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Journal of Organometallic Chemistry 487 (1995) C8–C14

Journal of Organometallic Chemistry

Preliminary communication

Formation, Structure, Spectra, and Reactivity of the Adduct between (η^5-Cyclopentadienyl)(1,2-dimethoxycarbonyl-1,2-ethylenedithiolato)-rhodium(III) and Dimethyl Acetylenedicarboxylate

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Received 18 May 1994; in revised form 20 July 1994

Abstract

A dithiolatorhodium complex [Rh(Cp)($S_2C_2Z_2$)] (**2**, Z=COOMe) reacts with dimethyl acetylenedicarboxylate (DMAD) to give a 1:1 adduct (**3**) in 85% yield. The same adduct is obtained in a prolonged reaction of [Rh(Cp)(cod)] (**1**) with S_8 and DMAD in 39% yield. In the adduct, DMAD adds between Rh and S. The adduct has been characterized by spectroscopic and by X-ray diffraction techniques. Red–brown crystals of the adduct are triclinic $P\bar{1}$, with $a = 11.789(4)$, $b = 10.789(3)$, $c = 7.960(1)$ Å, $\alpha = 92.33(2)$, $\beta = 94.07(2)$, $\gamma = 101.51(2)°$, and $D_c = 1.736$(calcd) g cm^{-1} for $Z = 2$. Least-squares refinement gives a final conventional R value of 0.028 for 4091 independent observed reflections. The adduct has a piano-stool structure consisting of a four-membered ring of Rh-S-C=C and a five-membered ring of rhodiadithiolene. The adduct is pyrolyzed to afford the decomposition product, tetramethyl 2,3,4,5-thiophenetetracarboxylate (TTME), together with a dissociation product, [Rh(Cp)($S_2C_2Z_2$)] (**2**). Adduct **3** is also photochemically dissociated to regenerate [Rh(Cp)($S_2C_2Z_2$)] **2**.

Keywords: Rhodium; Alkyne; Metallacycle; Thiolate; Cyclopentadienyl; X-ray diffraction

1. Introduction

Transition metal complexes with 1,2-ethylenedichalcogenolato as ligands have interesting chemical and physical properties [1–4]. A feature of the metalladichalcogenolene ring (five-membered ring consisting of a metal atom, two chalcogen atoms, and two unsaturated carbon atoms) in dichalcogenolatometal complexes ([M(Cp)(E_2C_2X,Y)]) is the unsaturated metal and chalcogen atoms.

We report the addition reactions of several organic compounds to the metalladichalcogenolene rings [5–8]. Phosphines and phosphites coordinate to the metal [9]. Addition reactions between metal and chalcogen atoms are reactions characteristic of the metalladithiolene rings. Additions of alkylidenes (CR^1R^2) by diazo compounds ($N_2CR^1R^2$) [5], of imino groups by azides [6], and of quadricyclane [7] are typical.

Previously we reported that (η^5-cyclopentadienyl)(1,2-dimethoxylcarbonyl-1,2-ethylenedithiolato)rhodium(III) [Rh(Cp)($S_2C_2(COOMe)_2$], which is prepared by a one-pot reaction of (η^5-cyclopentadienyl)(1,5-cyclooctadiene)rhodium(I) ([Rh(Cp)(cod)]: Cp = cyclopentadienyl, cod = 1,5-cyclooctadiene), dimethyl acetylenedicarboxylate (DMAD=Z-C≡C-Z, Z=COOMe), and elemental sulfur (S_8), reacts further with DMAD to give the 1:1 adduct [8]. In this paper, we report the full details of the adduct formation between [Rh(Cp)($S_2C_2Z_2$)] and DMAD. In addition, we describe the molecular structure of the adduct which is determined by single-crystal X-ray diffraction. We describe also the spectral properties as well as its thermal and photochemical behavior.

