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Electrochemical Behavior of Nickeladithiolene *S*,*S*′-Dialkyl Adducts: Evidence for the Formation of a Metalladithiolene Radical by Electrochemical Redox Reactions

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The electrochemical behavior of nickeladithiolene *S*,*S*′-dialkyl adducts (alkyl = benzyl, methyl, *tert*-butyl) was investigated by using cyclic voltammetry (CV), visible, near-IR, and ESR spectroscopies and bulk electrolyses. The redox potentials of the *S*,*S*′-dialkyl adducts were influenced by the electron-donating effect of the functional group on the sulfur atoms. The nickeladithiolene *S*,*S*′-dibenzyl adduct $[Ni\{S(SCH_2Ph)C_2Ph_2\}_2]$ (**2**) eliminated one benzyl radical by one-electron reduction, and then the monobenzyl adduct anion $[Ni(S_2C_2Ph_2)\{S_2(CH_2Ph)C_2Ph_2\}]^-$ (**3**$^-$) was formed. Anion **3**$^-$ was also formed by the reaction of nickeladithiolene dianion $[Ni(S_2C_2Ph_2)_2]^{2-}$ (**1**$^{2-}$) with 1 equiv of benzyl cation. When anion **3**$^-$ was oxidized, the long-lived nickeladithiolene radical $[Ni(S_2C_2Ph_2)\{S_2(CH_2Ph)C_2Ph_2\}]$ (**3**) was formed. The visible, near-IR, and ESR spectra of radical **3** could be measured and assigned. When radical **3** was further oxidized, the oxidant **3**$^+$ eliminated one benzyl cation, and then free nickeladithiolene (**1**) was generated.

Introduction

Many studies of square planar metalladithiolene complexes have been reported.[1] These complexes are interesting because of their unique redox and optical properties and "noninnocent" properties. The reactivities of metalladithiolene complexes are also well-known. The metalladithiolene ring undergoes electrophilic and radical substitution reactions due to its aromaticity.[2] The aromaticity can be also explained by noting that this ring has delocalized 6π electrons and exhibits $\pi-\pi^*$ transitions (in the near-IR area). Such a metalladithiolene complex undergoes cycloaddition by the reactions with an olefin and a conjugated diene, forming the metalladithiolene adducts.[3] This reaction always occurs on the two sulfur atoms rather than on the center metal. (In this paper, such adducts are described as *S*,*S*′-adducts.)

Recently, Wang and Stiefel have reported that the nickeladithiolene complex with electron-withdrawing groups even reacts with simple olefins to give olefin-bound *S*,*S*′-adducts. They proposed that it is reversible olefin binding controlled electrochemically. When the olefin-bound adduct is reduced, the reductant dissociates and forms an olefin and the metalladithiolene anion. When this anion is oxidized, the oxidant (neutral complex) binds the olefin again. This reversible olefin binding is proposed as a separation and purification system of an olefin gas.[4] Quite recently, the cycloaddition of a simple olefin and the structure of the olefin adduct have also been investigated by theoretical studies.[5] Geiger has reinvestigated the electrochemical behavior of the norbornene-bridged nickeladithiolene *S*,*S*′-adduct. This adduct similarly dissociates norbornene by an electrochemical reduction.[6]

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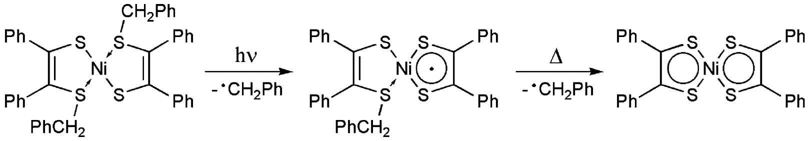
Scheme 1



Many metalladithiolene *S,S′*-adducts lead to photodissociation. The norbornene-bridged *S,S′*-adducts of metalladithiolene complexes, $[M(S_2C_2R_2)_2(C_7H_8)]$ (M = Ni, Pd, Pt; C_7H_8 = norbornene), lead to photodissociation in dichloromethane solution,[7] forming free metalladithiolene complex and norbornadiene. The norbornene-bridged *S,S′*-adduct of platinum complex shows emission in benzene solution.[8] On the other hand, the metalladithiolene *S,S′*-dibenzyl adducts,[9] $[M\{S(SCH_2Ph)C_2Ph_2\}_2]$ (M = Ni, Pd, Pt), eliminate one benzyl radical by photodissociation, and then the long-lived metalladithiolene radical[10] $[M(S_2C_2Ph_2)\{S_2(CH_2Ph)C_2Ph_2\}]$ is formed (Scheme 1). This unique complex radical has a lifetime on the order of 10^3 s; it is further converted to free nickeladithiolene complex by a thermal dissociation.

