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Formation and reaction of three-membered cobaltathiaziridine ring in (η^5-cyclopentadienyl)(substituted imido-κ*N*-thio-κ*S*-ethene-2-thiolato-κ*S*)cobalt(III). Ring opening and closure and transfer of imido group

Mitsushiro Nomura, Takayoshi Yagisawa, Chikako Takayama, Toru Sugiyama, Yasuo Yokoyama, Kunio Shimizu, Akira Sugimori, Masatsugu Kajitani *

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

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Abstract

Three-membered cobaltathiaziridine rings are formed in the reactions of [CpCo{$S_2C_2(COOMe)_2$}] either with some azides (RN_3: *p*-toluenesulfonyl azide (TsN_3), methanesulfonyl azide (MsN_3), and ethyl azidoformate ($EtOOCN_3$)) or with *N*-(phenyliodonio)-*p*-toluenesulfonamidate (PhI = NTs) to afford imido-bridged complexes, [CpCo{$S_2C_2(COOMe)_2$}(NR)]. The ring undergoes unique ring opening and reforming reactions. Hydrogen chloride brings about the cleavage of the Co–N bond to give *S*-iminodithiolato-cobalt(III) complexes [Cp(Cl)Co{S(NR)–C(COOMe)–C(COOMe)–S)}], which very easily regenerates the cobaltathiaziridine ring on treatment with bases, such as pyridine and even with the very weak base, water. The reaction with triphenylphosphine at room temperature results in the ring opening to give an ylide. The heating of a benzene solution of the ylide at 80°C (under reflux) gives a product in which a sulfonylimido moiety migrates to a carbon atom of the cyclopentadienyl ring. The reduction halfwave potential values of the imido-bridged complexes depend on the substituent of bridging moiety. The CV of sulfonylimido-bridged complex shows one-electron two-step reduction processes. We found that the reductant of the original complex is regenerated not by the first reduction, but by the second reduction according to CV and OTTLE measurements. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Cobaltathiaziridine; Cobaltadithiolene; Sulfonyl azide; *N*-(phenyliodonio)-*p*-toluenesulfonamidate; Ring opening; Migration

1. Introduction

A metalladithiolene ring is a very interesting metal chelate ring [1]. It is a conjugated ring with six π electrons. In some cases, the ring behaves as an aromatic ring and undergoes substitution reactions [2], while, under other conditions, the ring undergoes addition reactions due to unsaturation.

A typical addition reaction is the bridging between Co and S by alkylidene groups in the reaction with diazo compounds [3]. Similar addition reactions occur with dimethyl acetylenedicarboxylate [4] or with quadricyclane [5].

The alkylidene adducts further undergo various types of bond cleavage. UV-irradiation causes the elimination of alkylidene group to give free cobaltadithiolene complexes [3]. In the cases of the norbornadiene adducts, the adducts are photocleaved to afford free cobaltadithiolene complexes and norbornadiene [5,6].

The attack of hydrogen halide to the three-membered cobaltathiirane ring of alkylidene adducts gives rise to the cleavage of Co–C bond [7]. The halide atom is bonded to the cobalt atom and the hydrogen atom is bonded to the bridging alkylidene carbon to give three-component-adducts among cobaltadithiolene, alkylidene, and hydrogen halide [3d].

The addition of phosphines or phosphites to the cobalt atom in alkylidene adducts causes the cleavage of either Co–C or Co–S bond depending on the elec-

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* Corresponding author. Fax: + 81-3-2383361.
E-mail address: kajita-m@hoffman.cc.sophia.ac.jp (M. Kajitani).

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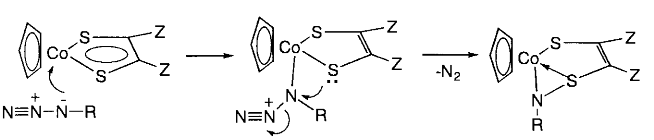


Scheme 1.

tronic structure of the bridging alkylidene groups to give *S*-ylide complexes or ring expansion complexes having a six-membered dihydro-1,2,5-cobaltadithiine ring [8,9]. Upon UV-irradiation, the dihydro-1,2,5-cobaltadithiine complex regenerates the three-membered cobaltathiirane ring [3b].

On the other hand, organic azides [10] react with the cobaltadithiolenes in two fashions. One is the replacement of sulfur by imido group. Phenyl azide brings about this type of reaction, in which nitrenes act as reactants [11b]. The other type reaction is the bridging between Co and S by imido group. This type reaction is similar to the reaction of diazo compounds with cobaltadithiolene complexes and is caused by 1,3-dipolar addition of sulfonyl azides to a Co–S bond. The latter type reaction has been reported preliminarily [11a]. Similar to the diazo compounds, some organic azides react with cobaltadithiolene complexes to give imido-bridged compounds (Chart 1).

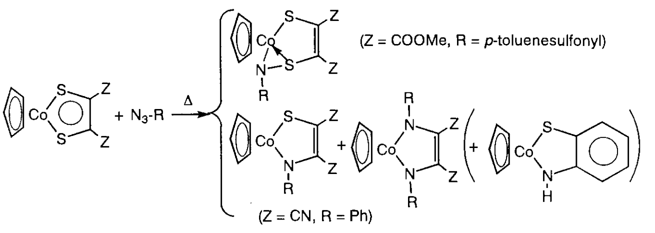


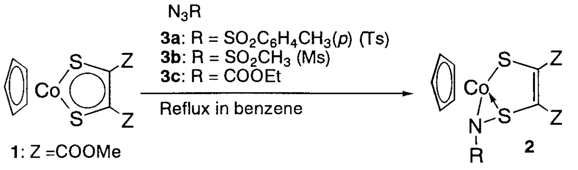
Chart 1.

We report here the formation of substituted imido-bridged cobaltadithiolene complexes [CpCo{S_2C_2-$(COOMe)_2$}(NR)] in the reactions of [CpCo{S_2C_2-$(COOMe)_2$}] either with some azides (RN_3: *p*-tolylsulfonyl azide (TsN_3), methanesulfonyl azide (MsN_3), and ethyl azidoformate ($EtOOCN_3$)) or with *N*-(phenyliodonio)-*p*-toluenesulfonamidate (PhI = NTs). Reactivities of three-membered cobaltathiaziridine rings in imido-bridged complexes were investigated in the reactions with hydrogen chloride and triphenylphosphine. The comparison of the chemical and electrochemical behavior of the imido-bridged cobaltadithiolenes with that of alkylidene-bridged cobaltadithiolenes is of interest in the chemistry of this type of bridged complexes. Sulfonylimido-bridged cobaltadithiolene complexes show remarkable reactions which are different from those of alkylidene-bridged complexes.

