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Formation, structure, and reactivities of 1:1 adducts between quadricyclane and (η^5-cyclopentadienyl)(1,2-diphenyl- or -dimethoxycarbonyl-1,2-ethenedithiolato)rhodium(III)

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Abstract

The rhodiadithiolene complexes [Rh(Cp)($S_2C_2Z_2$)] (Z = Ph (**1a**) and COOMe (**1b**)) reacted with quadricyclane (Q) to give 1:1 adducts [Rh(Cp)($S_2C_2Z_2$) (C_7H_8)] (Z = Ph (**2a**) and COOMe (**2b**)) in which Rh and S of the complexes are bridged by C(7) (bridge carbons) and C(5) (edge carbons) of norbornene (C_7H_8), respectively. The structure of the adduct **2a** was re-investigated and determined by X-ray structural analysis. The rhodiadithiolene complexes and those adducts showed the catalytic activities for the thermal isomerization from Q to norbornadiene (NBD). Adduct **2a** photochemically dissociated to give the original complex **1a** and NBD upon irradiation with a high-pressure mercury lamp. Skeletal rearrangements of the hydrocarbon moiety were confirmed in the formation of these adducts and in their photo-dissociation, according to deuterium labeling experiments.

Keywords: Rhodiadithiolene; Quadricyclane; Norbornadiene; Adduct; Isomerization

1. Introduction

A five-membered metallacycle, metalladichalcogenolene, which consists of one transition metal atom, two coordinated chalcogen atoms, and two unsaturated carbon atoms, has unique physical and chemical properties [1]. The remarkable features of this metalladichalcogenolene ring result from the coexistence of aromatic character due to a conjugated system with 6π electrons [2], and unsaturation especially at the central metal and at the chalcogen atoms in the ring [3].

In spite of their interesting electronic structure, the chemistry of the metalladichalcogenolenes has not so far been investigated extensively from the standpoint of their reactivities. We have thus attempted to elucidate the unique reactivities of metalladichalcogenolene rings.

Characteristic addition reactions due to their unsaturation occur at the central metal or at the metal–chalcogen bond. We have reported a variety of such addition reactions in (η^5-cyclopentadienyl)(substituted 1,2-ethenedichalcogenolato)cobalt(III) and rhodium(III) complexes: the additions of phosphines and phosphites to the central metal [4], those of diazo compounds [5] or organic azides [6] to the metal–chalcogen bonds to form the three-membered metallacycles, and that of an electron deficient alkyne [7] to the metal–chalcogen bond to form the four-membered metallacycle.

We have also reported the addition reactions of quadricyclane (Q) to the metal–chalcogen bonds to form the five-membered metallacycles [8,9]. It has been known that the square planar bis(1,2-diphenyl-1,2-ethenedithiolato)metal complexes (metal = Ni, Pd, and Pt) form 1:1 adducts with dienes, such as norbornadiene (NBD) [10] and 2,3-dimethyl-1,3-butadiene [11], and

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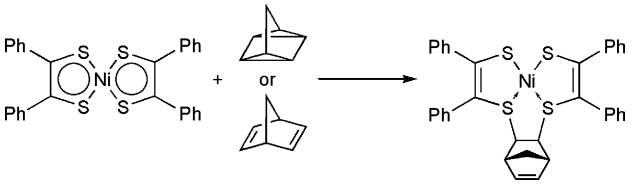
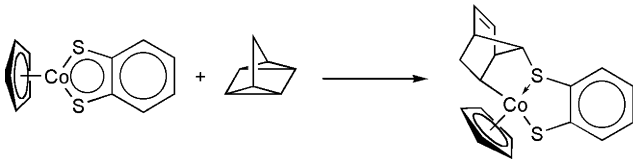
with strained molecules, such as quadricyclane (Eq. (1)) [12]. However, the reports on the adduct formation between the dithiolato-metal complexes and NBD or Q are mainly limited to bis(dithiolato)metal complexes, except for our studies [8,9] concerning the mono(dithiolato)metal complexes with a cyclopentadienyl ligand. Recently, as an extension of our results, Kang and coworkers [13] have reported that the reaction of the (*o*-carboranedithiolato)iridium(III) complex, [Ir(Cp*)($S_2C_2B_{10}H_{10}$)], with quadricyclane affords an interesting 1:1 addition product, and undergoes the unique isomerization of a quadricyclane unit



(1)

In the previous paper, as a first example of addition (insertion) of strained hydrocarbons into a metal–sulfur bond, we reported that the reaction between Q and (η^5-cyclopentadienyl)(1,2-benzenedithiolato)cobalt(III) gives several 1:1 adducts, the main one of which has a unique structure: the 5(edge carbon)- and the 7(bridge carbon)-positions of norbornene are bonded to the Co–S bond of the (dithiolato)cobalt complex, respectively (Eq. (2)) [9]. The anormalous structure of the Co adduct led us to reinvestigate the structure of the Rh adduct reported previously [8].