We focused on the electrochemical behavior of the nickeladithiolene *S,S′*-dialkyl adducts $[M\{S(SR)C_2Ph_2\}_2]$ (R = benzyl,[10] methyl,[11] and *tert*-butyl). Some of these adducts dissociated by electrochemical redox reactions, and the metalladithiolene radical was also observed in this work. This paper describes in detail the electrochemical behavior of *S,S′*-dialkyl adducts and the formation mechanisms of long-lived metalladithiolene radicals by electrochemical redox reactions.

Results and Discussion

The cyclic voltammetry (CV) of the nickeladithiolene *S,S′*-dialkyl adducts $[Ni\{S(SCH_2Ph)C_2Ph_2\}_2]$ (**2**), $[Ni\{S(SMe)C_2Ph_2\}_2]$ (**4**), and $[Ni\{S(S\text{-}t\text{-}Bu)C_2Ph_2\}_2]$ (**5**) and of the free nickeladithiolene complex $[Ni(S_2C_2Ph_2)_2]$ (**1**)[3a,12] was measured (Figures 1a−e). The redox potentials of these complexes are shown in Table 1. The reduction potentials of all adducts were more negative than that of complex **1**. Although free nickeladithiolene complex **1** showed two reversible reduction waves ($E_{1/2}$ = −0.51 and −1.33 V), all of the adducts showed only one reduction wave in the potential window of dichloromethane containing TBAP. The redox potentials of nickeladithiolene *S,S′*-dialkyl adducts were influenced by the electron-donating effect of the functional group on the sulfur atom.

Table 1. Redox Potentials (vs Fc/Fc^+)[a]

complex	temp	1st redn $E_{1/2}$/V	1st oxidn $E_{1/2}$/V
1	rt	-0.51^{r}	0.78^{ir}
2	rt	-1.74^{ir}	0.38^{ir}
3	rt	-0.54^{r}	0.30^{ir}
4	rt	-1.76^{r}	0.36^{ir}
5	rt	-1.83^{ir}	0.34^{r}
6	−40 °C	-1.88^{r}	0.34^{r}

[a] rt: room temperature. r: reversible wave. ir: irreversible wave. $E_{1/2} = (E_p + E_{p/2})/2$.

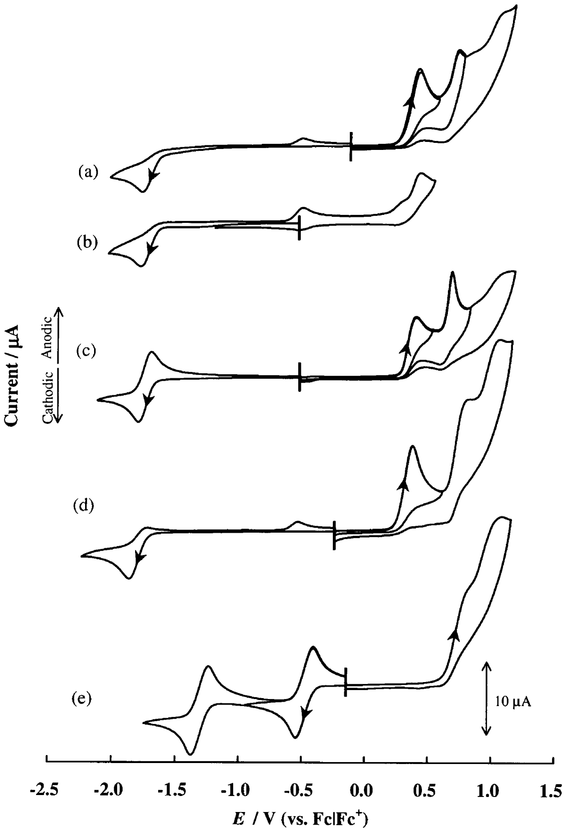


Figure 1. (a−e) Cyclic voltammograms (v = 100 mV·s^{-1}, Φ = 1.6 mm Pt disk) of 1 mM (a, b) complex **2**, (c) complex **4**, (d) complex **5**, and (e) complex **1**.