2. Results and discussion

2.1. Formation of imido-bridged complexes **2a**, **2b**, and **2c**

Sulfonyl azides (RN_3, **3a**: R = *p*-toluenesulfonyl and **3b**: R = methanesulfonyl) and ethyl azidoformate (**3c**: $EtOOCN_3$) react with (η^5-cyclopentadienyl)(1,2-dimethoxycarbonyl-1,2-ethenedithiolato)cobalt(III) (**1**) affording (η5-cyclopentadienyl)(sulfonylimido-κ*N*-thio-κ*S*-ethene-2-thiolato-κ*S*)cobalt(III) (**2a** and **2b**) and the corresponding ethoxycarbonylimido-bridged complex (**2c**) in reasonable yields, respectively (Chart 2). The reactions proceeds in boiling benzene. The mechanism of the imido-bridging should be similar to that of the alkylidene-bridging by diazo compounds, in which the initial step is the attack of the negative center (N atom) of an azide to the positive center (Co atom) of the cobaltadithiolene ring and the succeeding process is the attack of a negatively charged S atom to the positively charged N of azide moiety to cause S_N2-type elimination of N_2 (Scheme 1).



	React. time / h	Yield / %
2a: R = $SO_2C_6H_4CH_3$(*p*) (Ts)	2	78
2b: R = SO_2CH_3 (Ms)	5	76
2c: R = COOEt	24	64

Chart 2.

N-(Phenyliodonio)-*p*-toluenesulfonamidate (**4a**) gives also **2a** in the reaction with **1**. *N*-(Phenyliodonio)-*p*-toluenesulfonamidate (**4a**) has been reported as good nitrene precursor which generates nitrene under the catalysis of copper complexes at elevated temperatures [12]. However, even at room temperature and without any catalyst the complex **2a** is formed in good yield (Chart 3).

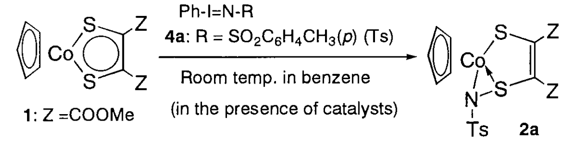
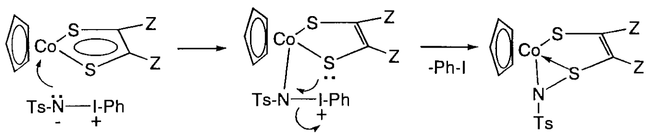


Chart 3.

In the reaction between equimolar **1** and **4a**, the yields of **2a** and the recovery of **1** (in parentheses) are as follows: in the presence of 1/20 molar CuI, 21% (70%); in the presence of 1/20 molar [$Cu(OTf)_2$], 27% (71%); in the presence of 1/20 molar [$Cu(acac)_2$], 24% (70%); and in the absence of catalyst, 27% (64%). This fact indicates that nitrene species does not participate in the formation of the imido-bridged compound. Thus, the bridging reaction by **4a** should proceed in an ionic reaction via dipolar addition similar to the process for the formation of methylene-bridged complexes in the reaction of **1** with diazo compounds (Scheme 2).



Scheme 2.

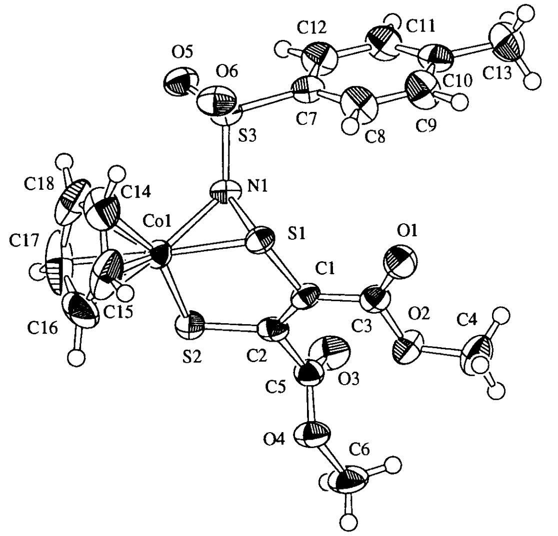


Fig. 1. ORTEP drawing of $[(Cp)Co(S_2C_2(COOMe)_2)(NTs)]$ (**2a**). Selected bond lengths (Å): Co–S1 2.176(1), Co–S2 2.230(1), Co–N1 1.961(4), S1–N1 1.714(4), S1–C1 1.750(5), S2–C2 1.704(5), C1–C2 1.365(7). Selected bond angles (°): S1–Co–S2 90.74(5), Co–S1–C1 105.0(2), Co–S2–C2 102.2(2), S1–C1–C2 117.4(4), S2–C2–C1 124.2(4), S1–Co–N1 48.6(1), Co–S1–N1 59.1(1), Co–N1–S1 72.3(1). Plane angles (°): Cp ring/dithiolene ring 110.9(3), plane of Co–S1–S2/plane of Co–S1–N1 89.89.

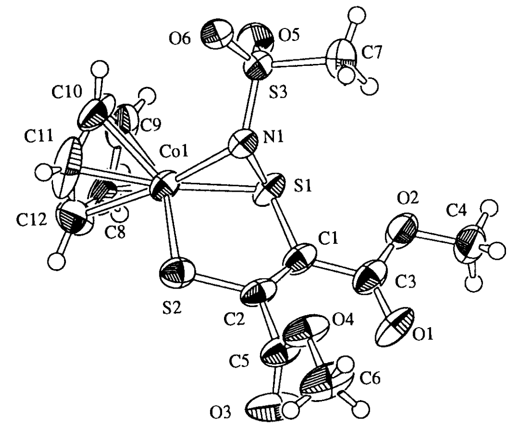


Fig. 2. ORTEP drawing of $[(Cp)Co(S_2C_2(COOMe)_2)(NMs)]$ (**2b**). Selected bond lengths (Å): Co–S1 2.196(1), Co–S2 2.220(1), Co–N1 1.959(3), S1–N1 1.720(3), S1–C1 1.754(4), S2–C2 1.708(4), C1–C2 1.346(5). Selected bond angles (°): S1–Co–S2 90.75(6), Co–S1–C1 104.4(1), Co–S2–C2 102.2(1), S1–C1–C2 117.8(3), S2–C2–C1 124.7(3), S1–Co–N1 48.51(6), Co–S1–N1 58.6(2), Co–N1–S1 72.9(1). Plane angles (°): Cp ring/dithiolene ring 111.88, dithiolene ring/plane of Co–S1–N1 91.37.

2.2. *X-ray structures of imido-bridged complexes*

The structures of the imido-bridged complexes **2a** and **2b** were determined by single-crystal X-ray diffraction. The ORTEP drawings are shown in Figs. 1 and 2, together with selected bond lengths and angles.