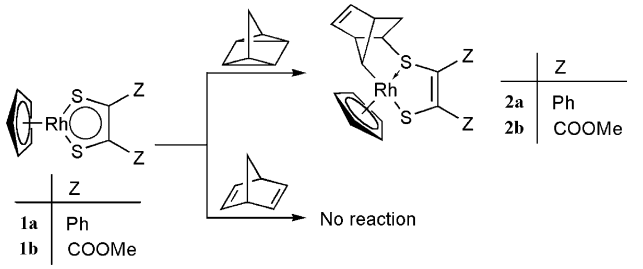
(2)

We report here the true structure of the 1:1 adduct between (η^5-cyclopentadienyl)(1,2-diphenyl-1,2-ethenedithiolato)rhodium(III) and Q by X-ray structure analysis, the formation mechanism of these adducts, and the thermal, electrochemical, and photochemical behavior of these adducts. This paper explains that the manner of the addition of Q to the Rh complex is similar to that of Q to (η^5-cyclopentadienyl)(1,2-benzenedithiolato)cobalt(III) [8], but the positions of the addition of Q to the metal–S bond are different.

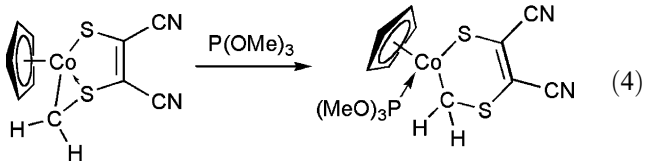
2. Results and discussion

2.1. Formation of adduct

The adducts were prepared by heating [Rh(Cp)($S_2C_2Ph_2$)] (**1a**) and [Rh(Cp)(S_2C_2(COOMe)$_2$)] (**1b**) complexes in neat quadricyclane (Q) under Ar atmosphere. The norbornene adducts [Rh(Cp)($S_2C_2Ph_2$) (C_7H_8)] (**2a**) and [Rh(Cp)(S_2C_2(COOMe)$_2$)(C_7H_8)] (**2b**) were obtained in 85% and 81% yields (Eq. (3)), respectively, as a sole product under refluxing for 6 and 2 h, respectively. During the reactions, Q was isomerized in part to norbornadiene (NBD). Under the same conditions, complex **1a** did not react with NBD (Eq. (4))



(3)



(4)

2.2. Structure of adduct

The ORTEP drawing of **2a** is given in Fig. 1. The selected bond angles and the bond lengths are summarized in Table 1. Adduct **2a** had a unique structure: (1) The hydrocarbon moiety bridges between metal (Rh) and sulfur (S) of the rhodiadithiolene ring without breaking the Rh–S bond. This is a marked difference

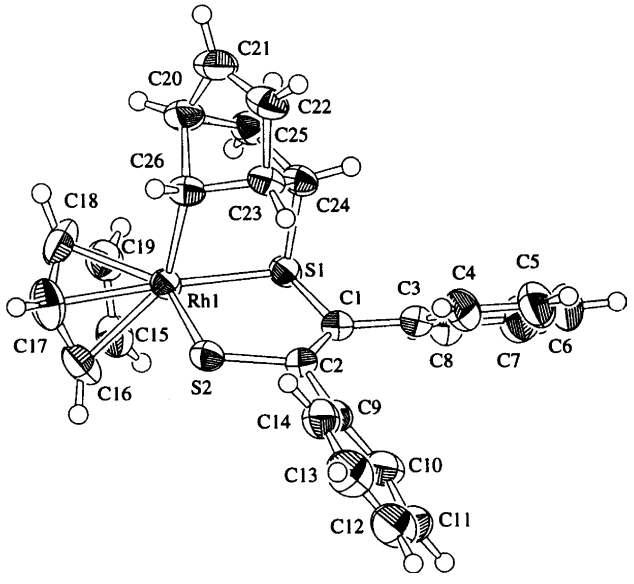


Fig. 1. ORTEP drawing of adduct **2a**.

Table 1
Selected bond distances (Å) and bond angles (°) of adduct **2a**

(a) Bond distances			
Rh1–S1	2.273(2)	S1–C24	1.818(8)
Rh1–S2	2.321(2)	C1–C2	1.35(1)
Rh1–C26	2.067(8)	C24–C25	1.54(1)
S1–C1	1.791(8)	C20–C21	1.53(1)
S2–C2	1.746(8)		
(b) Bond angles			
S1–Rh1–C2	86.93(7)	Rh1–S2–C2	104.6(3)
S1–Rh1–C26	82.3(2)	S1C1–C2	118.1(6)
S2–Rh1–C26	90.8(2)	S2C2–C1	123.3(6)
Rh1–S1–C1	106.8(3)	C20–C26–C23	92.9(6)

from the case of **2a** and from the reported cases of bis(dithiolato)metal complexes (metal = Ni, Pd, and Pt) [2,12], in which the hydrocarbon bridges between two sulfur atoms of two different dithiolene rings. (2) The position of bridging was unusual: Rh and S are bridged by the C26 (bridge carbon) and the C24 (edge carbon) of C_7H_8, respectively.

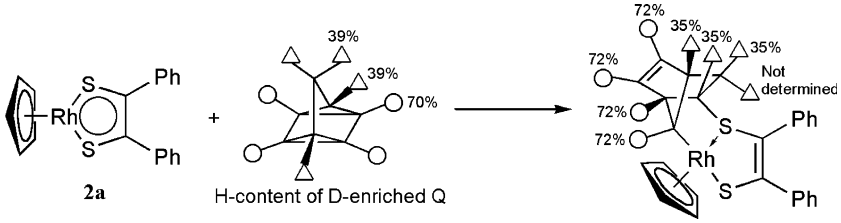
Adduct **2a** had a piano-stool structure and was a six-coordinate complex, in which the central metal was coordinatively saturated. The rhodiadithiolene ring was folded at two sulfur atoms, and the angle of the plane consisting of S–Rh–S and of S–C–C–S was 174.5°. The bond angle of S1–Rh1–S2 was 86.93(7)°. The bond length of 2.273(2) between Rh1 and S1 bonded to C_7H_8 was somewhat shorter than that of 2.321(2)Å between Rh1 and S2. The bond length of C1–C2 was 1.35(1), which showed its double bond character. The structure of adduct **2b** having ester groups was also suggested to be similar to that of adduct **2a** having phenyl groups, on the basis of the similarity of the NMR spectra.

