF solution. To a benzene solution of the complex **1c** (0.2 g, 0.35 mmol in 50 cm^3) was added a THF solution of tetrabutylammonium fluoride ($(C_4H_9)_4NF$, Aldrich, GR grade) and the mixture was refluxed for 24 h. The reaction mixture was directly chromatographed on silica gel (Wakogel C-300, eluent: benzene) and the green fraction was collected. Further purification was performed on GPLC (eluent: $CHCl_3$). Green solid; ^1H NMR ($CDCl_3$) δ = 5.33 (10H, s, $Co(C_5H_5)$) and 9.29 (2H, s, vinyl H of $Co(S)_2(C{=}C{-}H)$ ring); MS (EI, 70 eV) *m*/*z* (rel intensity) 426 (M^+; 100), 393 ($M^+ - SH$; 3), 360 ($M^+ - (SH)_2$; 19), 327 ($M^+ - (SH)_3$; 4), 270 ($M^+ - Co(Cp)(S)$; 45), 189 ($Co(Cp)(S)_2H^+$; 24), 188 ($Co(Cp)(S)_2{}^+$; 10), and 124 ($Co(Cp)^+$; 8). Found: C, 38.43; H, 3.51%. Calcd for $C_{14}H_{12}S_4Co_2$: C, 39.44; H, 2.84%.

μ-(1,4-Dimethyl-1,3-butadiene-1,2,3,4-tetrathiolato)-bis[(η^5-cyclopentadienyl)cobalt(III)] (1b). This compound was prepared from 2,4-hexadiyne (Tokyo Kasei, EP grade, 0.36 g, 4.61 mmol), elemental sulfur (0.80 g, 3.13 mmol as S_8), and $[Co(Cp)(CO)_2)]$) (2.0 cm^3, 14.2 mmol) by the same procedure as described for **1c**

Table 1. Crystallografic Data for **1b** and **1d**

	1b	**1d**
Formula	$C_{16}H_{16}S_4Co_2$	$C_{26}H_{20}S_4Co_2$
Fw	454.41	578.55
Crystal size/mm	0.13 × 0.20 × 0.40	0.03 × 0.13 × 0.33
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c* (#15)	*C*2/*c* (#15)
a/Å	16.719(3)	15.590(6)
b/Å	9.571(2)	9.220(5)
c/Å	13.284(3)	16.545(5)
β/deg	121.117(9)	95.24(3)
V/Å^3	1819.8(5)	2368(1)
Z	4	4
D (calcd)/g cm^{-3}	1.658	1.622
Radiation, λ/Å	Mo $K\alpha$, 0.71069	Mo $K\alpha$, 0.71069
Scan speed/deg min^{-1}	6	6
2θ range/deg	55	55
μ/cm^{-1}	22.74	17.67
No. of obsd reflns	1575 ($IF > 3\sigma(F_o)$)	1167 ($IF > 3\sigma(F_o)$)
No. of variables	108	155
$R/\%^{a)}$	3.1	4.1
$R_w/\%^{b)}$	2.8	2.8

a) $R = \sum||F_o| - |F_c||/\sum|F_o|$. b) $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)]^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Paramters for Non-Hydrogen Atoms of Complex **1b** and **1d** with Estimated Standard Deviation in Parentheses

Atom	x	y	z	B_{eq} $^{a)}$/Å^2
1b				
Co(1)	0.25429(3)	0.09863(5)	−0.13691(4)	2.584(9)
S(1)	0.22197(6)	−0.05167(10)	−0.04796(8)	3.21(2)
S(2)	0.11069(6)	0.1358(10)	−0.25508(8)	3.20(2)
C(1)	0.1020(2)	−0.0618(3)	−0.1210(3)	2.26(7)
C(2)	0.0513(2)	0.0240(3)	−0.2149(3)	2.26(7)
C(3)	0.0590(3)	−0.1663(5)	−0.0776(4)	5.1(1)
C(4)	0.3204(3)	0.1655(8)	−0.2201(4)	8.0(2)
C(5)	0.3235(3)	0.2680(5)	−0.1464(5)	6.1(1)
C(6)	0.3686(3)	0.2196(6)	−0.0358(4)	5.5(1)
C(7)	0.3953(3)	0.0853(6)	−0.372(5)	6.7(1)
C(8)	0.3652(3)	0.0503(6)	−0.1513(6)	8.1(1)
C(2*)	−0.0513(2)	0.0240(3)	−0.2851(3)	2.26(7)
S(2*)	−0.0107(6)	0.13658(10)	−0.24492(8)	3.20(2)
C(1*)	−0.1020(2)	−0.0618(3)	−0.3790(3)	2.72(7)
Co(1*)	−0.25429(3)	0.09863(5)	−0.36309(4)	2.584(9)
S(1*)	−0.22197(6)	−0.05166(10)	−0.45204(8)	3.21(2)
C(3*)	−0.0590(3)	−0.1663(5)	−0.4224(4)	5.1(1)
C(4*)	−0.3204(3)	0.1655(8)	−0.2799(4)	8.0(2)
C(5*)	−0.3235(3)	0.2680(5)	−0.3536(5)	5.1(1)
C(6*)	−0.3686(3)	0.2169(6)	−0.4642(4)	5.5(1)
C(8*)	−0.3652(3)	0.0503(6)	−0.3487(6)	8.1(1)
C(7*)	−0.3953(3)	0.0853(6)	−0.4628(5)	10(1)
1d				
Co(1)	0.86936(5)	0.44223(9)	0.55851(5)	3.12(2)
S(1)	0.93493(9)	0.2420(2)	0.55744(9)	3.29(4)
S(2)	0.9905(3)	0.2240(6)	0.67951(9)	3.40(4)
C(1)	0.1020(2)	−0.0618(3)	0.6516(3)	2.3(1)
C(2)	0.9805(3)	0.3316(5)	0.7078(3)	2.2(1)
C(3)	1.0455(3)	0.0928(6)	0.6673(3)	2.4(1)
C(4)	1.0154(3)	−0.0437(7)	0.6450(3)	3.2(1)
C(5)	1.0644(4)	−0.1656(7)	0.6648(4)	4.3(2)
C(6)	1.1434(4)	−0.1536(7)	0.7065(4)	4.4(2)
C(7)	1.1763(4)	−0.0198(7)	0.7278(4)	4.1(2)
C(8)	1.1277(4)	0.1053(6)	0.7089(3)	3.1(1)
C(9)	0.7892(4)	0.6167(7)	0.5483(4)	4.3(2)
C(10)	0.7444(4)	0.4940(7)	0.5198(4)	4.5(2)
C(11)	0.7869(4)	0.4376(8)	0.4538(4)	4.4(2)
C(12)	0.8582(4)	0.5269(8)	0.4428(4)	4.4(2)
C(13)	0.8593(4)	0.6356(7)	0.5020(4)	4.3(2)
C(2*)	1.0195(3)	0.3316(5)	0.7922(3)	2.2(1)
S(2*)	1.08349(10)	0.4772(2)	0.82049(9)	3.40(4)
C(1*)	1.0095(3)	0.2240(6)	0.8484(3)	2.3(1)
Co(1*)	1.13064(5)	0.44223(9)	0.94149(5)	3.12(2)
S(1*)	1.06507(9)	0.2420(2)	0.94256(9)	3.29(4)
C(3*)	0.9545(3)	0.0928(6)	0.8327(3)	2.4(1)
C(9*)	1.2108(4)	0.6167(7)	0.9517(4)	4.3(2)
C(10*)	1.2556(4)	0.4940(7)	0.9802(4)	4.5(2)
C(11*)	1.2131(4)	0.4376(8)	1.0462(4)	4.4(2)
C(12*)	1.1418(4)	0.5269(8)	1.0572(4)	4.4(2)
C(13*)	1.1407(4)	0.6356(7)	0.9980(4)	4.3(2)
C(4*)	0.9846(3)	−0.0437(7)	0.8550(3)	3.2(1)
C(8*)	0.8723(4)	0.1053(6)	0.7911(3)	3.1(1)
C(5*)	0.9356(4)	−0.1656(7)	0.8352(4)	3.0(9)
C(7*)	0.8237(4)	−0.0198(7)	0.7722(4)	4.1(2)
C(6*)	0.8566(4)	−0.1536(7)	0.7935(4)	4.4(2)