The structure of the imido-bridged complex is similar to that of the alkylidene-bridged complex. These adducts are coordinatively saturated six-coordinate species. The almost planar five-membered cobaltadithiolene rings are retained and the three-membered cobaltathiaziridine rings are almost perpendicular to the dithiolene rings in the these complexes (**2a**: 89.89; **2b**: 91.37°). The imido-bridged complexes, **2a** and **2b**, have a shape based on the 111.9 and 111.88° angles formed by the Cp rings and the dithiolene rings, respectively. These Co–S bond lengths in the imido-bridged complexes become longer than those of the original complex (Co–S, 2.108(2) and 2.104(2) Å), resulting from the formation of a bridging structure (**2a**: Co–S1, 2.176(1), Co–S2, 2.230(1); **2b**: Co–S(1), 2.196(1), Co–S(2), 2.220(1) Å). Their C–C bond lengths in cobaltadithiolene rings are shorter than normal C–C bonds and longer than normal C=C bonds; the bond length of the original complex is 1.369(6) [3e].

2.3. *Reactivities of imido-bridged complexes*

2.3.1. *Thermolysis*

The imido-bridged complex **2a** underwent thermal dissociation in the solid state at 177–178°C to yield the original dithiolene complex **1** (88%) and *p*-toluenesulfonamide (43%). The imido-bridged complex **2c** underwent also thermal dissociation in the solid state at 160°C to afford the original complex **1**, but the corresponding amine (urethane) did not appear. The thermal reactions of the complexes **2a** and **2c** in cyclohexene did not give any nitrene-trapping products (7-azanorcarane and methylcyclohexene) [13].

On the other hand, the alkylidene-bridged complexes dissociate thermally to give quantitatively the original dithiolene complexes. Pyrolysis of the methylene-bridged complexes in cyclohexene yielded the corresponding original dithiolene complexes and cyclohexene derivatives. This result gives some evidence for the generation of methylene from the adducts; the alkylidene-bridged complexes are regarded as precursors for free carbene species [3b].

2.3.2. *Cleavage of the cobaltathiaziridine ring with HCl and its reformation in the reaction of the resulting three-component adduct with bases*

A unique reaction of the cobaltathiaziridine ring was found in the reaction with HCl: the cleavage of Co–N bond by hydrogen chloride and the reformation of the cobaltathiaziridine ring by the action of a very weak base such as water.

Similar to the methylene-adducts, the imido-bridged complex reacts with hydrogen chloride[3d,7]. When the imido adduct **2a** was treated with an equal amount of hydrogen chloride in a dichloromethane solution, the color of the solution was rapidly changed from green to brown and a product was obtained. The ^{1}H-NMR spectrum and elemental analysis show that the product **5a** has an *S*-NHTs structure of (η^5-cyclopentadienyl)(chloro)(*p*-toluenesulfonylimidothio-κ*S*-ethene-2-thiolato-κ*S*)cobalt(III) (**5a**), a three-component-adduct consisting of cobaltadithiolene, *p*-toluenesulfonylimino group, and hydrogen chloride. Other imido-bridged complexes **2b** and **2c** reacted similarly. The proton may either attack directly to the bridging nitrogen or may attack to the basic sulfur atom first and then migrate to the bridging nitrogen.

Along with the ring opening, the elimination of the bridging group also takes place by the action of excess HCl. Free cobaltadithiolene complex **1** and *p*-toluenesulfonamide were identified by ^{1}H-NMR spectral data. Thus, complex **5** is not stable enough in an acidic solution (Chart 4).

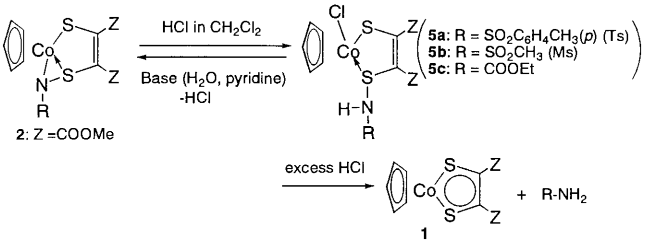


Chart 4.

The Co–S bond of the cobaltadithiolene rings in the alkylidene-bridged cobaltadithiolenes is also easily cleaved by hydrogen halides to give the corresponding three-component-adducts among cobaltadithiolene, alkylidene, and hydrogen halide. But the three-component-adducts are stable in the presence of an excess amount of hydrogen halides at room temperature. These facts suggest that the ring-opened three-component-adducts from the imido-bridged adducts are less stable than those from the alkylidene-bridged adducts [3d].

The most remarkable reaction of **5a** and **5b** is the reformation of **2a** and **2b**, respectively on the treatment with water. When we shake a dichloromethane solution of **5** with a small amount of water, we obtain the imido-bridged complex **2**. When we use a small amount of pyridine, the reformation of the imido-bridged adduct also occurs. These facts indicate that the highly acidic proton at the nitrogen atom is abstracted by bases and the negatively charged nitrogen attacks the cobalt atom to kick off the chloride anion. The facile reformation of a strained three membered ring is a characteristic reaction for this type of complex. The reformation of the strained three-membered ring by a very weak base such as water is a characteristic reaction for the cobaltaziridine ring. Namely, a feature of ring opening product **5** is its strong base. Similar behavior is not observed in the three-component-adducts from alkylidene-bridged adducts.

2.3.3. Cleavage of the cobaltathiaziridine ring with PPh_3

The addition of triphenylphosphine to a benzene solution of **2** at room temperature results in the ring opening to give quantitatively the three-component adduct which has an *S*-ylide structure, **6** (Chart 5). The formation of a six-membered ring complex as another three-component adduct was denied by the results of ^{1}H-NMR, UV–vis, and CV measurement, although in the reactions of alkylidene-bridged complexes with trimethylphosphine or trimethyl phosphite, we observed ylide complexes along with six-membered ring complexes, depending on the substituents at the bridging carbon atom [9] (Chart 6).

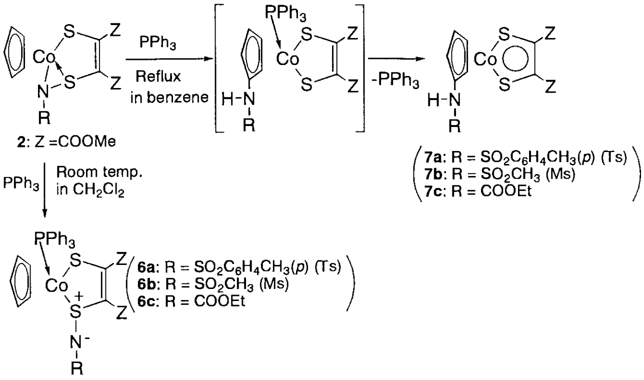


Chart 5.

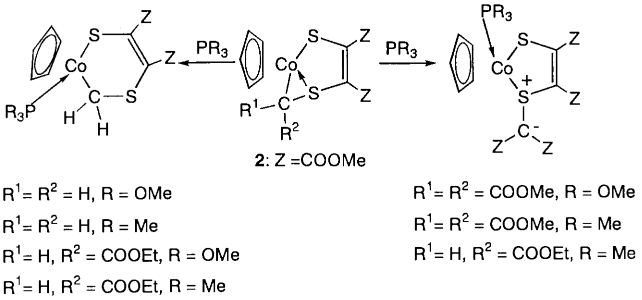


Chart 6.