The CV of complex **2** showed an irreversible reduction wave ($E_{1/2}$ = −1.74 V) and some irreversible oxidation waves. The oxidation process of complex **2** was complicated, and the reaction mechanism has not yet been made clear. The reductant of complex **2** was unstable on the CV time scale, and it was converted to an unknown species $\mathbf{X}^-$ by the following chemical reaction. When the potential was scanned to positive after the reduction, a reversible reoxidation wave ($\mathbf{X}/\mathbf{X}^-$) appeared at −0.54 V (Figure 1b). Therefore, the unknown redox species $\mathbf{X}^-$ and **X** were stable on the CV time scale. This reoxidation wave does not correspond to the redox wave of complex **1** (Figure 1e). When the potential was scanned to positive after the

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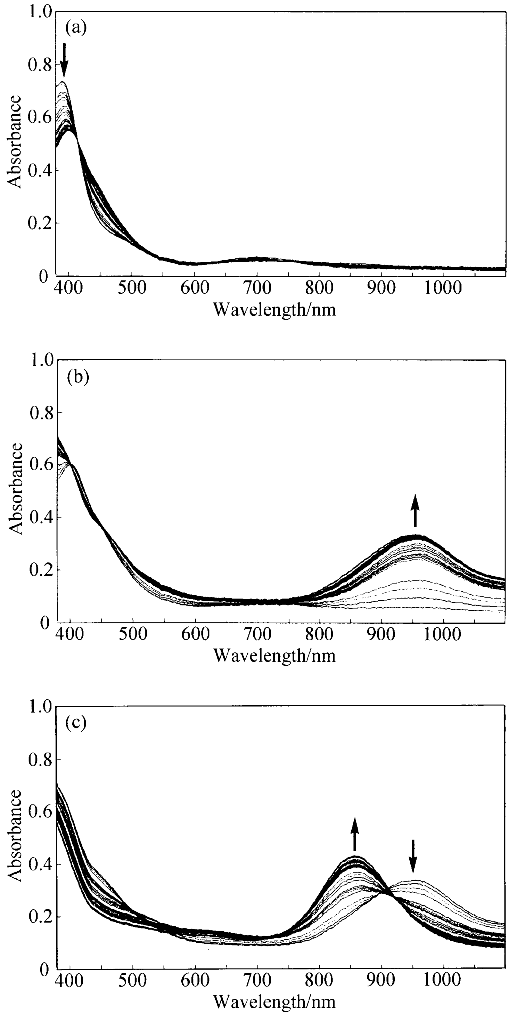
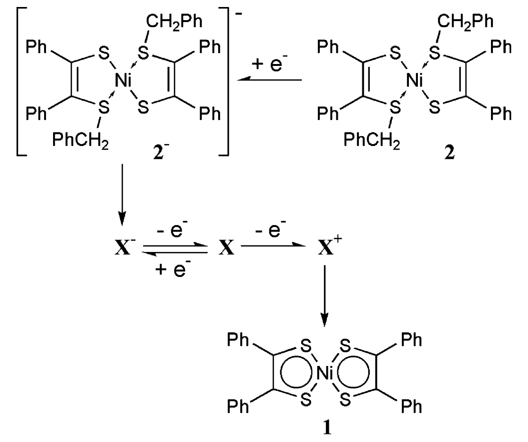


Figure 2. (a−c) Visible and near-IR spectral changes of complex **2** during (a) one-electron reduction (−1.90 V, sampling time 2 min, sampling interval 4 s), (b) reoxidation (−0.30 V, sampling time 1 min, sampling interval 2 s), and (c) reoxidation (+0.50 V, sampling time 1 min, sampling interval 2 s) using an OTTLE cell.