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SSDI 0022-328X(94)05122-4

2. Results and discussion

2.1. Formation of the adduct

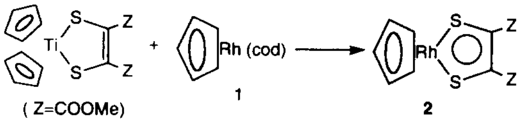
Boennemann et al. [10] have reported that novel (η^5-cyclopentadienyl) (substituted 1,2-ethylenedithiolato)cobalt(III) complexes ([Co(Cp)(S_2C_2X,Y)]) with a variety of substituents (X and Y) have been prepared by one-pot reactions of [Co(Cp)($CO)_2$] or [Co(Cp)(cod)] with elemental sulfur (S_8) and alkynes (X-C≡C-Y). In the reaction of [Co(Cp)(cod)] with S_8 and DMAD the complex [Co(Cp)($S_2C_2Z_2$)] was formed quantitatively. By replacing the starting complex [Co(Cp)(cod)] with [Rh(Cp)(cod)], we obtained two dithiolatorhodium complexes; one was [Rh(Cp)($S_2C_2Z_2$)] (**2**), the other was an adduct between **2** and DMAD.

These air-stable complexes were isolated by controlling the reaction time, as shown in Table 1.

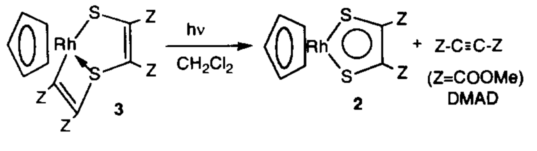
In a one pot reaction of [Rh(Cp)(cod)] (10 mmol) with S_8 (12.5 mmol as S_2) and DMAD (12 mmol) at 80°C in benzene, with a prolonged reaction time (13 h), the adduct **3** was formed in 39% yield, while the yield of **2** was very low (< 1%). With a shorter reaction time (20 min), **2** was predominant (11% yield) through a trace amount of **3** was formed. From the reaction mixture we isolated a small amount of tetramethyl 2,3,4,5-thiophenetetracarboxylate (TTME) which was expected in the "[CpRh(I)]"-catalyzed reaction of S_8 and Z-C≡C-Z [8].

The processes for the formation of these two novel dithiolatorhodium complexes are shown in Scheme 1.

The original complex [Rh(Cp)($S_2C_2Z_2$)], which was prepared by a one-pot reaction (Scheme 1) or the ligand exchange reaction between [Ti(Cp)$_2$($S_2C_2Z_2$)] and [Rh(Cp)(cod)] (Eq. (1)), or the photochemical dissociation of the adduct (Eq. (2)), reacted with an excess amount of Z-C≡C-Z at 80°C for 4 h in benzene to afford the adduct **3** in 85% yield.



(1)



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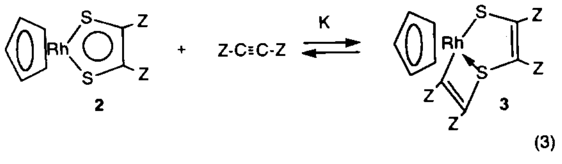


(3)

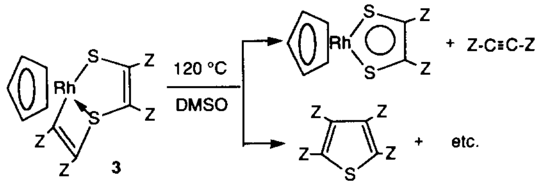
Table 1

Formation of Complex **2** [Rh(Cp)($S_2C_2Z_2$)] and Adduct **3** [CpRh{η^3(S,S,C′)-SC(Z)=CZS(C(Z)=C′Z)}] (Z=COOMe) in the one-pot reaction of [Rh(Cp)(cod)] **1** (10 mmol), elemental sulfur (12.5 mmol as S_2), and Z-C≡C-Z (DMAD, 12 mmol) at 80°C in 15 cm^3 benzene

Reaction time (h)	Yield of complexes (%)	
	Complex 2	Adduct 3
1/3	11	trace
13	0	39 [a]
20	0	37 [a]

[a] By-product: tetramethyl-2,3,4,5-thiophenetetracarboxylate (TTME).