2.3.4. Insertion of p-toluenesulfonylamino group into a C–H bond in the Cp ring in the reaction of the imido-bridged complex with PPh_3

In the reaction with phosphorus compounds at ca. 80°C (under reflux) in benzene or toluene, the sulfonylimido-bridged complex shows an interesting reaction which is not observed for the alkylidene-bridged complexes.

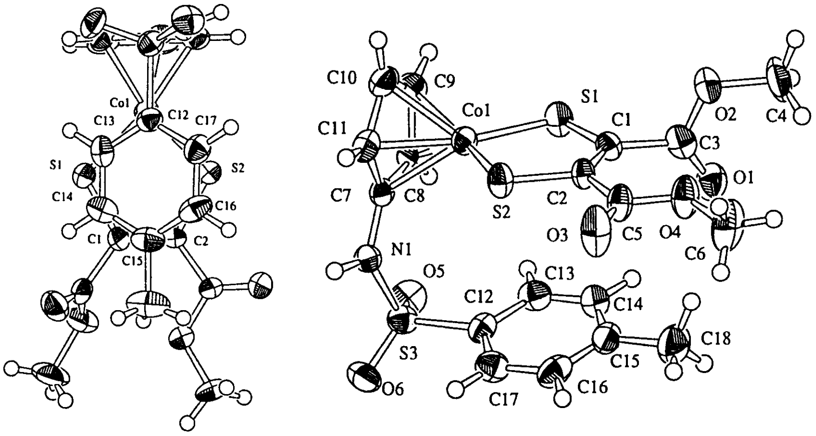


Fig. 3. ORTEP drawing of [(Cp–NH–SO_2–C_6H_4–CH_3)Co(S_2C_2(COOMe)$_2$)] (**7**). Selected bond lengths (Å): Co–S1 2.112(3), Co–S2 2.102(3), S1–C1 1.697(10), S2–C2 1.726(9), C1–C2 1.35(1), N1–C7 1.38(1). Selected bond angles (°): S1–Co–S2 91.8(1), Co–S1–C1 105.1(3), Co–S2–C2 104.7(3), S1–C1–C2 119.6(7), S2–C2–C1 118.9(7), S3–N1–C7 126.5(7), C7–N1–H11 116.8(8), S3–N1–H11 116.6(6). Plane angles (°): Cp ring/dithiolene ring 88.84, Cp ring/phenyl ring 89.4, dithiolene ring/phenyl ring 12.35.

The heating of **6a** in a benzene solution at ca. 80°C (under reflux) in the presence of triphenylphosphine gives another product, [(*p*-toluenesulfonylimino)cyclopentadienyl - (1,2 - ethylenedithiolato)cobalt(III)]. The structure of the isolated product was determined by X-ray diffraction analysis. The ORTEP drawing is shown in Fig. 3, together with selected bond lengths and angles. The structure of the cobaltadithiolene ring is analogous to that of the original complex **1**. Interestingly, as shown in Fig. 3, the cobaltadithiolene ring and the phenyl ring in the Ts group are situated face-to-face at a separation of ca. 3.5 Å. The distance suggests an intramolecular π–π interaction between the cobaltadithiolene ring and the phenyl ring.

In the product, *p*-toluenesulfonylamino group is bonded to a carbon atom of the cyclopentadienyl ring. Two different mechanisms are conceivable. One mechanism involves the intermediary formation of nitrene species and the other involves the intramolecular migration of the sulfonylimido group. We can not yet decide the mechanism.

The first step to form an ylide structure is similar to the reaction of di(methoxycarbonyl)-methylene-bridged complex with trimethyl phosphite to give the three-component adduct having *S*-ylide structure [9].

The second process of the reaction of the imido-bridged complex with trimethylphosphine is different from that of the di(methoxycarbonyl)methylene-bridged complex with trimethyl phosphite. In the reaction of alkylidene-bridged adducts, a similar alkylidene transfer has never been observed.

2.3.5. *Electrochemical behavior of the sulfonylimido-bridged adduct by CV and OTTLE*

The cyclic voltammogram of complex **2a** is shown in Fig. 4, together with that of the original complex.

The *p*-toluenesulfonylimido-bridged complex **2a** shows a reversible one-electron reduction wave at -0.79 V (reference, Fc|Fc$^+$) and an irreversible two-electron reduction wave at -1.80 V and an irreversible oxidation wave around 0.5 V. The reduction halfwave potential of -0.79 V is more positive than the original cobaltadithiolene **1** ($E_{1/2}$(red) = -0.94 V). This shows that the coordinated imido group lowers the electron density at the cobalt atom.

In the first reduction process, an in-situ measurement of the electronic absorption spectra during the electrolytic reduction using an optically transparent thin-layer electrode (OTTLE) showed the reversibility of the reduction and re-oxidation at -0.79 V.

On the other hand, after the irreversible second reduction process, the wave corresponding to the re-oxidation of **1a**$^-$ appeared; the reductant of the original complex is regenerated by the second reduction and the spectral change using OTTLE showed the regeneration of the original complex, as shown in Fig. 5.

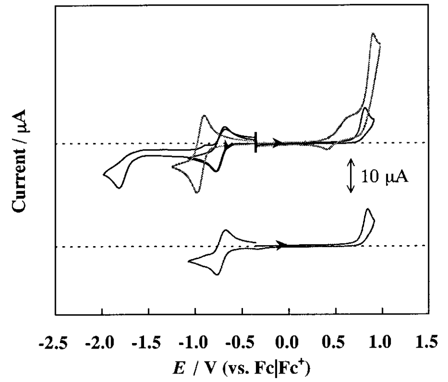


Fig. 4. Cyclic voltammograms ($v = 100$ mV s^{-1}, $\Phi = 1.6$ mm, Pt disk) of 1 mmol dm^{-3} complex in CH_3CN containing 0.1 mol dm^{-3} TEAP: **2a** (solid line) and **1**(dotted line).

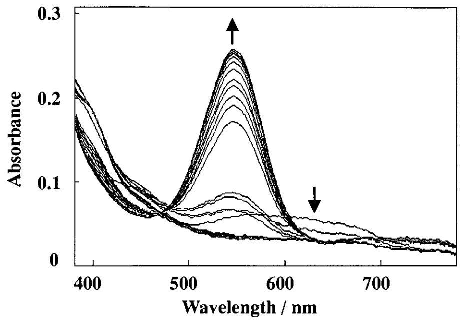
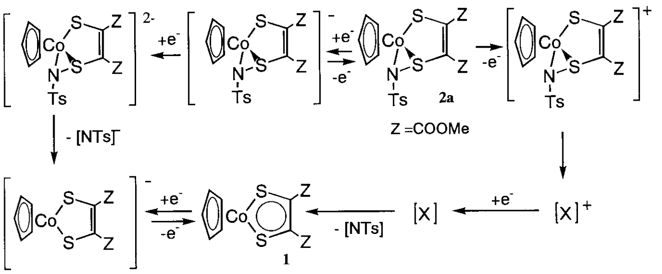


Fig. 5. Electronic spectral change of **2a** during reduction and re-oxidation: after the reduction at -1.8 V for 30 s, the potential was stepped from -1.8 (for 30 s) to -0.9 V (for 30 s); sampling interval, 2 s.