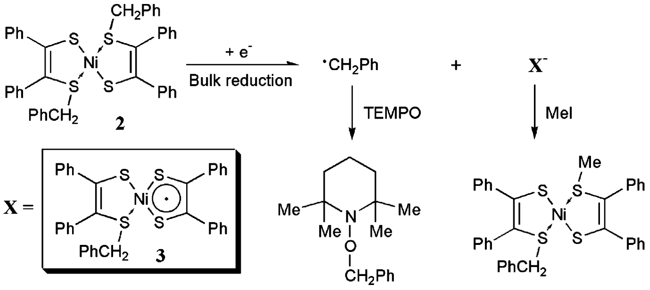
formation of **X**, the irreversible oxidation wave corresponding to $\mathbf{X}^+$/**X** couple appeared at +0.30 V (Figure 1b). The unknown species $\mathbf{X}^+$ was unstable on the CV time scale.

We attempted in situ measurements of the visible and near-IR absorption spectra following an electrochemical redox reaction using an optically transparent thin-layer electrode (OTTLE) cell. The spectral changes were not remarkable during the reduction of complex **2**. The spectrum of $\mathbf{X}^-$ was similar to that of complex **2** (Figure 2a). When the potential was jumped at −0.30 V, absorption appeared around 950 nm (Figure 2b), and this absorption was assumed to be that of **X** as an oxidant of $\mathbf{X}^-$. The absorption of **X** is similar to that of nickeladithiolene anion $\mathbf{1}^-$. However, the two redox potentials are different (Figure 1a,e). When the potential was jumped at +0.50 V, these spectral changes showed more blue shift than that of **X** and did not show an isosbestic point (Figure 2c). The maximum absorption was around 850 nm, and this absorption corresponds to free nickeladithiolene complex **1**.[3a] We assume the oxidant $\mathbf{X}^+$ was converted to complex **1** by elimination of the benzyl cation. This electrochemical behavior is summarized in Scheme 2.

Scheme 2



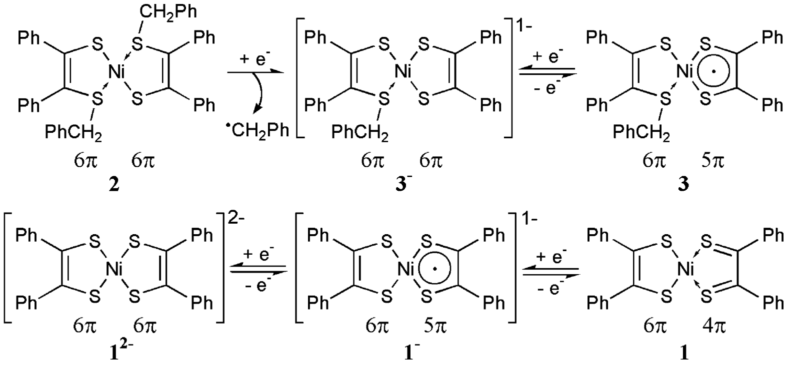
Scheme 3



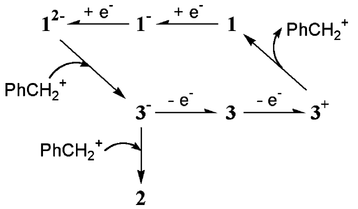
The bulk electrolysis of complex **2** was performed. The coulometry of complex **2** revealed 1.1 as the number of electrons/molecule passed in reduction. The bulk electrolysis of complex **2** in the presence of TEMPO at the same condition (1.0 F/mol) was also examined. We confirmed the generation of TEMPO−CH_2Ph (Scheme 3). Complex **2** did not react with TEMPO at all. These results suggest that the benzyl radical generates by the reduction process of complex **2**. In addition, complex **2** was reduced by the bulk electrolysis at −1.93 V (0.87 F/mol), and then methyl iodide was added to the solution. The nickeladithiolene adduct $[Ni\{S_2(CH_2Ph)C_2Ph_2\}\{S_2(Me)C_2Ph_2\}]$ was formed. This adduct had one benzyl group and one methyl group on the sulfur atoms of the dithiolene ring (Scheme 3). On the other hand, complex **2** did not react with methyl iodide at room temperature. We assumed that when complex **2** was reduced, the monobenzyl adduct anion $[Ni(S_2C_2Ph_2)\{S_2(CH_2Ph)C_2Ph_2\}]^-$ ($\mathbf{3}^-$) was formed. We identified the unknown species $\mathbf{X}^-$ as anion $\mathbf{3}^-$. The oxidant of anion $\mathbf{3}^-$, namely, the monobenzyl adduct $[Ni(S_2C_2Ph_2)\{S_2(CH_2Ph)C_2Ph_2\}]$ (**3**), has already been reported and is known as a long-lived metalladithiolene radical.[10] It can also be formed by the photodissociation of complex **2**.