a) $B_{i,j} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$.

(refluxed in xylene for 24 h). Separation of the complex was carried out by chromatography on silica gel (column, Wakogel C-300, 300 mesh; eluent: hexane–dichloromethane = 1/1, v/v) and centrifugal chromatography (eluent: hexane). Blue solid; 0.18 g (8.54%, based on 2,4-hexadiyne); ^{1}H NMR ($CDCl_3$) $\delta = 2.05$ (6H, s, CH_3) and 5.29 (10H, s, $Co(C_5H_5)$); MS (EI, 70 eV) *m*/*z* (rel intensity) 454 (M^+; 96), 298 ($M^+ - Co(Cp)S$; 100), 266 ($M^+ - Co(Cp)S_2$; 16), 188 ($Co(Cp)S_2{}^+$; 26), and 124 ($Co(Cp)^+$; 16). Found: C, 42.54; H, 3.65%. Calcd for $C_{16}H_{16}S_4Co_2$: C, 42.29; H, 3.55%.

μ-[1,4-Bis(trimethylsilyl)-1,3-butadiene-1,2,3,4-tetrathiolato]-bis[(η^5-cyclopentadienyl)cobalt(III)] (1c). In an argon-purged 300 cm^3 three-necked flask with a condenser and a gas-inlet tube (with a stop cock) was placed a xylene solution (40 cm^3) of 1,4-bis(trimethylsilyl)-1,3-butadiyne (Tokyo Kasei, G.R.; 0.97 g, 5 mmol). To the xylene solution were added 0.64 g of elemental sulfur and $[Co(Cp)(CO)_2)]$ (3 cm^3, 21.4 mmol) under stirring and the solution was refluxed for 48 h under a stream of argon. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Wakogel, C-300, 300 mesh, eluent: hexane–dichloromethane = 1 : 1, v/v) and further purification was done by an GPLC (eluent: $CHCl_3$). Blue solid; ^{1}H NMR ($CDCl_3$) $\delta = -0.11$ (18H, s, $Si(CH_3)_3$) and 5.30 (10H, s, C_5H_5); MS (EI, 70 eV) *m*/*z* (rel intensity) 570 (M^+; 100), 382 ($M^+ - Co(Cp)(S)_2$; 31), 189 ($Co(Cp)(S)_2{}^+$ +H; 45), 188 ($Co(Cp)(S)_2{}^+$; 43), and 124 ($Co(Cp)^+$; 4.7). HRMS, M^+: 569.9275 (0.2%). Found: C, 41.84; H, 4.97%. Calcd for $C_{20}H_{28}S_4Si_2Co_2$: C, 42.09; H, 4.95%.

μ-(1,4-Diphenyl-1,3-butadiene-1,2,3,4-tetrathiolato)-bis[(η^5-cyclopentadienyl)cobalt(III)] (1d). This compound was prepared from 1,4-diphenyl-1,3-butadiyne (0.8 g, 3.96 mmol), elemental sulfur (0.1 g), and $[Co(Cp)(CO)_2]$ (0.5 cm^3, 3.56 mmol) by the same procedure as used for complex **1c**. Blue-violet solid. Yield: 0.038 g (1.7% based on 1,4-diphenylbutadiyne). ^{1}H NMR ($CDCl_3$) $\delta = 5.33$ (10H, s, C_5H_5), 6.32 (4H, d, $J = 7.33$ Hz, H_3, H_5 of phenyl), 6.76 (4H, t, $J = 7.33$ Hz, H_2, H_6 of phenyl), and 6.96 (2H, t, $J = 7.33$ Hz, H_4 of phenyl); MS (EI, 70 eV) *m*/*z* (rel intensity) 578 (M^+; 59), 422 ($M^+ - Co(Cp)(S)$; 100), 390 ($M^+ - Co(Cp)(S)_2$; 38), and 266 ($M^+ - 2Co(Cp)(S)_2$; 27). Found: C, 53.74; H, 3.50%. Calcd for $C_{26}H_{20}S_4Co_2$: C, 53.98; H, 3.48%.