Scheme 3.

From these results, we propose the redox mechanism shown in Scheme 3: the sulfonyl-imido-bridged complex **2a** showed reversible redox behavior on these CV time scales at -0.79 V. Reversibility in cyclic voltammogram shows that one-electron reduction does not cause any bond cleavage. Two-electron reduction of **2a** affords an anion radical having a lifetime of a few seconds and then it eliminates the imido moiety to give more stable **1a**$^-$. Then, we could see the regeneration of the original complex by an OTTLE measurement. In the irreversible oxidation process, the cation radical **2a**$^+$ has a lifetime of a few seconds, and then it is converted to a species X^+, of which the re-reduction potential value is around -0.6 V. When the species X^+ was re-reduced, **1a** was rapidly generated. The complex X^+ is relatively stable, but the neutral X is very unstable. The structure of the complex X formed by the oxidation has not yet been clarified, but it would be an S–C bond cleaved product, because X easily regenerates the original complex **1a**. In contrast, the coordinated methylene increases the electron density of the cobalt atom.

In Fig. 6, the electrochemical behavior of a series of the imido-bridged complexes **2** is compared with those of methylene-bridged adduct, substituted Cp complexes, and the original complex. The reversible reduction half-wave potentials were shifted to the positive side as follows: $[(Cp–H)Co–\{S_2C_2(COOMe)_2\}(CH_2)] < [(Cp–NHTs)Co\{S_2C_2(COOMe)_2\}] < [(Cp–H)Co\{S_2C_2(COOMe)_2\}] < [(Cp–H)Co\{S_2C_2(COOMe)_2\}(N\text{–}COOEt)] < [(Cp–NHMs)Co\{S_2C_2(COOMe)_2\}] < [(Cp–H)Co\{S_2C_2(COOMe)_2\}(N–T_s)] < [(Cp–H)\text{-}Co\text{-}\{S_2C_2(COOMe)_2\}(N–Ms)]$. Electrochemical behavior of the imido-bridged complexes is now under detailed investigation by using CV and OTTLE measurements.

3. Experimental

3.1. General

Reactions were carried out under argon by means of standard Schlenk techniques.

NMR spectra were measured with a JEOL JNM-GX270, LA300, or LA500 spectrometer. Mass and FT IR spectra were recorded on a JEOL JMS-SX102A and Shimadzu model FTIR 8600PC, respectively. UV–vis spectra were recorded on Hitachi model U-3210 or Shimadzu model UV-2500PC. Cyclic voltammograms were measured with model CV-50W of BAS Co. Elemental analyses were determined by using a Shimadzu PE2400-II instrument. Products were purified by preparative HPLC, model LC-908 or model LC-08, produced by Japan Analytical Industry Co.

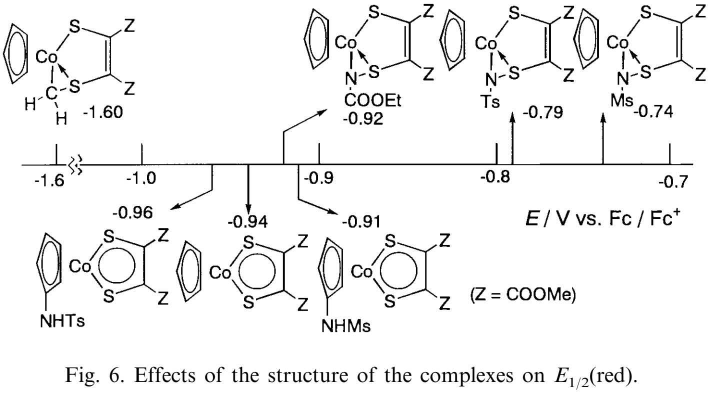


Fig. 6. Effects of the structure of the complexes on $E_{1/2}$(red).

3.2. Materials

The starting cobaltadithiolene complex [CpCo(S_2C_2-$(COOMe)_2$)] (**1**) was synthesized in a one-pot reaction of [CpCo$(CO)_2$], DMAD, and elemental sulfur [14].

p-Toluenesulfonyl azide (N_3Ts), methanesulfonyl azide (N_3Ms), and ethyl azidoformate (N_3COOEt) were synthesized in the reaction of *p*-toluenesulfonyl chloride, methanesulfonyl chloride, and ethyl chloroacetate with sodium azide, respectively, [15]. *N*-(Phenyliodonio)-*p*-toluenesulfonamidate (**4a**) was prepared according to the report by Okawara et al. [12b].

3.3. Formation of imido-bridged complexes ([CpCo($S_2C_2(COOMe)_2$)(NR)] 2)

3.3.1. Reaction with p-toluenesulfonyl azide

The cobaltadithiolene complex **1** (1.0 mmol) was treated with *p*-toluenesulfonyl azide (1.0 mmol) under reflux in benzene (10 cm^3) under a stream of Ar for 2 h. After the solvent was removed under reduced pressure, the residue was chromatographed by flush column chromatography using silica gel (Wako-gel C-300; eluent, mixed solvent of CH_2Cl_2–Et_2O (5:1 v/v). An *p*-toluenesulfonylimido-bridged complex **2a** was obtained as crystalline solid in 76% yield. Green crystals; m.p. 177–178°C (dec.). IR (KBr disk) 1736 and 1703 cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 2.39$ (s, 3H, CH_3), 3.57 (s, 3H, OCH_3), 3.79 (s, 3H, CH_3), 5.77 (s, 5H, Cp), 7.23 (d, $J = 7.94$ Hz, 2H, Ar), 7.73 (d, $J = 7.94$ Hz, 2H, Ar). ^{13}C-NMR ($CDCl_3$): $\delta = 21.6$ (CH_3), 52.1 (OCH_3), 53.4 (OCH_3), 84.4 (Cp), 127.2 (CH), 128.4 (dithiolene ring carbon), 129.4 (CH), 137.5, 143.4, 161.3 (CO), 165.8 (CO), and 185.3 (dithiolene ring carbon). MS (EI, 70 eV) *m*/*z* (rel. intensity) 499 (3.7, [M^+]), 330 (94, [$M^+ -$ NTs]), 188 (100, [$CpCoS_2^+$]), 124 (34, [$CpCo^+$]). *Anal.* Found: C, 43.11; H, 3.58; N, 2.74. Calc. for $C_{18}H_{18}NO_6S_3Co$: C, 43.29; H, 3.63; N, 2.80%.