The visible and near-IR absorptions of dithiolene complexes can be distinguished from the π-electron numbers of the dithiolene ring. The π-electron numbers of the dithiolene ring in complexes **2** and $\mathbf{3}^-$ are same. Furthermore, complexes $\mathbf{1}^-$ and **3** have the same number of π-electrons in dithiolene rings. We have reported the electron counting in the metalladithiolene rings of complex **3**.[10b] These support the spectra observed using the OTTLE (Figures 2a−c). The

Scheme 4



Scheme 5



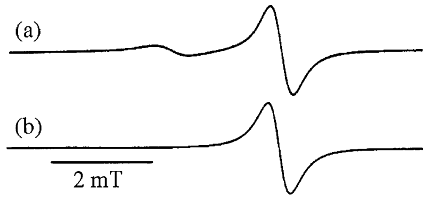


Figure 3. ESR spectra after electrolysis of complex **2**: (a) observed spectrum; (b) simulated spectrum of **3**.

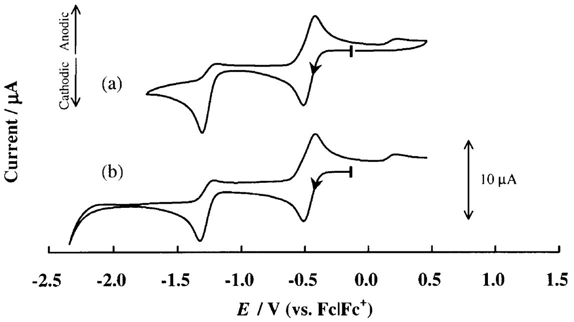


Figure 4. Cyclic voltammograms (v = 100 mV·s^{-1}, Φ = 1.6 mm Pt disk) of complex **1** in the presence of benzyl bromide: (a) in two-electron reduction and reoxidation processes; (b) until measurement limit in a negative potential window.

redox states and the π-electron numbers of dithiolene rings are shown in Scheme 4.

We also measured the ESR spectrum of radical **3**, after radical **3** was formed by electrolysis. The two signal mixture of the isotropic spectra appeared (Figure 3). A smaller signal corresponds to the isotropic spectrum of anion $\mathbf{1}^-$ (g = 2.057),[12a,13] and a larger signal corresponds to the isotropic spectrum of radical **3**. The g value of radical **3** (2.044) was the same as that previously reported[10] (2.042). This result also suggests that **X** is monobenzyl adduct **3**, as did the results of visible and near-IR spectra. We assume that anion $\mathbf{1}^-$ was formed by the decomposition of complex **3**.

The CVs of complexes **4** and **5** are shown in Figure 1c,d. The CV of *S*,*S*′-dimethyl adduct **4** showed a reversible reduction wave and three irreversible oxidation waves. The reductant of complex **4** was stable on the CV time scale. The oxidation process of complex **4** was complicated. Complex **5** showed three irreversible oxidation waves. The second and third oxidation waves corresponded to the oxidation waves of complex **1**. Therefore, when complex **5** was oxidized, the oxidant rapidly eliminated two *tert*-butyl groups, and complex **1** was generated. On the other hand, though the CV of adduct **5** showed a slightly irreversible reduction wave, a reoxidation wave appeared at −0.55 V. Therefore, since the electrochemical behavior of complex **5** is similar to that of complex **2**, we assumed the formation of the corresponding metalladithiolene radical [$Ni(S_2C_2Ph_2)\{S_2(t\text{-}Bu)C_2Ph_2\}$]. In the CV of complex **5** at −40 °C, a reversible reduction wave was confirmed. On the other hand, the reduction wave of complex **2** was irreversible even at −40 °C. The reductant of complex **5** was stable at low temperature on the CV time scale. Therefore, the reductant of complex **5** is more stable than that of complex **2** and less stable than that of complex **4**. We assumed that the lifetime of the reductant relates to the stability of an eliminated radical (stability: benzyl radical > *tert*-butyl radical > methyl radical). If a reductant becomes less stable, the radical eliminated from a reductant becomes more stable (stability: $\mathbf{4}^- > \mathbf{5}^- > \mathbf{2}^-$).