1,4-Bis(4-acetylphenyl)-1,3-butadiyne. This compound was prepared by the acetylation of phenyl groups on 1,4-diphenyl-1,3-butadiyne, of which two carbon–carbon triple bonds were protected by two hexacarbonyldicobalt units as described in the literature.[13)]

The dichloromethane solution (70 cm^3) of bis(hexacarbonyldicobalt) complex of 1,4-diphenyl-1,3-butadiene (2.92 g, 3.77 mmol) was added dropwise to the dichloromethane solution (70 cm^3) of $AlCl_3$ (2.52 g, 18.85 mmol) and acetyl chloride (1.34 cm^3, 18.9 mmol) and the mixed solution was stirred at room temperature for 30 min under a stream of argon. The reaction mixture was washed with 200 cm^3 of water and the water layer was extracted three times with dichloromethane. The combined dichloromethane solution was dried and was concentrated under reduced pressure. The residue was chromatographed on alumina (Merck, Aluminium oxide 90). Yield 2.66 g (82%).

To the acetone solution (100 cm^3) of bis(hexacarbonyldicobalt) complex of 1,4-bis(4-acetylphenyl)-1,3-butadiyne[13)] (2.4 g, 2.8 mmol) was added cerium(IV) ammonoum nitrate (CAN) (9.3 g, 16.9 mmol) and this mixture was stirred for 2 h. The color of the solution changed from dark-brown to orange. After the reaction, the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and this solution was washed with water and then the water layer was extracted with dichloromethane. Pale green crytalline solid was obtained after removal of the solvent. Yield 0.51 g (64%).

μ-[1,4-Bis(4-acetylphenyl)-1,3-butadiene-1,2,3,4-tetrathiolato]-bis[(η^5-cyclopentadienyl)cobalt(III)] (1e). This complex was prepared from 1,4-bis(4-acetylphenyl)-1,3-butadiyne (0.28 g, 1.0 mmol) elemental sulfur (0.13 g, 0.51 mmol), and $[Co(Cp)(CO)_2]$ (0.51 cm^3, 3.55 mmol) by the same procedure (refluxed in xylene for 48 h) described for **1c**. The separation and purification were done by column chromatography (Wakogel C-300, eluent: dichloromethane) and centrifugal chromatography (eluent: dichloromethane). Blue solid; Yield: 0.12 g (18% based on 1,4-di(4-acetyl)-1,3-butadiyne). ^{1}H NMR ($CDCl_3$) $\delta = 2.49$ (6H, s, CH_3), 5.41 (10H, s, C_5H_5), 6.38 (4H, d, H_2, H_6 of 4-acetylphenyl), and 7.34 (4H, d, H_3, H_5 of 4-acetylphenyl); MS (EI, 70 eV), *m*/*z* (rel intensitry), 662 (M^+; 6.4), 530 ($M^+ - 132$; 7.6), 506 ($M^+ - Co(Cp)S$; 9.0), 474 ($M^+ - Co(Cp)S_2$; 19.6), 188 ($Co(Cp)S_2{}^+$; 62.1), 124 ($Co(Cp)^+$; 13.6), 66 (100). Found: C, 54.36; H, 3.66%. Calcd for $C_{30}H_{24}S_4Co_2$: C, 54.38; H, 3.65%.

μ-[1,4-Bis(4-nitrophenyl)-1,3-butadiene-1,2,3,4-tetrathiolato]-bis[(η^5-cyclopentadienyl)cobalt(III)] (1f). The compound was prepared from 1,4-bis(4-nitropheny)butadiyne (0.1 g, 0.34 mmol), elemental sulfur (0.2 g), and $[Co(Cp)(CO)_2]$ (0.5 cm^3, 3.56 mmol) by the same procedure as described above. Separation was performed on silica-gel chromatography (Wakogel C-300, eluent: hexane/dichloromethane = 1 : 1, v/v). Blue-violet solid. Yield: 0.15 g {66% based on 1,4-bis(4-nitrophenyl)butadiyne}. ^{1}H NMR ($CDCl_3$) $\delta = 5.45$ (5H, s, C_5H_5), 6.45 (2H, d, $J = 8.8$ Hz, H_α of 4-nitrophenyl), and 7.64 (2H, d, $J = 8.8$ Hz, H_β of 4-nitrophenyl); MS (EI, 70 eV) *m*/*z* (rel intensity) 668 (M^+; 90.8), 512 ($M^+ - Co(Cp)(S)$; 84.2), 482 ($M^+ - Co(Cp)(S)_2$; 35.3), and 188 ($Co(Cp)(S)_2{}^+$; 100). Found: C, 46.78; H, 2.70; N, 4.20%. Calcd for $C_{26}H_{18}N_2O_4S_4Co_2$: C, 46.71; H, 2.71; N, 4.19%.

[(η^5-Cyclopentadienyl)(1,2-ethylenedithiolato)cobalt(III)] (2a). This compound was obtained as a by-product of the complex **2c**. Violet needle; ^{1}H NMR ($CDCl_3$) $\delta = 5.30$ (5H, s, $Co(C_5H_5)$) and 8.73 (2H, s, vinyl H of $CoS_2C_2H_2$ ring); MS (EI, 70 eV) *m*/*z* (rel intensity) 214 (M^+; 100), 188 ($Co(Cp)(S)_2{}^+$; 100), and 124 ($Co(Cp)^+$; 42). Found: C, 38.92; H, 3.35%. Calcd for $C_7H_7S_2Co$: C, 39.25; H, 3.29%.