3.3.2. Reaction with methanesulfonyl azide

The cobaltadithiolene complex **1** (0.3 mmmol) was treated with methanesulfonyl azide (1.0 mmol) under reflux in benzene (10 cm^3) under a stream of Ar for 5 h. After the solvent was removed under reduced pressure, the residue was chromatographed by flush column chromatography using silica gel (Wako-gel C-300; eluent, mixed solvent of CH_2Cl_2–hexane (10:1 v/v). A methanesulfonylimido-bridged complex **2b** was obtained as crystalline solid in 75% yield. Green crystals; m.p. 165–167°C (dec.). ^{1}H-NMR ($CDCl_3$): $\delta = 3.07$ (s, 3H, CH_3), 3.77 (s, 3H, OCH_3), 3.85 (s, 3H, CH_3), 5.73 (s, 5H, Cp). ^{13}C-NMR ($CDCl_3$): $\delta = 41.9$ (CH_3), 52.6 (OCH_3), 53.4 (OCH_3), 84.3 (Cp), 115.0 (dithiolene ring carbon), 161.4 (CO), 165.7 (CO), and 185.2 (dithiolene ring carbon). MS (EI, 70 eV) *m*/*z* (rel. intensity) 423 (2.9, [M^+]), 330 (87, [$M^+ -$ NMs]), 188 (100, [$CpCoS_2^+$]), 124 (29, [$CpCo^+$]). *Anal.* Found: C, 33.99; H, 3.21; N, 3.50: S, 22.72. Calc. for $C_{12}H_{14}NO_6S_3Co$: C, 34.04; H, 3.33; N, 3.31: S, 22.81%.

3.3.3. Reaction with ethyl azidoformate azide

The cobaltadithiolene complex **1** (0.17 mmmol) was treated with ethyl azidoformate (0.97 mmol) under reflux in benzene (30 cm^3) under a stream of Ar for 24 h. After the solvent was removed under reduced pressure, the residue was chromatographed by flush column chromatography using silica gel (Wako-gel C-300; eluent, mixed solvent of CH_2Cl_2–Et_2O (1:3 v/v). An ethoxycarbonylimido-bridged complex **2c** was obtained as crystalline solid in 64% yield. m.p. 160–162°C. ^{1}H-NMR ($CDCl_3$): $\delta = 2.39$ (t, $J = 6.71$ Hz, 3H, CH_3), 3.82 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 4.06 (q, $J = 6.71$ Hz, CH_2), 5.53 (s, 5H, Cp). ^{13}C-NMR ($CDCl_3$): $\delta =$ 14.7 (CH_3), 52.7 (OCH_3), 53.3 (OCH_3), 67.4 (CH_2), 86.2 (Cp), 128.1 (dithiolene ring carbon), 161.7 (CO), 166.2 (CO), 176.4 (CO), and 179.3 (dithiolene ring carbon). MS (EI, 70 eV) *m*/*z* (rel. intensity) 417 (4.3, [M^+]), 330 (87, [$M^+ -$ NCOOEt]), 188 (100, [$CpCoS_2^+$]), 124 (32, [$CpCo^+$]). *Anal.* Found: C, 40.34; H, 3.89; N, 3.25. Calc. for $C_{14}H_{16}NO_6S_2Co$: C, 40.29; H, 3.89; N, 3.36%.

3.3.4. Reaction of **1** *with N-(phenyliodonio)-p-toluenesulfonamidate* ***(4a)*** *in the absence of catalyst or in the presence of catalysts*

A dichloromethane solution (20 cm^3) of **1** (0.34 mmol) and **4a** (0.34 mmol) was stirred in benzene (10 cm^3) at room temperature. Reaction time of five minutes was enough for the formation of the imido-bridged complex. The reaction mixture was submitted to flush column chromatography using silica gel column (Wako-gel C-300) and dichloromethane–hexane (5:1 v/v) as an eluent. A *p*-toluenesulfonylimido-bridged complex **2a** was obtained in 27% yield.

Similar reactions were carried out in the presence of catalysts (0.03 mmol). The results are shown in the text.

3.4. Reaction of imido-bridged adducts with hydrogen chloride

3.4.1. Ring opening reaction of imido-bridged complex with hydrogen chloride

To a dichloromethane solution (20 cm^3) of imido-bridged complex (**2**) (0.10 mmol) was added 20 μl of concentrated hydrochloric acid. The suspension was stirred under Ar for 5 min. The water was removed with anhydrous $MgSO_4$ and the solvent was distilled under reduced pressure and the HCl adduct was obtained as brown crystals. The three-component adduct [CpCo($S_2C_2(COOMe)_2$)(NTs)(HCl)] (**5a**) of **2a** and HCl was obtained in 81% yield: Brown crystals, m.p. 88–90 °C (dec.). ^{1}H-NMR ($CDCl_3$): $\delta = 2.50$ (s, 3H, CH_3), 3.53 (s, 3H, OCH$_3$), 3.86 (s, 3H, OCH$_3$), 5.39 (s, 5H, Cp), 7.45 (d, $J = 7.93$ Hz, 2H, Ar), 7.86 (s, 1H, NH), and 7.97 (d, $J = 7.93$ Hz, 2H, Ar). MS (FAB, 70 eV) m/z 536 ([M$^+$ + 1]). *Anal.* Found: C, 40.11; H, 3.81; N, 2.60. Calc. for C$_{18}$H$_{19}$ClCoNO$_6$S$_3$: C, 40.34; H, 3.57; N, 2.61%. The three-component adduct [CpCo(S$_2$C$_2$(COOMe)$_2$)(NMs)(HCl)] (**5b**) of **2a** and HCl was obtained in 80% yield: Brown crystals. ^{1}H-NMR (CDCl$_3$): $\delta = 3.33$ (s, 3H, CH$_3$), 3.77 (s, 3H, OCH$_3$), 3.86 (s, 3H, OCH$_3$), 5.70 (s, 5H, Cp), and 7.87 (s, 1H, NH). The three-component adduct [CpCo(S$_2$C$_2$(COOMe)$_2$)(NCOOEt)–(HCl)] (**5c**) of **2a** and HCl was obtained in 80% yield: MS (FAB, 70 eV) m/z 454 ([M$^+$ + 1]). ^{1}H-NMR (CDCl$_3$): $\delta = 1.30$ (t, $J = 6.71$ Hz, 3H, CH$_3$), 3.76 (s, 3H, OCH$_3$), 3.87 (s, 3H, OCH$_3$), 4.26 (q, $J = 6.71$ Hz, 3H, CH$_3$), 5.63 (s, 5H, Cp), and 6.94 (s, 1H, NH).

3.4.2. Regeneration of the imido-bridged adduct due to ring reformation t with bases

A dichloromethane solution of [CpCo(S$_2$C$_2$(COOMe)$_2$)(NTs)(HCl)] (**5a**) was shaken with water in a separatory funnel. The organic layer was dried over MgSO$_4$ and the solvent was removed under reduced pressure. The formation of the imido-bridged complexes **2a** was confirmed by ^{1}H-NMR. The reaction of **5a** with pyridine was also performed in a dichloromethane solution by adding a small amount of pyridine. After evaporation of solvent, the imido-bridged complex **2a** was identified by ^{1}H-NMR.