The CV of complex **1** in the presence of benzyl bromide (10 equiv) was measured. Although the first reduction wave (−0.51 V) was reversible, the second reduction wave (−1.33 V) was irreversible (Figure 4a). These results suggest that dianion $\mathbf{1}^{2-}$ reacted with benzyl bromide on the CV time scale. However, the reduction wave of dibenzyl adduct **2** was not observed (Figure 4b). When the potential was scanned to positive after the two-electron reduction of complex **1**, two reoxidation waves appeared around −0.54 and +0.3 V. (The former reoxidation wave could be confirmed as the shoulder of the wave of $\mathbf{1}/\mathbf{1}^-$.) These reoxidation waves correspond to the waves of the redox couples of $\mathbf{3}^-/\mathbf{3}$ and $\mathbf{3}/\mathbf{3}^+$. These results suggest that dianion $\mathbf{1}^{2-}$ reacts with one benzyl cation to give the anion of monobenzyl adduct $\mathbf{3}^-$ on the CV time scale (Scheme 5).

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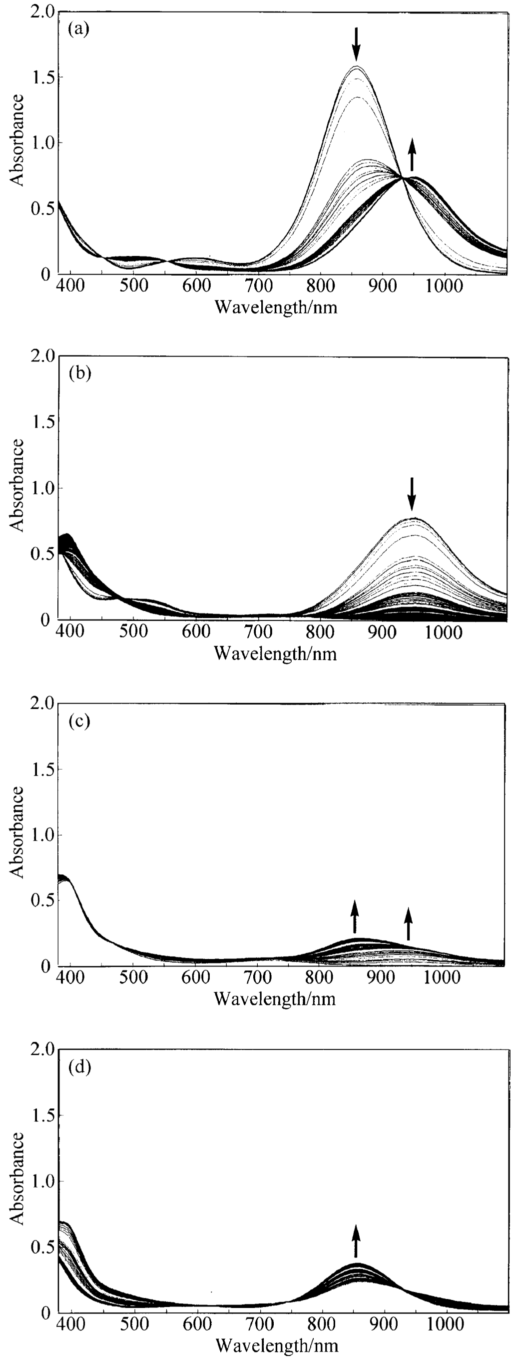
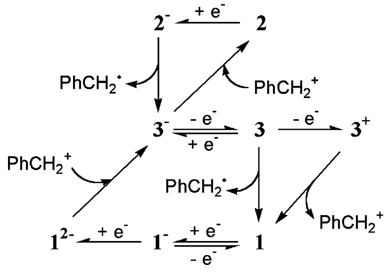


Figure 5. (a−d) Visible and near-IR spectral changes of complex **1** in the presence of benzyl bromide during (a) one-electron reduction (−0.90 V, sampling time 1 min, sampling interval 2 s), (b) two-electron reduction (−1.50 V, sampling time 5 min, sampling interval 2 s), (c) reoxidation (−0.10 V, sampling time 1 min, sampling interval 2 s) after two-electron reduction, and (d) reoxidation (+0.50 V, sampling time 1 min, sampling interval 2 s) after two-electron reduction.