[(η^5-Cyclopentadienyl)(1-trimethylsilyl-1,2-ethylenedithiolato)cobalt(III)] (2c). This compound was prepared from trimethylsilylacetylene (Tokyo Kasei, G.R.; 5.0 g, 51 mmol), elemental sulfur (1.7 g), and $[Co(Cp)(CO)_2]$ (7 cm^3, 50 mmol) in xylene solution (40 cm^3) by refluxing for 48 h under a stream of argon. The solvent was removed under reduced pressure. The separation and purification procedures are similar to the those described for **1c**. From the first fraction was obtained **2c** and from the second fraction was obtained **2a**. Violet needle; ^{1}H NMR ($CDCl_3$) $\delta = 0.33$ (9H, s, $Si(CH_3)_3$), 5.37 (5H, s, C_5H_5), and 8.81 (1H, s, vinyl H of $Co(S)_2(Me_3Si{-}C{=}C{-}H)$); MS (EI, 70 eV) *m*/*z* (rel intensity) 286 (M^+; 100), 271 ($M^+ - CH_3$; 33), 188 ($Co(Cp)(CO)_2{}^+$; 71), and 124 ($Co(Cp)^+$; 17). Found: C, 41.25; H, 5.16%. Calcd for $C_{10}H_{15}S_2SiCo$: C, 41.94; H, 5.28%.

[(η^5-Cyclopentadienyl){1-(4-nitrophenyl)-1,2-ethylenedithiolato}cobalt(III)] (2f). The compound was prepared from 4-nitrophenylacetylene (0.6 g, 4.1 mmol), elemental sulfur (0.2 g), and $[Co(Cp)(CO)_2]$ (0.5 cm^3, 3.56 mmol) was refluxed for 24 h in a xylene solution (50 cm^3). Separation was done by chromatography on silica gel (Wakogel C-300, eluent: hexane/dichloromethane = 1/1—1/3, v/v). Yield: 7.6 mg (0.5%). ^{1}H NMR ($CDCl_3$) $\delta = 5.44$ (5H, s, $Co(C_5H_5)$), 7.96 (2H, d, $J = 8.8$ Hz, H_3, and H_5 of 4-nitrophenyl), and 8,18 (2H, d, $J = 8.8$ Hz, H_2 and H_6 of 4-nitrophenyl), and 9.10 (1H, s, vinyl H of $CoS_2(NO_2{-}C_6H_4{-}C{=}C{-}H)$

ring); MS (EI, 70 eV) *m*/*z* (rel intensity) 335 (M^+; 57.8), 188 (Co-(Cp)$(S)_2{}^+$; 100). Found: C, 47.98; H, 2.95; N, 4.76. Calcd for $C_{13}H_{10}NO_2S_2Co$: C, 46.56; H, 2.98; N, 4.18%.

Results and Discussion

The dinuclear and the corresponding mononuclear cobaltadithiolene complexes used in this study are shown in Chart 1.

Structure. The ORTEP drawings of X-ray structures of dimethyl (**1b**) and diphenyl derivative (**1d**) are shown in Fig. 1. Selected bond lengths, bond angles, torsion angles, and dihedral angles of **1b** and **1d** are listed in Table 3, together with those of a mononuclear (η^5-cyclopentadienyl)(1,2-diphenyl-1,2-ethenedithiolato)cobalt(III) (**3**).[14]

The bond lengths and bond angles of the cobaltadithiolene rings in **1b**, **1d**, and **3** are very similar. There are only slight structural differences between mononuclear and dinuclear complexes and between dimethyl and diphenyl derivatives of the dinuclear complexes.

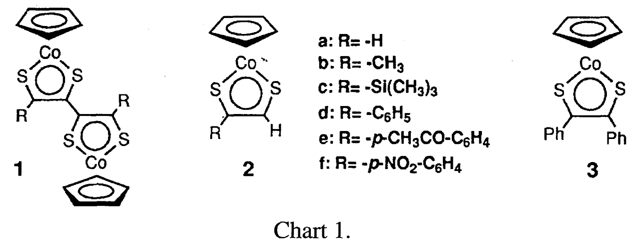


Chart 1.

Table 3. Selected Bond Lengths (Å) and Bond, Dihedral, and Tortion Angles (deg) of Bimetallic and Monometallic Cobaltadithiolene Complexes (**1b**, **1d**, and **3**[13])

	1b	**1d**	**3**[13]
Bond length			
Co(1)–S(1)	2.102(1)	2.111(2)	2.110(4)
Co(1)–S(2)	2.1129(9)	2.093(2)	2.098(4)
S(1)–C(1)	1.721(3)	1.720(5)	1.75(1)
S(2)–C(2)	1.727(3)	1.712(5)	1.73(1)
C(1)–C(2)	1.362(4)	1.377(7)	1.35(2)
Cp–Co[a]	1.662	1.657	1.6392
Bond angle			
S(1)–Co(1)–S(2)	90.68(4)	90.83(4)	91.0(2)
Co(1)–S(1)–C(1)	106.6(1)	106.3(2)	105.5(4)
Co(1)–S(2)–C(2)	106.1(1)	106.6(2)	106.7(5)
C(1)–C(2)–S(2)	118.3(2)	118.6(4)	118(1)
C(2)–C(1)–S(1)	118.4(2)	117.6(4)	118.6(9)
Dihedral angles			
Cp-dithiolene	91.63	92.08	88.91
Tortion angles			
C(1)–C(2)–C(2*)–C(1*)	87.3(6)	56(1)	
S(2)–C(2)–C(2*)–S(2*)	89.9(4)	58.4(7)	

a) Distance between Co and the center of pentagonal Cp.