3.5. Reaction of imido-bridged adducts with triphenylphosphine

The p-toluenesulfonylimido-bridged complex **2a** (0.1 mmol) was treated with triphenylphosphine (0.11 mmol) in dichloromethane at room temperature. The reaction occurs at once and the color changed from green to brown. The products were separated by flush column chromatography using silica gel (C-300) (eluent, acetone-diethyl ether (1:1 v/v)). The dark-brown solid was obtained in 95% yield as a three-component adduct [CpCo(S$_2$C$_2$(COOMe)$_2$)(NTs)(PPh$_3$)]. Brown crystals: m.p. 127–129°C (dec.). IR (KBr disk) 1736 and 1703 cm^{-1}. ^{1}H-NMR (CDCl$_3$): $\delta = 2.37$ (s, 3H, CH$_3$), 2.72 (s, 3H, OCH$_3$), 3.67 (s, 3H, CH$_3$), 5.40 (s, 5H, Cp), 7.18 (d, $J = 7.93$ Hz, 2H, Ph), 7.31–7.34 (m, Ph), 7.46–7.52 (m, Ph), 7.76 (m, Ph), and 7.78 (d, $J = 7.93$ Hz, 2H, Ph). MS (FAB, 70 eV) m/z 762 ([M$^+$ + 1]), 500 ([M$^+$ − PPh$_3$ + 1]), and 262 ([PPh$_3^+$]). *Anal.* Found: C, 56.47; H,4.46; N, 1.93%. Calc. for C$_{36}$H$_{33}$NO$_6$PS$_3$Co: C, 56.76; H, 4.37; N, 1.84%.

The methanesulfonylimido-bridged complex **2b** (0.1 mmol) was treated with triphenylphosphine (0.11 mmol) in dichloromethane at room temperature for 30 min. The color changed from green to brown. The products were separated by flush column chromatography using silica gel (C-300) (eluent, acetone-diethyl ether (1:1 v/v)). The dark-brown solid was obtained in 94% yield as a three-component adduct [CpCo(S$_2$C$_2$(COOMe)$_2$)(NMs)(PPh$_3$)] (**6b**). Brown crystals: ^{1}H-NMR (CDCl$_3$): $\delta = 2.93$ (s, 3H, CH$_3$), 3.51 (s, 3H, OCH$_3$), 3.70 (s, 3H, CH$_3$), 5.34 (s, 5H, Cp), 7.43–7.71 (m, 15H, Ph), MS (FAB, 70 eV), m/z 686 ([M$^+$ + 1]).

For the reaction at elevated temperature, a benzene solution of complex **2a** (0.1 mmol) and triphenylphosphine (0.2 mmol) was refluxed for 5 h. The products were separated by flush column chromatography using silica gel (C-300) (eluent, CH$_2$Cl$_2$–diethyl ether 2:1 v/v)). The blue–violet solid was obtained in 44% yield as a substituted Cp complex [(Cp–NHTs)Co(S$_2$C$_2$(COOMe)$_2$)]. Blue crystals; m.p. 209–211°C (dec.). UV–vis (CH$_2$Cl$_2$) $\lambda(\varepsilon)$ 717 (557), 572 (5350), 362 (3110), 294 (16700). ^{1}H-NMR (CDCl$_3$): $\delta = 2.25$ (s, 3H, CH$_3$), 3.89 (s, 6H, OCH$_3$), 5.07 (t, $J = 2.44$ Hz, 2H, Cp), 5.66 (t, $J = 2.44$ Hz, 2H, Cp), 6.98 (d, $J = 7.94$ Hz, 2H, Ar), 7.21 (s, 1H, NH), 7.37 (d, $J = 7.94$ Hz, 2H, Ar). ^{13}C-NMR (CDCl$_3$): $\delta = 21.2$ (CH$_3$), 52.7 (OCH$_3$), 69.5 (Ar), 74.6 (Ar), 112.0 (Ar), 127.1 (Ar), 129.1 (Cp), 131.0 (C–SO$_2$), 144.1 (Cp–N), 158.1 (dithiolene C), and 165.4 (C=O). MS (EI, 70 eV) m/z (rel. intensity) 499 ([M$^+$], 94), 356 ([CpNHTsS$_2^+$ − 1], 24), 91 ([C$_6$H$_4$CH$_3^+$], 100). *Anal.* Found: C, 41.36; H, 3.37; N, 2.83. Calc. for C$_{18}$H$_{20}$NO$_7$S$_3$Co: C, 41.78; H, 3.90; N, 2.71%.

The reaction of methanesulfonylimido-bridged complex (0.1 mmol) with triphenylphosphine (0.3 mmol) was refluxed in benzene (10 cm^3) for 5 h to give 32% of a blue crystalline product which is a methanesulfonyl substituted Cp complex. M.p.: 181–183°C. ^{1}H-NMR (CDCl$_3$) 5.85 (t, $J = 2.0$ Hz, 2H, Cp), 5.16 (t, J = 2.0 Hz, 2H, Cp), 3.89 ($_s$, 6H, OCH$_3$), 2.72 (s, 3H, CH$_3$). 13C-NMR (CDCl$_3$) 165.9 (C=O), 158.4 (dithiolene C), 132.2 (Cp(C–N), 75.2 (Cp(C–H)), 69.7 (Cp(C–H)) 53.2 (OCH$_3$), 37.7 (CH$_3$). UV–vis (CH$_2$Cl$_2$) $\lambda_{\max}$ (ε) 712 (687), 571 (6150), 361 (3670), 291 (17300). MS (EI, 70 eV) m/z (rel. intensity) 423 ([M$^+$], 100), 280 ([(CpNHMs)CoS$_2^+$ − 1], 34). *Anal.* Found: C, 34.05; H, 3.15; N, 3.17, Calc. for C$_{12}$H$_{14}$O$_6$NS$_3$Co: C, 34.00; H, 3.33; N, 3.33%.

*3.6. Crystal data and structure determination of complexes **2a**, **2b**, and **7a***

Detail are given in Table 1. Suitable crystals of complexes **2a**, **2b**, and **7a** were grown from CH$_2$Cl$_2$–hexane solution at room temperature. All measurements were made on Rigaku AFC5S four-circle diffractometers with graphite- monochromated Mo Kα radiation. The structures were solved by direct methods and expanded using Fourier techniques [16]. The non-