The visible and near-IR absorption spectra of the mixture of complex **1** with benzyl bromide (10 equiv) were measured using the OTTLE cell. The spectrum changed to that of anion $\mathbf{1}^-$ at −0.90 V, and the spectral changes showed an isosbestic point around 930 nm (Figure 5a). This result suggests no reaction of anion $\mathbf{1}^-$ with benzyl cation. In a second reduction at −1.50 V, the absorption based on $\pi-\pi^*$ transition disappeared, and then the analogue spectra of anion $\mathbf{3}^-$ appeared (Figure 5b). At this potential, the formations of dianion $\mathbf{1}^{2-}$ and complex **2** are also conceivable. However, the spectra of three species could not be distinguished, because these complexes contain the same numbers of π-electrons in the dithiolene ring (see Scheme 4). When the potential was jumped at −0.10 V, maximum absorptions appeared around 850 and 950 nm (Figure 5c). These spectra correspond to those of complexes **1** and **3**, respectively. In this potential, although anion $\mathbf{3}^-$ is oxidized to neutral adduct **3**, dianion $\mathbf{1}^{2-}$ should be also oxidized to neutral complex **1**. It is conceivable that dianion $\mathbf{1}^{2-}$ did not completely react with benzyl cation. In addition, when the potential was jumped at +0.50 V, the absorption of complex **3** decreased and the absorption of complex **1** increased (Figure 5d). This can be explained by the fact that cation $\mathbf{3}^+$ was converted to complex **1** by the elimination of benzyl cation (Scheme 5).

Scheme 6



Conclusion

We investigated the electrochemical behavior of the nickeladithiolene *S,S′*-dialkyl adducts (alkyl = benzyl, methyl, and *tert*-butyl) using various electrochemical measurements. The *S,S′*-dibenzyl adduct **2** eliminated one benzyl radical by one-electron reduction, and then the monobenzyl adduct anion $\mathbf{3}^-$ was formed. Anion $\mathbf{3}^-$ was also generated by the reaction of dianion $\mathbf{1}^{2-}$ with one benzyl cation. Complex **2** can be synthesized by dianion $\mathbf{1}^{2-}$ with two benzyl cations.[10] Therefore, anion $\mathbf{3}^-$ reacts with another benzyl cation, and then nickeladithiolene *S,S′*-dibenzyl adduct **2** is formed. The stepwise formation of complex **2** via monobenzyl adduct was revealed for the first time in this work.

When anion $\mathbf{3}^-$ was oxidized, the long-lived metalladithiolene radical **3** was formed by electrochemical redox reactions. This complex radical also forms in the photodissociation of *S,S′*-dibenzyl adduct.[10] In addition, when radical **3** was further oxidized, the corresponding cation $\mathbf{3}^+$ became unstable, and then free nickeladithiolene complex **1** was formed by the elimination of benzyl cation. Therefore, the dissociation mechanism of complex **2** was revealed to be a stepwise process for the first time. The lifetime of the reductant of *S,S′*-adduct is influenced by the group on the sulfur atoms of the dithiolene ring; therefore, if the radical eliminated from sulfur becomes more stable, the reductant of the *S,S′*-dialkyl adduct becomes less stable. Such electrochemical behavior of the nickeladithiolene *S,S′*-dialkyl adducts is summarized in Scheme 6.