Table 4. Characteristic Visible Absorption of Mononuclear and Dinuclear Cobaltadithiolene Complexes in Dichloromethane Solutions

Substituent	Absoption maxima/nm		Shift
	Dinuclear	Mononuclear	$\Delta\lambda_{max}$/nm
a (R = H)	643	550	93
b (R = $-CH_3$)	598	566	32
c (R = $-Si(CH_3)_3$)	586	556	30
d (R = $-C_6H_5$)	628	592	36
e (R = $-p$-CH_3CO–C_6H_4–)	620	—	—
f (R = $-p$-NO_2–C_6H_4–)	618	589	29

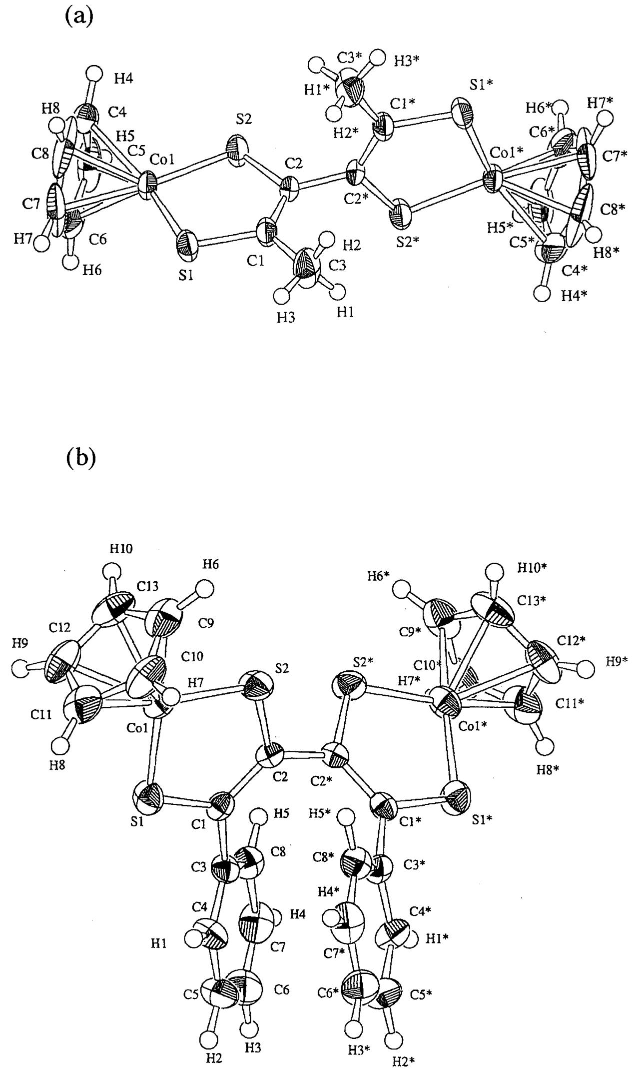


Fig. 1. ORTEP drawings of dinuclear cobaltadithiolene complexes, (a) **1b** and (b) **1d**.

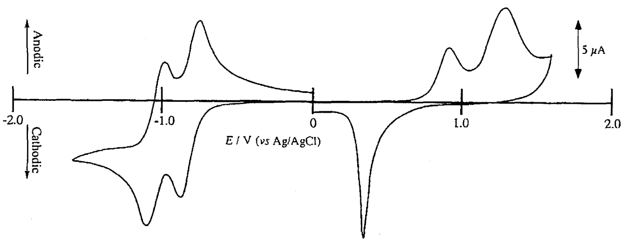


Fig. 2. Cyclic voltammogram of **1b** in a dichloromethane solution at 25 °C (scan rate, 100 mV s^{-1}).

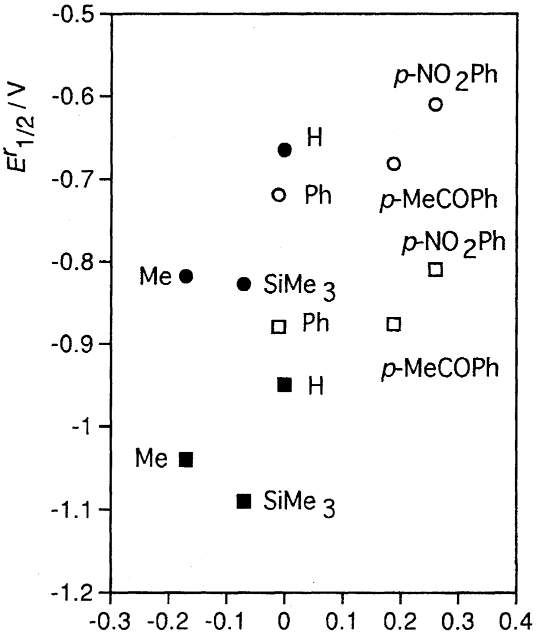


Fig. 3. Hammett's plots for $E^r_{1/2}$(red.1) and $E^r_{1/2}$(red.2). $E^r_{1/2}$(red.1): ○, **1** having aryl substituent; ●, **1** having non-aryl substituent. $E^r_{1/2}$(red.2): □, **1** having aryl substituent; ■, **1** having non-aryl substituent.