2.3. Mechanism of adduct formation

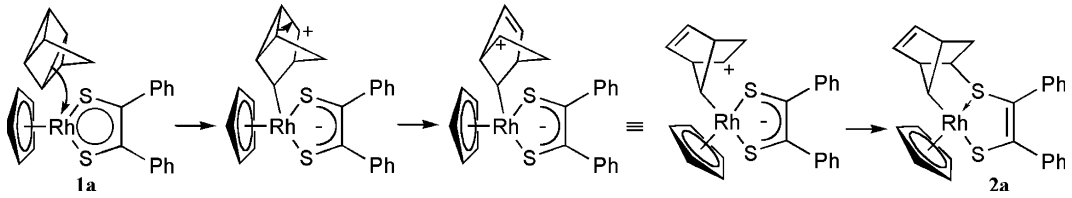
For the elucidation of the reaction mechanism for adduct formation, we used a deuterium labeled quadricyclane that has 70% of 1H content (averaged content) at the edge positions (marked as circles in Scheme 1), and 39% 1H content (averaged content) at the bridge and the bridgehead positions (marked as triangles in Scheme 1). The analysis of ^{1}H NMR of the adducts **2a** from deuterated Q and complex **1a** gave the following results: (1) Two geminal hydrogens at the edge (bonded to C(6)) in adduct **2a** have the same 1H content as that at the bridge in the deuterated Q. (2) Two bridgehead hydrogens have different 1H contents.

These results strongly suggest that only one skeletal rearrangement was involved and that no hydrogen atom shift takes place in the formation of the adducts. A possible mechanism for the formation of adduct **2a** is shown in Scheme 2. The addition of Q to complex **1a** can be considered as the following stepwise processes. (1) The initial step is the attack of electron-rich carbons of Q to the positively charged Rh metal: The bond between the edge carbons of three-membered rings of Q is cleaved to form the singly bonded intermediate. A positively charged C_7H_8 moiety and a negatively charged metalladithiolene ring are produced. (2) The skeletal carbon rearrangement occurs in the hydrocarbon moiety to form a more stabilized carbenium ion. (3) The positively charged C binds with a negatively charged sulfur atom of the dithiolene ring.

The mechanism in which Q approaches to complex **1a** from the back side of four-membered ring can be excluded, since the four-membered ring side approach requires a shift of hydrogen atoms in order to produce adduct **2a**.



Scheme 1.



Scheme 2.

Comparison of the above results with the cycloaddition reactions of Q or NBD with organic unsaturated compounds is of interest in view of the elucidation of the characteristic features of rhodiadithiolene: Sasaki et al. [14] reported that the reaction of NBD with chlorocyanoacetylene affords the [2 + 2] cycloadduct (**4**) and its skeletal rearrangement product (**5**) via an ionic intermediate (**6**), together with homo-Diels–Alder adduct (**3**) (Scheme 3). Thus, the formation of compound **5** suggests that an ionic cycloaddition initiated by an exo approach of chlorocyanoacetylene to NBD is competing with the homo-Diels-Alder reaction. This fact could be reasonably explained by assuming the initial formation of a zwitterionic intermediate **6**, which can cyclize to compound **5** after a Wagner–Meerwein rearrangement. Also, as expected from the report of Tabushi et al. [15], Q reacts with an alkyne or with an alkene to afford a [2 + 2 + 2] cycloadduct like compound **4**. Interestingly, in the reaction between Q and the Rh complex **1a**, the structure of the Rh adduct **2a** is an analogue of compound **5**, not of compound **6**. As seen in Scheme 3, the mechanism of adduct formation seems to be similar to that of compound **5**, although NBD does not react with the original Rh complex **1a**. Therefore, the intermediate in the first step in Scheme 3 should be very important to give the Rh adduct.

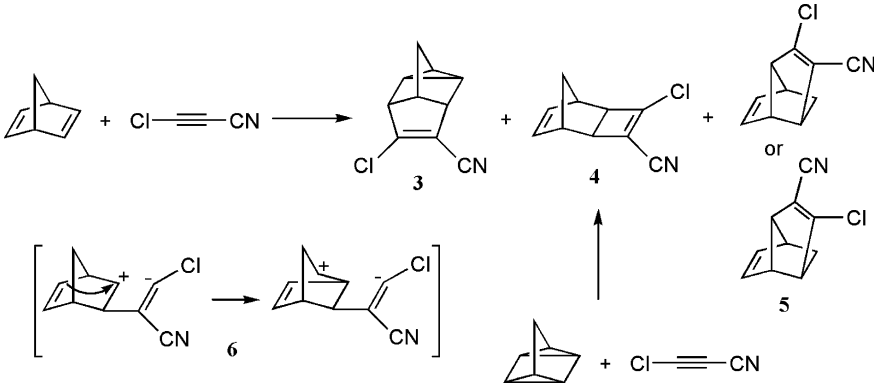
In the reaction of (η^5-cyclopentadienyl)(1,2-benzenedithiolato)cobalt(III) and Q, the main adduct has also a unique structure, in which the 5- and 7-positions of norbornene are bonded to Co and S of the cobalt complex [8,9], respectively. Namely, the positions of the addition to Co and S atoms in the norbornene form differ from those of the Rh complex. Based on a study using deuterium-labeled Q, we proposed a possible mechanism shown in Scheme 4. The mechanism in which Q approaches to the cobalt complex from the front side of the four-membered ring can be excluded, as the four-membered ring side approach requires the shift of a hydrogen atom to produce the adduct of the Co complex.