The formation of the adduct is an equilibrium reaction (Eq. (3)). The equilibrium constant in the reaction at 80°C was estimated as $K_{80°C} = 60 \pm 4.5$ mol^{-1} dm^3 by ^{1}H-NMR in DMSO-d_6. Therefore, the free complex formed reacted further with an excess amount of DMAD to afford the adduct almost quantitatively. When the reaction temperature was raised to 120°C, a decomposition reaction yielding a thiophene derivative (TTME) occurred in parallel with the dissociation reaction (Eq. (4)).

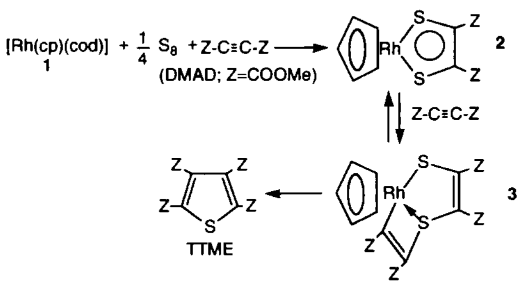


(4)

2.2. Structure of the adduct

The structure of the adduct **3** was determined using single-crystal X-ray analysis. Fig. 1 and Tables 2–4 show the ORTEP drawing and selected structural parameters of the adduct.

The adduct has a unique structure in which the alkyne adds between Rh and S of the rhodiadithiolene ring. The adduct has a piano-stool structure consisting of a four-membered and a five-membered ring. In the adduct, the central Rh atom has a coordination number of six. However, the original dithiolatorhodium complex has a structure in which the rhodiadithiolene ring is perpendicular to the cyclopentadienyl ring and the central Rh atom is five-coordinate, as expected from the molecular structure of the free dithiolato-



Scheme 1.

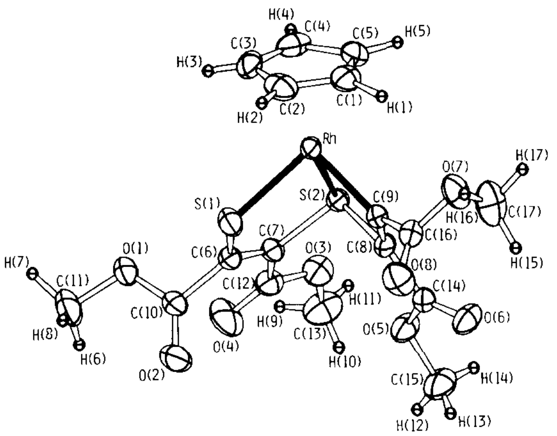


Fig. 1. Molecular structure of [CpRh{η^3-(S,S,C')-SC(Z)=CZS-(C(Z)=C'Z)}] (Z=COOMe) along with the numbering scheme. The atoms are displayed as 50% probability spheres for heavy atoms and as arbitrary spheres for hydrogen atoms.

Table 2
Crystal data and experimental details

Formula	$C_{17}H_{17}O_8S_2Rh$
Formula weight	516.348
a, Å	11.788(4)
b, Å	10.789(3)
c, Å	7.960(1)
α, deg	92.33(2)
β, deg	94.07(2)
γ, deg	101.51(2)
V, Å^3	987.9(4)
Z	2
Space group	$P\bar{1}$
Density, g cm^{-3}	1.736 (calcd)
Crystal shape and dimensions	plates; 0.15 × 0.35 × 0.38 mm^3
F(000), electrons	520
Radiation	MoKα (λ = 0.71073 Å) from graphite monochromater
Temp, °C	25
μ(MoKα), cm^{-1}	10.44
Transmissn factors	0.93–1.16 [a]
Scan speed, deg	4.0 in 2θ min^{-1}
Scan range, deg	1.2 + 0.5 tan θ
Background count, s	5 at the lower and upper limits of each scan
2θ limits, deg	3.0–55.0
Scan mode	ω scan for 2$\theta \le$ 45.0° ω-2θ scan for 2θ < 45.0°
Diffractometer	Rigaku
Unique data measured	4523
Unique data used (NO) ($F_o > 3\sigma(F_o)$)	4091
Final no. of variables (NV)	321
R [b]	0.028
R_{wF} [c]	0.035
GOF [d]	1.03