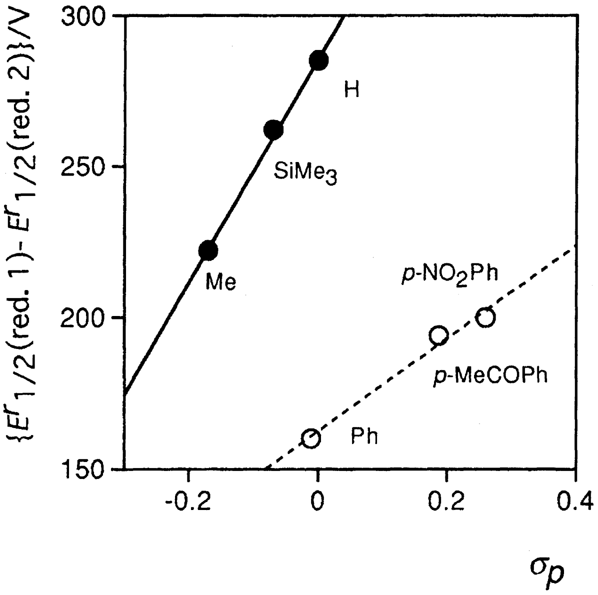


Fig. 4. Hammett's plots for $\Delta E^r_{1/2}$ (= $E^r_{1/2}$(red.1) − $E^r_{1/2}$(red.2)). ○, **1** having aryl substituent; ●, **1** having non-aryl substituent.

A remarkable difference in the crystal structures of dinuclear dimethyl (**1b**) and dinuclear diphenyl derivative (**1d**) is the conformation of the substituents: In the diphenyl derivative, two phenyl groups are situated face-to-face in a distance of 3.5 Å, while in the dimethyl derivative, two methyl groups are situated at the remote positions.[15] The distance between two phenyl groups in **1d** suggests a π–π interactions between two phenyl groups in the crystals.

However, the intramolecular π–π interaction between two aryl groups is not significant in solutions. In the ^{1}H NMR spectra, the protons of the 2- and the 6-positions, and the 3- and the 5-positions of 4-nitrophenyl and 4-acetylphenyl groups (in **1e** and **1f**) are equivalent. This result suggests that these aryl groups can, at least, rotate freely along the C–C bond in a solution at room temperature.

The torsion angles of C(1)–C(2)–C(2)*–C(1)* which can be a measure of the coplanarity between two cobaltadithiolene rings in dinuclear complexes are 87.3° and 56° for **1b** and **1d**, respectively. It indicates that the conjugation between two cobaltadithiolene rings is incomplete at least

Table 5. Reduction Half-Wave Potentials[a] of the Bimetallic Complexes (**1a**—**1f**) and Corresponding Monometallic Complexes (**2a**, **2c**, **2d**, and **2f**)

Complex	$E^r_{1/2}$(red.1) V	$E^a_p - E^c_p$ mV	$E^r_{1/2}$(red.2) V	$E^a_p - E^c_p$ mV	$\Delta E^r_{1/2}$ mV
1a (R = –H)	−0.665	95	−0.950	100	285
1b (R = –CH$_3$)	−0.818	84	−1.040	85	222
1c (R = –Si(CH$_3$)$_3$)	−0.828	90	−1.090	100	262
1d (R = –C$_6$H$_5$)[b]	−0.720	80	−0.880	70	160
1e (R = –p-CH$_3$CO–C$_6$H$_4$)	−0.682	70	−0.876	72	194
1f (R = –p-NO$_2$–C$_6$H$_4$)[b]	−0.610	90	−0.810	73	200
2a (R = –H)	−0.790	110	—	—	—
2c (R = –Si(CH$_3$)$_3$)	−0.810	100	—	—	—
2d (R = –C$_6$H$_5$)	−0.760	310	—	—	—
2f (R = –p-NO$_2$-C$_6$H$_4$)	−0.630	104	—	—	—

a) Half-wave reduction potentials were obtained from cyclic voltammograms measured in CH$_2$Cl$_2$ (25 °C; Scan rate = 100 mV s^{-1}). The peak differences ($|E^a_p - E^c_p|$) of the first and the second reduction waves of **1** appear to be larger (70—110 mV) than the theoretical reversible process (60—70 mV), but they are comparable to those of ferrocene in the same system as an internal standard. A similar results in the same solvent were obtained by Cowan et al.[3g] b) Potentials are obtained by normal pulse voltammograms.

within such electrically neutral dinuclear cobaltadithiolene complexes (in the oxidation state of Co(III)–Co(III)).

The UV-visible absorption spectra would give information on the conjugation between two cobaltadithiolene rings. The spectral shapes of **1** are similar to those of the corresponding mononuclear complexes **2**, but the shifts of absorptions are observed. The λ_{max} values of the characteristic absorptions in the visible region (550—650 nm) of complexes **1** and **2** are listed in Table 4. These absorptions have been assigned to the π–π^* transition of the metalladithiolene ring.[16)] The band is diminished when the ring loses aromaticity by forming 1 : 1 adduct with quadricyclane, dimethyl acetylenedicarboxylate, trimethyl phosphite, or alkylidene or when it is reduced by an electron.[17)] The π–π^* absorption bands of **1b**, **1c**, **1d**, and **1f** appear at about 30 nm longer wavelength region than those of the corresponding mononuclear complexes **2**. The shifts in the complexes having non-aryl substituents (**1b-2b**, **1c-2c**) are similar to those having aryl substituents (**1d-2d**, **1f-2f**). This suggests that the two aryl groups in the complexes having aryl substituents slightly interact with each other in solutions.

The complex having hydrogen in the cobaltadithiolene ring (**1a** and **2a**) is an exception. The shift of π–π^* absorption from mononuclear to dinuclear complexes is 93 nm, much larger than those of the other complexes. This shows the larger conjugation in **1a**, because of less steric hindrance.

Electrochemical Property. A typical cyclic voltammogram of bimetallic complex (**1a**) is shown in Fig. 2. The cyclic voltammograms (CV) of the dinuclear complexes (**1**) show two reversible reduction waves in the region of -0.6—-1.1 V, which are ascribed to the reduction of Co(III) to Co(II), and two irreversible oxidation waves in the region of 0.8—1.2 V, which are ascribed to the oxidation[11)] of cobaltadithiolene moiety. The cyclic voltammogram of the mononuclear complexes **2**, show only one reversible reduction wave ascribed to Co(III)/Co(II) and one irreversible oxidation wave.