2.4. Reactivities of adduct

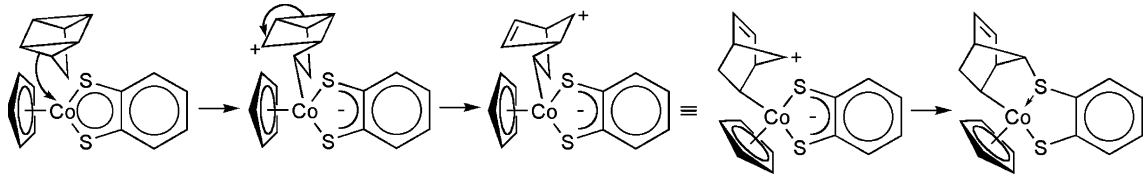
2.4.1. Thermal reactivity: catalysts for isomerization from Q to NBD

The Rh adducts **2a** and **2b** are thermally stable in the solid state and in DMSO or Q solution, while the Co adducts were dissociated thermally under the same conditions to regenerate the original Co complex and NBD, which is an isomerization product of Q [16]. Even if the deuterium-labeled adduct **2b′**, which was formed in the reaction of complex **1b** and deuterium-labeled Q ($C_{76}H_2$), is refluxed in unlabeled Q, the hydrocarbon unit of adduct **2b′** did not exchange with unlabeled Q.

During the adduct formation in the reaction of complex **1a** or **1b** with Q, the Q used as a solvent was isomerized to NBD. The result suggests that the complexes used showed the catalytic activities for the isomerization from Q to NBD. The catalytic activities can be embodied in the turnover number (TN = amount of NBD formed/amount of complex used), which is dependent on the reduction potentials ($E_{1/2}$ (red) vs. Ag|$AgClO_4$) of the original complexes used, as listed in Table 3. The rhodiadithiolene complex



Scheme 3.



Scheme 4.

Table 2
Crystal data for the adduct **2a**

[Rh(Cp)($S_2C_2Ph_2$)(C_7H_8)] (**2a**)	
Formula	$C_{26}H_{23}S_2Rh$
Formula weight	502.49
T (K)	296
Crystal color	orange
Crystal habit	platelet
Crystal system	monoclinic
Space group	$P2_1/a$(#14)
a (Å)	15.0365(3)
b (Å)	11.4270(3)
c (Å)	15.1250(5)
β (°)	101.7370(8)
V (Å^3)	2544.5(1)
Z	4
D_{calc} (g cm^{-3})	1.312
μ(Mo Kα) (cm^{-1})	8.42
Crystal size (mm)	$003 \times 0.23 \times 0.33$
$2\theta_{max}$ (°)	54.9
Unique data (R_{int})	5800 (0.052)
Observations ($I > 3.00\sigma(I), 2\theta < 54.89°$)	3976
Variables	285
R_1, wR_2	0.066, 0.095
Goodness-of-fit on F^2	2.78
Largest difference peak and hole (e Å^{-3})	1.18, −0.49

Using Rigaku RAXIS-RAPID Imaging Plate; Mo Kα (λ = 0.71069 Å).

Table 3
Turnover number (TN) of complexes used for isomerization from Q to NBD and their reduction potentials ($E_{1/2}$ (red) vs. Ag|$AgClO_4$)

Complex	TN[a] (h)	$E_{1/2}$(red) (V)
[Rh(Cp)($S_2C_2Ph_2$)] (**1a**)	3.2	−1.40
[Rh(Cp)(S_2C_2(COOMe)$_2$)] (**1b**)	42	−1.17
[Rh(Cp)(S_2C_2(CN)$_2$)] (**1c**)	258	−0.90
[Rh(Cp)($S_2C_2Ph_2$)(C_7H_8)] (**2a**)	1.7	[b]
[Rh(Cp)(S_2C_2(COOMe)$_2$)(C_7H_8)] (**2b**)	32	[b]

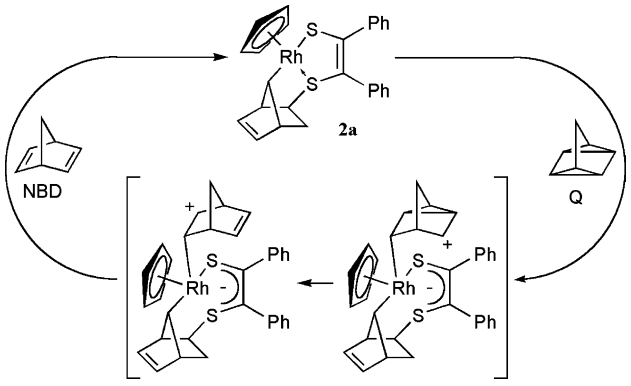
[a] Q (1 cm^3: 1×10^{-2} mol) was heated for 6 h at 120 °C in the presence of complexes (3×10^{-5} mol).
[b] Not observed in the potential window of TBAP-CH_2Cl_2.