[a] Normalized to an average of unity;
[b] $R = \Sigma |F_o - |F_c|| / \Sigma F_o$;
[c] $R_{wF} = [\Sigma w |F_o - |F_c||^2 / \Sigma w F_o^{\,2}]^{1/2}$;
[d] GOF = $[\Sigma w(F_o - |F_c|)^2 / (\text{NO-NV})]^{1/2}$.

Table 3
Final atomic parameters [a]

Atom	X	Y	Z	B_{eq} or B (Å^2)
Rh	12053(2)	21150(2)	35165(3)	1.93(0.01)
S(1)	2080(1)	959(1)	5483(1)	2.80(0.05)
S(2)	2445(1)	3927(1)	4900(1)	2.08(0.04)
O(1)	4794(2)	1024(3)	6752(3)	3.7(0.1)
O(2)	3854(3)	1280(4)	9059(4)	4.7(0.1)
O(3)	4492(2)	5392(3)	6767(3)	3.3(0.1)
O(4)	5196(3)	3830(3)	8000(4)	4.8(0.1)
O(5)	2181(2)	5235(3)	8285(3)	3.3(0.1)
O(6)	222(2)	4844(3)	8059(3)	3.3(0.1)
O(7)	−1546(2)	2928(3)	4701(4)	3.5(0.1)
O(8)	−1098(3)	1936(3)	7005(4)	3.8(0.1)
C(1)	−266(3)	1559(4)	1666(5)	3.3(0.1)
C(2)	288(4)	525(4)	1891(5)	3.5(0.1)
C(3)	1398(4)	845(4)	1297(5)	3.6(0.1)
C(4)	1562(3)	2073(4)	763(5)	3.4(0.1)
C(5)	529(4)	2549(4)	1011(5)	3.2(0.1)
C(6)	3230(3)	2044(3)	6435(4)	2.4(0.1)
C(7)	3459(3)	3306(3)	6223(4)	2.3(0.1)
C(8)	1205(3)	3843(3)	6102(4)	2.1(0.1)
C(9)	407(3)	2902(3)	5337(4)	2.1(0.1)
C(10)	4000(3)	1434(4)	7614(4)	2.9(0.1)
C(11)	5565(4)	364(5)	7708(7)	5.1(0.2)
C(12)	4468(3)	4182(4)	7085(4)	2.9(0.1)
C(13)	5353(4)	6323(5)	7759(6)	4.3(0.1)
C(14)	1132(3)	4694(3)	7553(4)	2.2(0.1)
C(15)	2218(4)	6073(5)	9765(6)	4.2(0.1)
C(16)	−806(3)	2534(3)	5812(4)	2.4(0.1)
C(17)	−2771(4)	2574(5)	5015(7)	4.6(0.1)
H(1)	−119(5)	153(5)	215(7)	7.7(1.4)
H(2)	−8(4)	−31(5)	232(6)	6.4(1.3)
H(3)	185(4)	28(4)	144(6)	4.9(1.1)
H(4)	225(4)	267(4)	36(6)	4.7(1.1)
H(5)	36(4)	343(5)	73(7)	6.3(1.3)
H(6)	593(4)	96(4)	868(6)	5.3(1.1)
H(7)	604(5)	−5(5)	679(7)	6.5(1.3)
H(8)	502(4)	−32(5)	804(6)	6.6(1.2)
H(9)	614(4)	604(5)	771(6)	5.8(1.2)
H(10)	518(5)	652(5)	878(7)	6.5(1.3)
H(11)	546(4)	705(4)	716(6)	5.3(1.1)
H(12)	280(5)	607(6)	1044(7)	8.3(1.6)
H(13)	161(5)	572(5)	1054(7)	7.1(1.3)
H(14)	225(5)	692(5)	933(7)	8.0(1.4)
H(15)	−300(4)	292(4)	618(6)	5.5(1.1)
H(16)	−303(4)	169(4)	476(6)	5.4(1.2)
H(17)	−314(4)	298(5)	411(6)	6.6(1.3)