The reversible half-wave reduction potentials of the complexes **1a**—**1f** and their corresponding mononuclear complexes **2a**, **2c**, **2d**, and **2f** are summarized in Table 5. The values of $E^{\mathrm{r}}_{1/2}$(red.1) and $E^{\mathrm{r}}_{1/2}$(red.2) are plotted against Hammett's σ_{p},[18)] in Fig. 3.

The data in Table 5 and Fig. 3 show the following tendencies: (1) the first reduction half-wave potentials ($E^{\mathrm{r}}_{1/2}$(red.1)) of **1** are similar to those of the corresponding mononuclear complexes **2** except **1a** and (2) both $E^{\mathrm{r}}_{1/2}$(red.1) and $E^{\mathrm{r}}_{1/2}$(red.2) of **1** shift to more positive side as the substituent becomes more electron-attracting, although the plots are dispersed.

The first feature can be explained by the small conjugation of two cobaltadithiolene rings due to the non-coplanar configurations of the two cobaltadithiolene rings as discussed earlier. At least at the first reduction, a cobaltadithiolene ring behaves independently on the other cobaltadithiolene ring. The large difference between $E^{\mathrm{r}}_{1/2}$(red.1) of **1a** and that of **2a** can be ascribed to the larger electronic interaction between two cobaltadithiolene rings in **1a** due to the small steric hindrance of hydrogen, as discussed earlier.

In the Hammett's plot of $E^{\mathrm{r}}_{1/2}$(red.1) and $E^{\mathrm{r}}_{1/2}$(red.2) (Fig. 3), we can not recognize any notable difference between the complexes having non-aryl substituents and the complexes having aryl substituents. This may reflect the fact that the intramolecular interactions between two aryl groups does not play an important role in a solution.

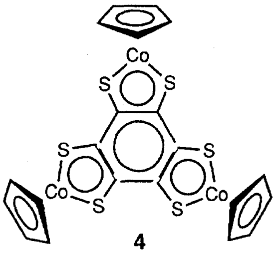
The fact that we observe two separate reduction waves shows that two cobaltadithiolene rings come to interact with each other more strongly when one cobaltadithiolene ring is reduced. The mixed-valence states (half reduced states) are stabilized.

The magnitude of $\Delta E^{\mathrm{r}}_{1/2}$ values ($= E^{\mathrm{r}}_{1/2}$(red.1) $-$ $E^{\mathrm{r}}_{1/2}$(red.2)) in dinuclear complexes has been the subject of discussion on the delocalization of valence electron,[3,4,7)] i.e. the value reflects the stability of mixed-valence state in dinuclear systems. In the case of (arene)chromoium tricarbonyl derivatives, both the distance between the two metal complex moieties and the π-system connecting the two metal complex moieties play important roles on the magnitude of $\Delta E^{\mathrm{r}}_{1/2}$ value.[7c)]

In the study on trinuclear cobaltadithiolene complex (**4**) (Chart 2), Nishihara et al.[12)] observed reversible three step reduction and intervalence transfer absorption in one- and two-electron reduction products. The reduction potentials of **4** are -1.06, -1.30, and -1.74 V in a THF solution in the presence of $\mathrm{Bu_4NClO_4}$ as a supporting electrolyte. It will be interesting to compare the results by Nishihara et al.,[12)] which were done in a planar system, with our results, which were obtained in a flexible system.

The difference in the first and second reduction potentials for **4** is 0.24 V and that for **1a** is 0.285 V. This suggests that the intervalence interaction in **1a** is larger than that in **4**, although the conjugation between two cobaltadithiolene moieties in the flexible systems is expected to be smaller than that in a rigid coplanar system. We do not yet have any satisfactory explanation for the observation.

Although there is no clear difference between aryl substituted and non-aryl substituted complexes in the Hammett's plots of $E^{\mathrm{r}}_{1/2}$(red.1) and $E^{\mathrm{r}}_{1/2}$(red.2) (Fig. 3), the plots of $\Delta E^{\mathrm{r}}_{1/2}$ versus σ_{p} (Fig. 4) show two different linear relationships: One is for the complexes having non-aryl substituents and the other is for the complexes having aryl substituents. We can see a tendency that the dinuclear cobaltadithiolene complexes having non-aryl substituents show larger $\Delta E^{\mathrm{r}}_{1/2}$



4

Chart 2.

and stronger dependence on σ_p values, while the complexes having aryl substituents show smaller $\Delta E^\mathrm{r}_{1/2}$ and weaker dependence on σ_p values. This suggests that in monoanioic states the conjugation becomes more important for the stabilization than in electrically neutral states and the inhibition of the conjugation by more bulky aryl groups may cause the decrease in $\Delta E^\mathrm{r}_{1/2}$ values.

The mixed-valence state of the anionic dinuclear cobaltadithiolene complexes is stabilized by the delocalization of an extra-electron in the two bound cobaltadithiolene rings. The electron-attracting substituents would contribute to the stabilization of the mono-anioic complex. The smaller substituent effects in aryl substituted dinuclear cobaltadithiolene complexes would be due to the smaller interactions between anionic and neutral cobaltadithiolene moieties because of larger steric hindrance.

The study was supported by Grants-in-Aid for Scientific Research Nos. 09440247 and 09640673 and Grants-in-Aid on Priority Area-Researches on "Interelement" No. 09239246 from the Ministry of Education, Science, Sports and Culture. We thank to Mr. Masahiro Shinkai of TDK, Co., Ltd. for the MM-2 calculation (CAChe system) of the complexes and to Dr Shozo Masuda of Science University of Tokyo for his helpful discussions on Hammett's substituent constants.

References

1) a) J.-P. Launay, S. Woitellier, M. Sowinska, M. Tourrel, and C. Joachim, in "Molecular Electronic Devices," ed by F. L. Carter, R. E. Siatkowski, and H. Wohltjen, Elservier Science Publishers, Amsterdam (1988), pp. 171—185; b) P. Jutzi, U. Siemeling, A. Müller, and H. Bögge, *Organometallics*, **8**, 1744 (1989); c) M.-T. Lee, B. M. Foxman, and M. Rosenblum, *Organometallics*, **4**, 539 (1985).