[Rh(Cp)(S_2C_2(CN)$_2$)] (**1c**), which has a more positive reduction potential (−0.90 V) than those of complexes **1a** and **1b**, showed larger TN than those of complexes **1a** and **1b**. However, the norbornene adduct between Q and complex **1c** was not identified in this work.

When adducts **2a** and **2b** were used as catalysts, it showed also the catalytic activity (TN), although the adducts have very negative reduction potentials than those of the corresponding original complexes **1a** and **1b** [16]. The catalytic activities of adducts were somewhat lower than those of the original complexes **1a** and **1b**. From the above results, we propose a possible mechanism for the catalytic valence isomerization from Q to NBD catalyzed by adduct **2a**, as shown in Scheme 5. Based on the results that the hydrocarbon unit of the adduct is not eliminated as a NBD and that the adduct itself has some activity, the following processes can be expected: (i) after the initial interaction between the adduct and Q, an electron transfer from Q to the adduct occurs, (ii) subsequent bond formation between Rh and a carbon atom of Q results in the ring expansion from 5 to 6 rings due to the Rh–S bond cleavage, accompanied by rearrangement of the carbon skeleton occurs, and (iii) the pre-adduct (1:2 adduct) with a corner-metalated cation [17] is formed, and then the norbornene unit of pre-adduct is eliminated by the intramolecular attack of the free sulfur atom. In another report, we have reported such ring expansion reaction by the reaction of the 1:1 alkylidene adduct with $P(OMe)_3$ to give the 1:2 (or 1:1:1) adduct [Co(Cp)(S_2C_2(CN)$_2$)(CH_2)($P(OMe)_3$)] (Eq. (4)) [18]. This reaction support that the M–S bond of 1:1 adduct is possible cleaved by a nucleophilic attack to the metal center.

2.4.2. Photodissociation

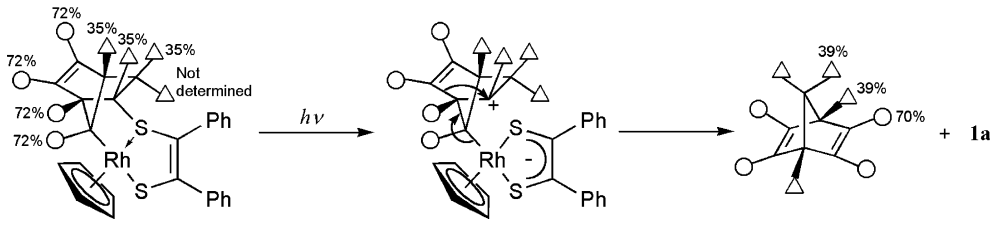
Upon irradiation in a dichloromethane solution with a medium pressure mercury lamp, adduct **2a** is dissociated to form the corresponding original complex **1a** and NBD, accompanied by skeletal rearrangement in the hydrocarbon moiety (C_7H_8). The photodissociation of adduct **2a** is wavelength-dependent. The quantum yields of the photoreaction are listed in Table 4.



Scheme 5.

Table 4
Quantum yields of photodissociation (photodecomposition) of [Rh(Cp)($S_2C_2Z_2$)(C_7H_8)] (Z = Ph (**2a**), COOMe (**2b**)) and photodecomposition of [Rh(Cp)($S_2C_2Ph_2$)] (**1a**) in CH_2Cl_2

λ (nm)	[Rh(Cp)($S_2C_2Z_2$)(C_7H_8)]		[Rh(Cp)($S_2C_2Ph_2$)] (**1a**)
	Z = Ph (**2a**)	Z = COOMe (**2b**)	
254	(0.41)	(0.05)	not determined
313	(0.01)	0	0
365	0.005	0	0
406	0.0008	0	0
436	0.0009	0	0



Scheme 6.

The types of photoreactions of adduct **2a** change depending on the wavelengths of the irradiating light. The irradiation with 365 nm light brought about the photodissociation ($\phi = 0.005$: quantum yield of photodissociation), whereas the irradiation with 254 and 313 nm causes the decomposition of the complex ($\phi = 0.41$ and 0.01, respectively: quantum yield of decomposition). On the other hand, the original complex **1a** and adduct **2b** were stable upon the irradiations with a medium pressure mercury lamp, except that with 254 nm light. A study using D-labeled adduct revealed that the norbornadiene was formed in a mechanism involving reverse skeletal rearrangement, as described in Scheme 6.

2.4.3. Electrochemical behavior of adduct *2a*

Fig. 2 shows the cyclic voltammograms (CV) of adduct **2a** in CH_2Cl_2, together with the corresponding original complex **1a**. Although the original complex **1a** exhibited a well-defined reversible reduction wave ($E_{1/2}$ (red) = −1.57 V vs. $Fc|Fc^+$) and an irreversible oxidation wave (Fig. 2(c)), the CV of adduct **2a** as a whole was shifted to more negative potential than that of the corresponding original complex **1a**. The reduction wave of adduct **2a** was not observed in the potential window (Fig. 2(a)). Namely, adduct **2a** is easier to oxidize and is more difficult to reduce than complex **1a**. This result can be explained by a potential gap between 16-electron metal complex **1a** and 18-electron metal complex **2a**. We have previously reported that the electronic effects of their substituents can control the catalytic activities for the isomerization from Q to NBD [16].