[a] Positional parameters are multiplied by 10^5 for Rh, 10^4 for the other heavy atoms, and 10^3 for hydrogen atoms. Equivalent temperature factors are of the form, $B_{eq}\frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}a_i \cdot a_j$ for the heavy atoms and isotropic temperature factors are of the form $T = \exp[-B(\sin\theta/\lambda)^2]$ for hydrogen atoms.

cobalt complexes such as [Co(Cp)($S_2C_2(CN)_2$] [11] and [Co(Cp)($S_2C_2(CF_3)_2$] [12]. The existence of the bond between Rh and S(2) is suggested by the fact that the bond length of Rh–S(2) in the adduct (2.372 Å) is shorter than the sum of the van der Waals radii of Rh and S atoms (2.61 Å), although the Rh–S(2) bond is somewhat longer than the Rh–S(1) bond (2.348 Å). The adduct has a distorted dithiolene ring, in which the S(1)–C(6) bond (1.712 Å) is shorter than the S(2)–

Table 4
Heavy-atom bond distances (Å) and angles (deg)

(a) *Coordination sphere*			
	Bond distances		
Rh–C(1)	2.165(4)	Rh–S(1)	2.3483(10)
Rh–C(2)	2.160(4)	Rh–S(2)	2.3716(8)
Rh–C(3)	2.244(4)	Rh–C(9)	2.030(3)
Rh–C(4)	2.261(4)	Rh–Cp* [a]	1.850
Rh–C(5)	2.197(4)		
	Bond angles		
Cp*–Rh–S(1)	123.4	Rh–S(1)–C(6)	104.06(13)
Cp*–Rh–S(2)	137.7	Rh–S(2)–C(7)	104.64(11)
Cp*–Rh–C(9)	131.8	Rh–S(2)–C(8)	80.26(10)
S(1)–Rh–S(2)	85.44(3)	Rh–C(9)–C(8)	106.2(2)
S(1)–Rh–C(9)	91.84(10)	Rh–C(9)–C(16)	129.2(2)
S(2)–Rh–C(9)	68.43(8)		
(b) *The $S_2C_4(COOMe)_4$ ligand*			
	Bond distances		
S(1)–C(6)	1.712(3)	O(3)–C(13)	1.442(5)
C(6)–C(7)	1.354(5)	C(12)–O(4)	1.214(5)
C(7)–S(2)	1.785(4)	C(8)–C(14)	1.465(5)
S(2)–C(8)	1.792(3)	C(14)–O(5)	1.338(4)
C(8)–C(9)	1.332(4)	O(5)–C(15)	1.449(5)
C(6)–C(10)	1.519(5)	C(14)–O(6)	1.209(5)
C(10)–O(1)	1.332(5)	C(9)–C(16)	1.486(5)
O(1)–C(11)	1.455(7)	C(16)–O(7)	1.339(5)
C(10)–O(2)	1.189(5)	O(7)–C(17)	1.460(5)
C(7)–C(12)	1.470(4)	C(16)–O(8)	1.201(5)
C(12)–O(3)	1.335(5)		
	Bond angles		
S(1)–C(6)–C(7)	126.2(3)	C(7)–C(12)–O(4)	122.9(4)
C(6)–C(7)–S(2)	117.7(2)	O(3)–C(12)–O(4)	124.0(3)
C(7)–S(2)–C(8)	104.4(2)	S(2)–C(8)–C(14)	125.1(2)
S(2)–C(8)–C(9)	104.8(3)	C(9)–C(8)–C(14)	130.1(3)
S(1)–C(6)–C(10)	111.9(3)	C(8)–C(14)–O(5)	112.1(3)
C(6)–C(10)–O(1)	109.7(3)	C(14)–O(5)–C(15)	117.2(3)
C(10)–O(1)–C(11)	115.8(3)	C(8)–C(14)–O(6)	123.3(3)
C(6)–C(10)–O(2)	124.2(4)	O(5)–C(14)–O(6)	124.5(3)
O(1)–C(10)–O(2)	126.0(4)	C(8)–C(9)–C(16)	124.6(3)
C(6)–C(7)–C(12)	123.1(3)	C(9)–C(16)–O(7)	110.9(3)
S(2)–C(7)–C(12)	119.1(3)	C(16)–O(7)–C(17)	115.4(3)
C(7)–C(12)–O(3)	113.1(3)	C(9)–C(16)–O(8)	125.1(3)
C(12)–O(3)–C(13)	116.4(3)	O(7)–C(16)–O(8)	124.0(3)
(c) *The cyclopentadienyl ligand*			
	Bond distances		
C(1)–C(2)	1.412(7)	C(4)–C(5)	1.435(6)
C(2)–C(3)	1.406(6)	C(5)–C(1)	1.416(6)
C(3)–C(4)	1.389(6)		
	Bond angles		
C(1)–C(2)–C(3)	108.0(4)	C(4)–C(5)–C(1)	106.8(4)
C(2)–C(3)–C(4)	108.8(4)	C(5)–C(1)–C(2)	108.1(4)
C(3)–C(4)–C(5)	108.2(4)		