2) a) J. W. Park, P. B. Mackenzie, W. P. Schaefer, and R. H. Grubbs, *J. Am. Chem. Soc.*, **108**, 6402 (1986); b) F. Ozawa, J. W. Park, P. B. Mackenzie, L. M. Henling, and R. H. Grubbs, *J. Am. Chem. Soc.*, **111**, 1319 (1989); c) M. Darensburg, R. Silva, J. Reibenspies, and C. K. Prout, *Organometallics*, **8**, 1315 (1989); d) G. Süss-Fink, *Angew. Chem., Int. Ed. Engl.*, **33**, 67 (1994).

3) a) C. LeVanda, K. Bechgaard, D. O. Cowan, T. U. Mueller-Westerhoff, P. Eilbracht, G. Candela, and R. L. Collins, *J. Am. Chem. Soc.*, **98**, 3181 (1976); b) C. LeVanda, K. Bechgaard, and D. O. Cowan, *J. Org. Chem.*, **41**, 2700 (1976); c) E. E. Bunel, P. Campos, P. Ruz, L. Valle, I. Chadwick, M. S. Ana, G. Gonzalez, and J. M. Manriquez, *Organometallics*, **7**, 474 (1988); d) H. Atzkern, B. Huber, F. H. Köhler, G. Müller, and R. Müller, *Organometallics*, **10**, 238 (1991); e) For [Fe(Cp)(CO)$_2$] derivatives: R. Chukwu, A. D. Hunter, B. D. Santarsiero, S. G. Bott, J. L. Atwood, and J. Chassaignac, *Organometallics*, **11**, 589 (1992); f) D. O. Cowan, P. Shu, F. L. Hedberg, M. Rossi, and T. J. Kistenmacher, *J. Am. Chem. Soc.*, **101**, 1304 (1979); g) D. C. O'Connor-Salazar and D. O. Cowan, *J. Organomet. Chem.*, **408**, 227 (1991).

4) a) R. Moulton, T. W. Weidman, K. P. C. Vollhardt, and A. J. Bard, *Inorg. Chem.*, **25**, 1846 (1986); b) M.-H. Delville-Desbois, D. S. Brown, K. P. C. Vollhardt, and D. Astruc, *J. Chem. Soc., Chem. Commun.*, **1991**, 1355.

5) D. Obendorf, H. Schottenberger, and C. Rieker, *Organometallics*, **10**, 1293 (1991).

6) B. Bachmann, F. Hahn, J. Heck, and M. Wünsch, *Organometallics*, **8**, 2523 (1989).

7) a) N. Van Order, Jr., W. E. Geiger, T. E. Bitterwolf, and A. L. Rheingold, *J. Am. Chem. Soc.*, **109**, 5680 (1987); b) W. E. Geiger, N. Van Order, Jr., D. T. Pierce, T. E. Bitterwolf, A. L. Rheigold, and N. D. Chasteen, *Organometallics*, **10**, 2403 (1991); c) J. W. Merkert, J. H. Davis, Jr., W. E. Geiger, M. N. Paddon-Row, A. M. Oliver, and A. L. Rheingold, *Organometallics*, **11**, 4109 (1992).

8) a) J. W. Merkert, J. H. Davis, Jr., W. E. Geiger, and R. N. Grimes, *J. Am. Chem. Soc.*, **114**, 9846 (1992); b) J. Edwin, W. E. Geiger, and A. L. Rheingold, *J. Am. Chem. Soc.*, **106**, 3052 (1984).

9) H. Schimanke and R. Gleiter, *Organometallics*, **17**, 275 (1998).

10) T. Akiyama, K. Nakamura, M. Tamada, H. Ushijima, M. Kajitani, K. Shimizu, and A. Sugimori, *Chem. Lett.*, **1990**, 1255.

11) a) M. Kajitani, T. Akiyama, A. Sugimori, K. Hirakata, Y. Hoshino, Y. Satsu, G. P. Sato, K. Shimizu, M. Kaise, and C. Nishihara, *J. Electroanal. Chem.*, **251**, 421 (1988); b) H. Ushijima, M. Kajitani, K. Shimizu, G. P. Sato, T. Akiyama, and A. Sugimori, *J. Electroanal. Chem.*, **303**, 199 (1991).

12) M. Okubo, K. Aramaki, S. Nakajima, T. Watanabe, and H. Nishihara, *Chem. Lett.*, **1995**, 585.

13) D. Seyferth, M. O. Nestle, and A. T. Wehman, *J. Am. Chem. Soc.*, **97**, 7417 (1975).

14) C. Takayama, M. Kajitani, T. Sugiyama, and A. Sugimori, *J. Organomet. Chem.*, in press.

15) An MM-2 calculation performed by using *CAChe Mechanics* system at TDK Co., Ltd. for **1d** gives two stable conformations: The most stable conformation is the structure in which two phenyl groups are situated in the remote position and the second stable one is the conformation in which two phenyl groups are situated in parallel.

16) R. T. Boeré, B. Klassen, and K. H. Moock, *J. Organomet. Chem.*, **467**, 127 (1994).

17) T. Akiyama, Y. Watanabe, A. Miyasaka, T. Komai, H. Ushijima, M. Kajitani, K. Shimizu, and A. Sugimori, *Bull. Chem. Soc. Jpn.*, **65**, 1047 (1992).

18) C. Hansch, A. Leo, and R. W. Taft, *Chem. Rev.*, **91**, 165 (1991). Except for **1e**, all of the σ_p values were taken from this reference. The σ_p value of **1e** was calculated according to the following literature: M. Charton, *J. Org. Chem.*, **28**, 3121 (1963).