The first oxidation wave of adduct **2a** was slightly irreversible ($i_{pc}/i_{pa} = 0.73$), and this result reveals that the oxidant $\mathbf{2a}^+$ is unstable on the CV time scale. The second oxidation wave of adduct **2a** was identical to the oxidation wave of complex **1a** (Fig. 2(a)). This fact suggests that complex **1a** was formed from the oxidant $\mathbf{2a}^+$, and that the complex **1a** formed at the electrode was further oxidized. In addition, the reduction wave of complex **1a** was confirmed after the oxidation of adduct **2a** (Fig. 2(b)). Therefore, adduct **2a** was dissociated by an electrochemical oxidation to form the corresponding original complex **1a**.

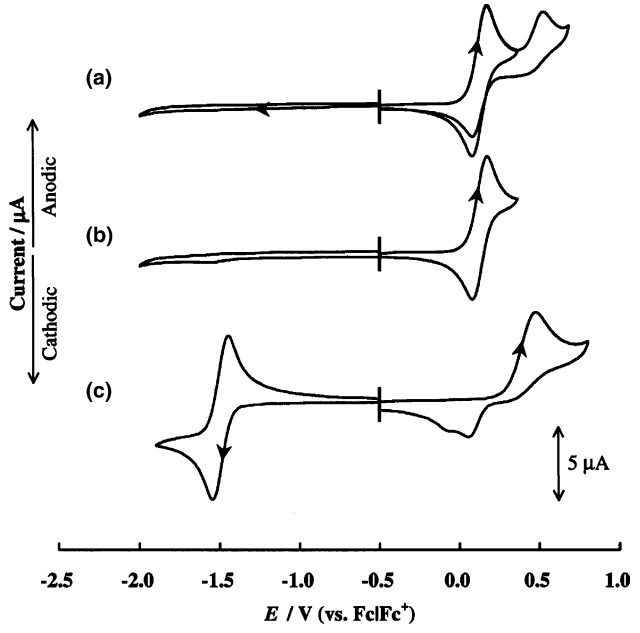


Fig. 2. Cyclic voltammograms of ($v = 100$ mV s^{-1}, $\Phi = 1.6$ mm Pt disk) of 1 mM (a, b) adduct **2a**, and (c) complex **1a** in TBAP-CH_2Cl_2 solution.

2.5. Conclusion

The norbornene adducts of rhodiadithiolene complexes, $[Rh(Cp)(S_2C_2Z_2)(C_7H_8)]$ (Z = Ph, COOMe), were formed from the rhodiadithiolene complexes having coordinatively unsaturated metal center and Q. Interestingly, the position of the addition of Q to the Rh–S bond was different from the case of the cobaltadithiolene adducts [9]. This reaction is also one example of the addition reactions due to the unsaturation of the metalladicalcogenolene ring [3–7]. This addition reaction was also unique because it thermally caused the catalytic isomerization from Q to NBD. The catalysis depended on the reduction potentials (the electron density of metal center) of rhodiadithiolene complexes. In addition, the norbornene adduct of rhodiadithiolene complex underwent unique dissociation reactions: photodissociation and electro-oxidative dissociation. These reactions always re-generated the corresponding original complex (aromatized complex) and NBD species. Skeletal rearrangements of the hydrocarbon moiety were confirmed in the formation of adducts and in their photo-dissoci-

ation according to deuterium labeling experiments. We conclude that such reversible addition and dissociation reactions of metalladicalcogenolene ring are caused by the coexistence of the aromaticity [2] and the unsaturation [3–7] of the metalladicalcogenolene ring.

3. Experimental

3.1. General remarks

Unless otherwise mentioned, all reactions were performed under an atmosphere of argon and all subsequent filtration, chromatography, and crystallization were carried out in an ambient atmosphere. Reaction solvents were purified by distillation from appropriate drying agents under argon. Quadricyclane was obtained from a commercial supplier (Aldrich). NMR spectra were obtained on a JEOL JNM GX-270 instrument and mass spectra on a JEOL JMS D300 instrument. UV–Vis and IR spectra were measured with a Hitachi spectrometer Model 228 and Hitachi spectrometer Model 260-50, respectively. Elemental analysis was carried out with a Perkin–Elmer Model 240C apparatus. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm downfield from TMS. Melting points were measured on a Yanaco model Micro melting point apparatus. HPLC was performed using model LC-908 produced by Japan Analytical Industry Co. All electrochemical measurements were performed under argon atmosphere. Cyclic voltammetry were measured on CV-50W of BAS Co.

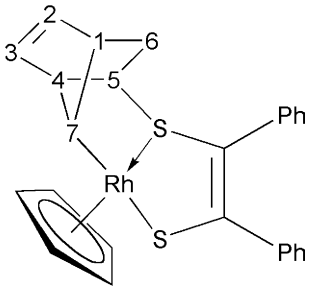
3.2. Preparations of complexes

3.2.1. Preparation of complex *1a*

Complex **1a** was prepared according to the method reported [8]. The complex **1a** was obtained by the one-pot reaction of [Rh(Cp)(cod)] (0.700 g, 2.53×10^{-3} mol), diphenylacetylene (0.680 g, 3.82×10^{-3} mol), and elemental sulfur (0.200 g, 6.25×10^{-3} mol as a S) in 10% yield (107 mg). Further purification of complex **1a** was carried out using preparative HPLC.