[a] The centroid of the cyclopentadienyl ring.

C(7) bond (1.785 Å). The bond angle of S(1)–C(6)–C(7) (126.20°) is greater than that of S(2)–C(7)–C(6) (117.73°). The bond length of S(1)–C(6) is close to that of normal C=S (1.71 Å) [11]. The C(8)–C(9) bond length of 1.332 Å corresponds to the normal C=C bond length (1.337 ± 0.006 Å), but the C(6)–C(7) bond length (1.354 Å) is somewhat longer than that of C(8)–C(9).

Recently, we reported another example of an addition reaction using the metal–sulfur bond in the metalladithiolene ring. The dithiolatocobalt complex [Co(Cp)(S_2C_2H,COOMe)] reacts with ethyl diazoacetate (N_2CH(COOEt)) to give a 1:1 alkylidene adduct containing a C–Co–S three-membered ring. In this adduct, the plane of the C–Co–S three-membered ring is almost perpendicular to the plane of the almost planar dithiolene ring [5].

2.3. *Spectral data of the adduct*

The spectral data (^{1}H- and ^{13}C-NMR, IR, and UV-vis) of the adduct **3** were compared with those of the original complex **2**.

In NMR, the adduct showed four non-equivalent ^{1}H signals of the OCH_3 in the ester (in DMSO-d_6) and four non-equivalent ^{13}C signals of the CO in the ester (in $CDCl_3$), as expected from the molecular structure of the adduct determined by single crystal X-ray analysis. The chemical shift for the C(6) ($\delta = 178.6$) in the dithiolene ring differed greatly from that for the C(7) dithiolene carbon ($\delta = 107.4$). The ^{13}C-NMR signal of the carbon (C(9)) attached to Rh metal appeared as a doublet at $\delta = 164.3$ (J(Rh–C) = 29.3 Hz).

The IR spectra of the adduct showed several peaks attributable to four non-equivalent ester groups in the range of 1750–1600 cm^{-1}, while **2** showed two peaks attributable to two equivalent ester groups at 1732 and 1691 cm^{-1}.