Table 1
Crystal data and data collection parameters

	2a	**2b**	**7a**
Formula	$C_{18}H_{18}NO_6S_3Co$	$C_{12}H_{14}NO_6S_3Co$	$C_{18}H_{18}NO_6S_3Co$
Formula weight	499.46	423.36	499.46
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$ (#15)	$P2_1/n$ (#14)	$P\bar{1}$ (#2)
Unit cell dimensions			
a (Å)	13.744(4)	10.297(8)	11.056(2)
b (Å)	19.832(4)	8.68(1)	11.775(2)
c (Å)	15.085(1)	18.75(1)	9.003(2)
β (°)	95.6900	93.52(6)	106.79(1)
V (Å^3)	4091(1)	1672(2)	1119.0(4)
Z	8	4	2
2θ Range (°)	25(20.2–24.8)	25(27.5–29.5)	25(28.6–29.9)
D_{calc} (g cm^{-3})	1.622	1.681	1.536
$F(000)$	2048.00	864.00	532.00
μ (Mo Kα) (cm^{-1})	11.81	14.27	10.85
T (K)	296	296	296
Crystal size (mm)	0.17 × 0.17 × 0.33	0.10 × 0.17 × 0.43	0.07 × 0.13 × 0.43
Scan type	ω–2θ	ω–2θ	ω–2θ
Scan speed (° min^{-1})	6.0	6.0	6.0
Scan width (°)	(1.05 + 0.30 tanθ)	(1.21 + 0.30 tanθ)	(1.37 + 0.30 tanθ)
$2\theta_{max}$ (°)	55.0	55.0	55.0
Unique data (R_{int})	4864 (0.033)	4102 (0.023)	5144 (0.021)
Number of observations	2588	2291	3149
Number of variables	280	222	289
R_1, wR_2 (all data)	0.046, 0.056	0.037, 0.030	0.067, 0.097
Goodness-of-fit on F^2	1.39	1.62	4.64
Largest difference peak and hole (e Å^{-3})	0.55, −0.81	0.27, −0.25	

hydrogen atoms were refined anisotropically. Idealized positions were used for the TEXSAN crystallographic software package of Molecular Structure Corp. [17].

3.7. CV measurements

All the electrochemical measurements were done in 1 (CV) or 1.0 mmol dm^{-3} (OTTLE) acetonitrile solutions containing 0.1 (CV) or 0.1 mmol dm^{-3} (OTTLE) [35] tetraethyl-ammonium perchlorate (TEAP) at 25°C. A stationary platinum disk (1.6 mm in diameter) (CV) or platinum wire served as a working electrode. A coiled platinum wire served as a counter electrode, with the reference electrode as Ag|AgNO$_3$ corrected for junction potentials by being referenced internally to the Fc|Fc$^+$.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 141220 for complex **2a**, 141180 for complex **2b**, and 141219 for complex **7a**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) G.N. Schrauzer, Acc. Chem. Res. 2 (1969) 72. (b) J.A. McCleverty, Prog. Inorg. Chem. 10 (1969) 49. (c) R.P. Burns, C.A. McAuliffe, Adv. Inorg. Chem. Radiochem. 22 (1979) 303. (d) U.T. Mueller Westerhoff, B. Vance, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty, (Eds.), Comprehensive Coordination Chemistry, vol. 2, Pergamon Press, Oxford, 1987, pp. 595–631. (e) A. Sugimori, Yuki Gosei Kagaku Kyokai Shi, 48 (1990) 788. (f) A. Sugimori, T. Akiyama, M. Kajitani, T. Sugiyama, Bull. Chem. Soc. Jpn. 72 (1999) 879.

[2] (a) M. Kajitani, G. Hagino, M. Tamada, T. Fujita, M. Sakurada, T. Akiyama, A. Sugimori, J. Am. Chem. Soc., 118 (1996) 489. (b) A. Sugimori, K. Yanagi, G. Hagino, M. Tamada, M. Kajitani, T. Akiyama, Chem. Lett. (1997) 807. (c) A. Sugimori, N. Tachiya, M. Kajitani, T. Akiyama, Organometallics, 15 (1995) 5664.

[3] (a) M. Kajitani, M. Sakurada, K. Dohki, T. Suetsugu, T. Akiyama, A. Sugimori, J. Chem. Soc. Chem. Commun. (1990) 19. (b) M. Sakurada, M. Kajitani, K. Dohki, T. Akiyama, A. Sugimori, J. Organomet. Chem. 423 (1992) 141. (c) M. Sakurada, J. Okubo, M. Kajitani, T. Akiyama, A. Sugimori, Phosphorus, Sulfur, Silicon, Related Elements 67 (1992) 145. (d) T. Harada, C. Takayama, M. Kajitani, T. Sugiyama, T. Akiyama, A. Sugimori, Bull. Chem. Soc. Jpn. 71 (1998) 2645. (e) C. Takayama, M. Kajitani, T. Sugiyama, A. Sugimori, J. Organomet. Chem. 563 (1998) 161. (f) C. Takayama, M. Kajitani, T. Sugiyama, T. Akiyama, K. Shimizu, A. Sugimori, Organometallics 16 (1997) 3498.

[4] M. Kajitani, T. Suetsugu, T. Takagi, T. Akiyama, A. Sugimori, K. Aoki, H. Yamazaki, J. Organomet. Chem. 487 (1995) C8.

[5] (a) M. Kajitani, Y. Eguchi, R. Abe, T. Akiyama, A.Sugimori, Chem. Lett. (1990) 359. (b) M. Kajitani, H. Hatano, T. Fujita, T. Okumachi, H. Nagao, T. Akiyama, A. Sugimori, J. Organomet. Chem. 430 (1992) C64.

[6] M. Kajitani, T. Fujita, N. Hisamatsu, H. Hatano, T. Akiyama, A. Sugimori, Coord. Chem. Rev. 132 (1994) 175.

[7] M. Kajitani, F. Kawakita, E. Chikuma, M. Sakurada, T. Akiyama, A. Sugimori, Chem. Lett. (1995) 85.

[8] M. Sakurada, M. Kajitani, H. Hatano, Y. Matsudaira, T. Suetsugu, S. Ono, T. Akiyama, A. Sugimori, Organometallics 11 (1992) 2337.

[9] C. Takayama, K. Takeuchi, S. Ohkoshi, G.C. Janairo, T. Sugiyama, M. Kajitani, A. Sugimori, Organometallics 18 (1999) 2843.

[10] E.F.V. Scriven, K. Turnbull, Chem. Rev. 88 (1988) 297.

[11] (a) H. Katsuta, N. Noguchi, Y. Inomata, M. Kajitani, T. Akiyama, A.Sugimori, Chem. Lett. (1994) 1165. (b) Preliminary report: M. Sakurada, M. Kajitani, T. Akiyama, A.Sugimori, Chemistry Express 6 (1991) 759.

[12] (a) D.A. Evans, M.M.;Faul, M.T. Bilodeau, J. Am. Chem. Soc. 116 (1994) 2742. (b) Y. Yamada, T. Yamamoto, M. Okawara, Chem. Lett. (1975) 361.

[13] W. Lwowski, T.W. Mattingly, Jr., J. Am. Chem. Soc. 87 (1965) 1947.

[14] H. Boennemann, B. Bogdanovic, W. Brijoux, R. Brinkmann, M. Kajitani, R. Mynott, G.S. Natarajan, M.G.Y. Samson, in: J.R. Kosak (Ed.), Catalysis of Organic Reactions, Marcel Dekker, New York, 1984, pp. 31–63.

[15] M. Regitz, J. Hocker, A. Liedhegener, Org. Syn. Coll. 5 (1973) 179.

[16] P.T. Beurstkens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Smykala, The DIRDIF Program System, Technical Report of the Crystallography Laboratory, University of Nijmegen, Nijmegen, The Netherlands 1992.

[17] TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, 1985, 1992.