3.2.2. Preparation of adduct *2a*

In a 50 cm^3 three-necked flask was placed complex **1a** (50 mg, 1.2×10cm^{-4} mol) and to this was added previously argon-purged Q (10 cm^3, 1.0×10^{-1} mol). The mixture was heated to reflux (120 °C, 6 h) under a stream of argon. After the reaction, excess Q was removed under reduced pressure and the residue was chromatographed on silica-gel (300 mesh; eluent: $C_6H_{14}/CH_2Cl_2 = 1{:}1$, v/v). Adduct **2a** was obtained as a sole product from the second brown band of the column chromatography (eluent: $C_6H_{14}/CH_2Cl_2 = 3{:}1$,v/v) in 85% yield (52 mg). Orange crystal (**2a**); m.p. 155–156 °C. *Anal.* Calc. for $C_{26}H_{23}S_2Rh$: C, 62.15; H, 4.61. Found: C, 62.02; H, 4.86%. ^{1}H NMR (270 MHz, $CDCl_3$, vs. TMS): 1.25 (ddd, $J_{gem} = 12.6$, $J_{6-5} = 6.8$, $J_{6-7} = 1.8$ Hz, 1H, $H_{6\text{-endo}}$), 1.60 (dd, $J_{gem} = 12.6$, $J_{6-1} = 4.2$ Hz, 1H, $H_{6\text{-exo}}$), 2.45 (dd, $J_{5-6} = 6.8$, $J_{7-5} = 1.5$ Hz, 1H, $H_{5\text{-endo}}$), 2.81 (ddd, $J_{1-6} = 4.2$, $J_{1-2} = 3.3$, $J_{1-3} = 0.7$ Hz, 1H, H_1), 3.15 (d, $J_{4-3} = 3.1$ Hz, 1H, H_4), 3.44 (dd, $J_{7-6} = 1.8$, $J_{7-5} = 1.5$ Hz, 1H, H_7), 5.33 (s, 5H, Cp), 5.95 (ddd, $J_{3-2} = 5.6$, $J_{3-4} = 3.1$, $J_{3-1} = 0.7$ Hz, 1H, H_3), 6.38 (dd, $J_{2-3} = 5.6$, $J_{2-1} = 3.3$ Hz, 1H, H_2), 7.14 (m, 8H, Ph), and 7.26 (m, 2H, Ph). ^{13} C{^{1}H} NMR (67.94 MHz, $CDCl_3$, vs. TMS): 35.2 ($C_6$of C_7H_8), 50.0 (C_5 of C_7 H_8), 51.7 (C_1 of C_7 H_8), 54.4 (C_4 of C_7H_8), 65.9 (d, $J_{Rh-C} = 25.6$ Hz, C_7 of C_7H_8), 89.6 (d, $J_{Rh-C} = 3.7$ Hz, Cp), 117.9 (dithiolene-C), 126.1, 127.4, 127.8, 128.1, 128.5, 129.8, 139.1, and 141.5 (Ph), 132.1 (C_3 of C_7H_8), 142.6 (C_2 of C_7 H_8), and 163.8 (dithiolene-C). Mass (EI$^+$, 70 eV) m/z (rel. intensity) 502 (M^+, 37), 410 (M^+–C_7 H_8, 60), and 232 ($Rh(Cp)S_2^+$, 100). UV–Vis (CH_2 Cl_2): λ_{max} (nm) (log ε) 236 (4.46), 384 (3.94), and 513 (2.78).



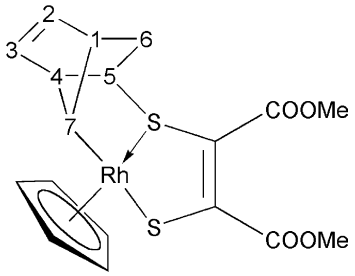
3.2.3. Preparation of complex *1b*

Complex **1b** [7] was prepared according to a modification of the literature method. At first, the mixture of [Rh(Cp)(cod)] (0.6 g, 2.2×10^{-3} mol), S_8 (0.12 g, 3.6×10^{-3} mol as a S), and Z–C≡C–Z (Z = COOMe) (0.22 cm^3, 1.8×10^{-3} mol) was heated at 110 °C for 3.5 h in 30 cm^3 of toluene. This reaction gave red-brown crystals of the alkyne adduct [Rh(Cp)($S_2C_2Z_2$)(C_2Z_2)] (Z = COOMe [7], 265 mg), and red crystals of the free complex **1b** (169 mg), respectively. Following this, the alkyne adduct isolated (265 mg, 5.1×10^{-4} mol)) was irradiated with a 400 W high pressure mercury lamp in 650 cm^3 of CH_2Cl_2 to form complex **1b** (175 mg) and Z–C≡C–Z. The overall yield of the free complex **1b** was 26% (344 mg).