2.4. *Thermal behavior of the adduct*

The adduct **3** is readily pyrolyzed in the solid state or in solution to give **2** and tetramethyl-2,3,4,5-thiophenetetracarboxylate (TTME). The time-course for the decomposition of the adduct and the formation of the complex **2** and TTME in the pyrolysis was followed by ^{1}H-NMR at 120°C in DMSO-d_6 (Fig. 2). The results in Fig. 2 suggest that the decomposition

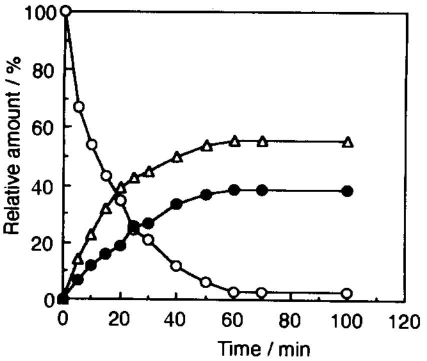


Fig. 2. Thermal behavior of the adduct [CpRh{η^3-(S,S,C')-SC(Z)=CZS(C(Z)=C′Z)}] (Z = COOMe): Time-course of disappearance of the adduct (○) and formation of the free complex (△), and TTME (●) in DMSO-d_6 at 120°C.

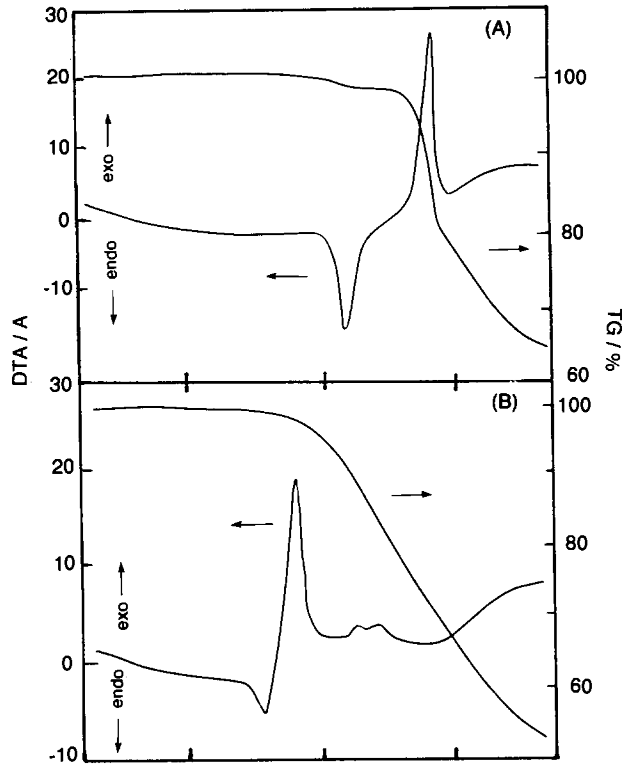


Fig. 3. DTA–TG of [Rh(Cp)($S_2C_2Z_2$)] (A) (7.900 mg) and the adduct [CpRh{η^3-(S,S,C′)-SC(Z)=CZS(C(Z)=C′Z)}] (Z = COOMe) (B) (5.740 mg) at 20–400°C (20°C $\min^{-1}$).

reaction giving TTME occurs in parallel with the dissociation reaction.

When the mass spectrum of the adduct was measured using a direct sample inlet system at 200–350°C, characteristic peaks appeared at $m/z = 374$, 316, and 111; these can be assigned to the cations of **2**, TTME, and [DMAD–OMe], respectively, although the parent peak of the adduct was not observed. These results suggest that adduct **3** is pyrolyzed in the probe of the mass spectrometer to give **2** and DMAD, together with TTME as a decomposition product.

The DTA–TG of the adduct showed an endothermic peak because of melting at a temperature about 50°C lower than the free complex, followed by an exothermic peak which can be ascribed to the decomposition reaction giving TTME together with the dissociation reaction giving the free complex and DMAD. Therefore, the weight loss (TG) of the adduct began gradually at lower temperature than for the original complex **2** (Fig. 3).