Experimental Section

All synthetic reactions were carried out under argon atmosphere by means of standard Schlenk techniques. Complexes **1**, **2**, **4**, and

5 were prepared by literature methods.[3a,10b] Solvents for chemical synthesis were dried by CaH_2 and distilled before use. Solvents for electrochemical measurements were dried by molecular sieve 4A before use. The reagents were used without further treatment. Silica gel and Wakogel C-300 were obtained from Wako Pure Chemical Industries, Ltd. Mass spectra were recorded on a JEOL JMS-D300. NMR spectra were measured with a JEOL LA500 spectrometer. All electrochemical measurements were performed under argon atmosphere. In all electrochemical measurements and syntheses, a coiled platinum wire served as a counter electrode, and the reference electrode was Ag|AgCl corrected for junction potentials by being referenced internally to the ferrocene/ferrocenium ($Fc|Fc^+$) couple. Cyclic voltammetry were measured with a CV-50W of BAS Co. Visible and near-IR absorption spectra during electrolysis were measured with MCPD-7000 and MC-2530 of Otsuka Electronics Co., Ltd. ESR spectra were recorded on a JEOL X-band JES-3X ESR spectrometer. Microwave frequencies and the magnetic field were directly determined by using a microwave counter, ADVANTEST TR5212, and a field measurement unit, JEOL NMR field meter ES-FC-5, respectively.

CV Measurements. CV measurements were done in 1 mmol·dm^{-3} dichloromethane solutions of complexes containing 0.1 mol·dm^{-3} tetrabutylammonium perchlorate (TBAP) at 25 °C. A stationary platinum disk (1.6 mm in diameter) was used as a working electrode.

Visible Absorption and Near-IR Spectral Measurements during Electrolysis. The visible and near-IR absorption spectra during electrolysis were obtained for 1 mmol·dm^{-3} dichloromethane solutions of complexes containing 0.1 mol·dm^{-3} TBAP at 25 °C in an optically transparent thin-layer electrode (OTTLE) cell by using a Photal MCPD-7000 rapid scan spectrometer. The working electrode was stationary platinum mesh.

ESR Spectral Measurements during Electrolysis. ESR spectra were obtained for ca. 5 mmol·dm^{-3} dichloromethane solutions of complexes containing 0.1 mol·dm^{-3} TBAP at 293 K by electrolysis.

Coulometry Measurement. Coulometry measurements were done in ca. 0.12 mmol·dm^{-3} dichloromethane solutions of complexes containing 0.1 mol·dm^{-3} TBAP at 25 °C. A stationary platinum plate was used as a working electrode.

Radical Trapping by 2,2,6,6-Tetramethylpiperidine *N*-Oxyl (TEMPO). The mixture of complex **2** and 100 equiv of TEMPO as a radical scavenger in dichloromethane solutions containing 0.1 mol·dm^{-3} TBAP was subjected to bulk electrolysis (−1.93 V, 1.0 F/mol). A stationary platinum plate was used as a working electrode. The product was separated by column chromatography on silica gel. Spectroscopic data for TEMPO−CH_2Ph were as follows: GC-mass (EI$^+$, 1.3 kV) *m*/*z* 156 (TEMPO$^+$), 91 (CH_2Ph^+); mass (FAB$^+$, 70 eV, NBA) *m*/*z* 248 (TEMPO − CH_2Ph^+ + 1), 156 (TEMPO$^+$), 91 (CH_2Ph^+); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26−7.39 (m, 5H, Ph), 4.83 (s, 2H, CH_2), 1.36−1.68 (m, 6H, CH_2), 1.26 (s, 6H, Me), 1.15 (s, 6H, Me).

Reaction of Anion 3$^-$ with Methyl Iodide. Complex **2** in dichloromethane solution containing 0.1 mol·dm^{-3} TBAP was subjected to bulk electrolysis. A stationary platinum plate was used as a working electrode. After the bulk electrolysis (−1.93 V, 0.87 F/mol), 10 equiv of methyl iodide was added to this solution and the mixture was stirred at room temperature for 20 h. The product was separated by column chromatography on silica gel and HPLC. Spectroscopic data for complex $[Ni\{S_2(CH_2Ph)C_2Ph_2\}\{S_2(Me)C_2Ph_2\}]$ were as follows: mass (FAB$^+$, 70 eV, NBA) *m*/*z* 649 (M$^+$ + 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95−7.49 (m, 25H, Ph), 4.04 (s, 2H, CH_2), 2.34 (s, 3H, Me).

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