3.2.4. Preparation of adduct *2b*

Adduct **2b** was prepared according to the method of adduct **2a**. Complex **1b** was heated to reflux (120 °C, 2 h) in 10 cm^3 of Q. Adduct **2b** was obtained in 81% yield. Orange crystal (**2b**); mp 196–197 °C. *Anal.* Calc. for $C_{18}H_{19}O_4$ RhS_2: C, 46.36; H, 4.11. Found: C, 45.98; H, 4.17%. ^{1}H NMR (270 MHz, $CDCl_3$, vs. TMS): 1.33 (ddd, $J_{gem} = 13.1$, $J_{6-5} = 6.7$, $J_{6-7} = 1.8$ Hz, 1H, $H_{6\text{-endo}}$), 1.51 (dd, $J_{gem} = 13.1$, $J_{6-1} = 3.9$ Hz, 1H, $H_{6\text{-exo}}$), 2.77 (dd, $J_{1-6} = 3.9$, $J_{1-2} = 3.3$ Hz, 1H, H_1), 2.86 (dd, $J_{5-6} = 6.7$,

$J_{3-2} = 1.9$ Hz, 1H, $H_{5\text{-endo}}$), 2.92 (d, $J_{4-3} = 3.3$ Hz, 1H, H_4), 3.34 (dd, $J_{7-6} = 1.9$, $J_{7-5} = 1.5$ Hz, 1H, H_7), 3.73 (s, 3H, OMe), 3.86 (s, 3H, OMe), 5.28 (s, 5H, Cp), 5.93 (dd, $J_{3-2} = 5.9$, $J_{3-4} = 3.3$ Hz, 1H, H_3), 6.35 (dd, $J_{2-3} = 5.9$, $J_{2-1} = 3.3$ Hz, 1H, H_2). $^{13}C\{^1H\}$ NMR (67.94 MHz, $CDCl_3$, vs. TMS): 35.5 (C_6 of C_7H_8), 51.4 (C_1 of C_7H_8), 52.0 (C_5 of C_7H_8), 52.4 (OMe), 53.1 (OMe), 54.5 (C_4 of C_7 H_8), 67.0 (d, $J_{Rh-C} = 25.3$ Hz, C_7 of C_7 H_8), 114.1 (dithiolene-C), 132.1 (C_3 of C_7 H_8), 142.5 (C_2 of C_7H_8), 179.7 (dithiolene-C), 89.5 (d, $J_{Rh-C} = 3.7$ Hz, Cp), 163.1 (C═O), and 168.3 (C═O). Mass (EI^+, 70 eV) m/z (rel. intensity) 466 (M^+, 33), 374 (M^+– C_7H_8, 100), 232 ($Rh(Cp)S_2^+$, 97), 168 ($Rh(Cp)^+$, 27), and 91 ($C_7H_8^+$–H, 25). UV–Vis (CH_2Cl_2): λ_{max} [nm] (ε) 390 (7148) and 240 (18890). IR (KBr disk): 1730, 1688, 1500, and 1430 cm^{-1}.



3.2.5. Preparation of complex *1c*

Complex **1c** [19] was prepared according to a ligand exchange reaction [20]. The methanol solution of $[Rh(Cp)I_2]$ [21] (0.130 g, 3.10×10^{-4} mol) and disodium mercaptomaleonitrile (0.060 g, 3.20×10^{-4} mol) was stirred for 3 h at room temperature. The red solution of complex **1c** was separated by an extraction from dichloromethane/water. The complex **1c** was obtained in 47% (0.045 g) yield.

3.3. Preparation of deuterium labeled quadricyclane

The deuterium labeled quadricyclane was prepared by Diels–Alder reaction of cyclopentadiene-d^6 with trans-1,2-dichloroethylene [22], followed by a dechlorination [23] and a cyclization [24] according to the literature methods.

3.4. Fraction of deuteration and distribution of hydrogen in deuterated Q

The hydrogen content was determined with ^1H NMR. The hydrogen content at the bridge (C(7)) position (39%) of Q was preserved at C(6) position ($H_{6\text{-exo}}$ and $H_{6\text{-endo}}$) in the case of **2a**(ca. 39 (not determined but estimated value) and 39%), and the hydrogen atom contents at C(2), C(3), C(5), and C(6) positions (70%) in Q are preserved at C(2), C(3), C(4), and C(7) positions (72%) in **2a**. One of the bridgehead position, C(4), the hydrogen content changed from 39% in Q to 72% in **2a**.

3.5. X-ray diffraction study

An orange single crystal ($0.03 \times 0.23 \times 0.33$ mm) was obtained by crystallization from ethanol at −30 °C. The reflection intensities were collected on a Rigaku RAXIS-RAPID Imaging plate with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$). The parameters used during the collection of diffraction data are given in Table 2. The structure was solved by the heavy atom method and refined by a full-matrix least-squares method. The weighting scheme was $w = 1/(\sigma^2 F_o)$. The final R value was 0.066 ($Rw = 0.095$) on 3976 intensities ($|F_o| > 3s|F_o|$). Idealized positions of adduct **2a** was used for the teXsan crystallographic software package of Molecular Structure Corp.

3.6. Isomerization of Q to NBD

After the reaction, the amount of NBD was analyzed by the GLC method: Shimazu-6A (detector: FID), Column: silicone OV-17 (5%) on Uniport B (mesh: 60/80), 3 m. Column temperature: 50 °C, Injection temperature: 75 °C. The catalytic activities for the isomerization of Q to NBD were determined on the basis of turnover number (TN = amount of NBD produced/amount of complex used).

3.7. Cyclic voltammetry (CV) measurement

All the electrochemical measurements were undertaken in dichloromethane solutions containing 0.1 $moldm^{-3}$ tetrabuthylammonium perchlorate (TBAP) at 25 °C. A stationary platinum disk (1.6 mm in diameter) was used as a working electrode. A platinum wire served as a counter electrode. The reference electrode is Ag|AgCl or $Ag|AgClO_4$ corrected for junction potentials by being referenced internally to the ferrocene/ferrocenium ($Fc|Fc^+$) couple.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Center, CCDC No. 217852 for complex **2a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EK (Fax: +44-1223-336033; deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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