2.5. *Photochemical behavior of the adduct*

The characteristic photochemical behavior of adduct **3** is photodissociation to regenerate the original complex **2** and DMAD.

Irradiation of the adduct in a dichloromethane solution with a high pressure mercury lamp at room temperature caused a color change from brown to red. The spectral change is due to the regeneration of the original complex which exhibits an absorption maximum at 487.2 nm, as shown in Fig. 4. The ^{1}H-NMR study showed that the adduct was photodissociated to afford the original complex and DMAD quantitatively. This photoreaction has the following benefit: the preparation of the original complex **2** in the reaction of [Rh(Cp)(cod)], S_8, and DMAD is accompanied by the formation of the adduct; therefore, the preparation of **2** in pure form requires elaborate work for separation and purification. Photo-irradiating the mixture of the original complex **2** and the adduct **3** (or only the adduct) in dichloromethane is a useful, practical method for the preparation of **2**.

3. Experimental

3.1. *Materials*

Commercially available dimethyl acetylenedicarboxylate (DMAD) and elemental sulfur were used as purchased. Toluene used as solvent was purified by distillation.

3.2. *Spectroscopy, DTA–TG, and elemental analysis*

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 a Hitachi spectrometer model 260-50, respectively. DTA–TG was performed with the Seiko I SSC-5000. Elemental analysis was carried out with Perkin-Elmer Model 240C apparatus.

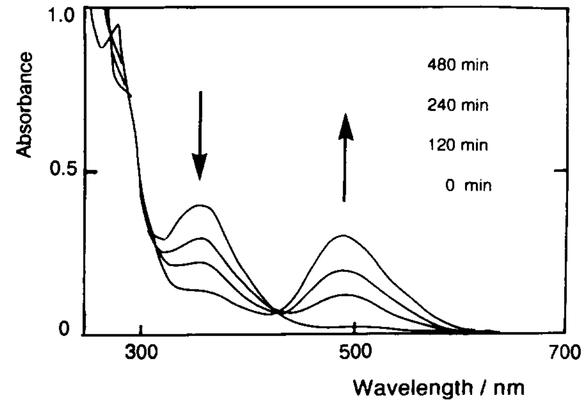


Fig. 4. UV–vis spectral change during irradiation of the adduct [CpRh{η^3-(S,S,C′)-SC(Z)=CZS(C(Z)=C′Z)}] (Z = COOMe) with a high-pressure Hg lamp at room temperature in CH_2Cl_2.

3.3. Synthetic procedure

All synthetic operations were conducted using the Schlenk tube technique under an atomosphere of Ar. The starting complex [Rh(Cp)(cod)] was prepared according to the method given in Ref. [13].

3.4. Reaction of [Rh(Cp)(cod)], S_8, and DMAD

A mixture of [Rh(Cp)(cod)] (10 mmol), S_8 (12.5 mmol as S_2), and DMAD (12 mmol) was heated at 80°C in benzene for 1/3–20 h under an atomosphere of Ar. Marked color change of the solution from yellow to red–brown was observed. The products were purified by flush column chromatography on silica gel (Wakogel, C-300). Air stable pale-red crystals (adduct **3**) and red–brown crystals (original complex **2**) were isolated.

The mixture of [Rh(Cp)(cod)] (0.90 g, 1.94 mmol) and [Ti(Cp)$_2$(S$_2$C$_2$(COOMe)$_2$)] (0.148, 0.385 mmol) [14] was heated in refluxing xylene (12 cm^3). The color of the solution changed from green to red. After 14 h, the solution was evaporated to dryness under reduced pressure and the unreacted [Rh(Cp)(cod)] was recovered by sublimation for ca. 1 at 90°C under < 10 mmHg. From the resulting residue, the red–black crystals of [Rh(Cp)(S$_2$C$_2$(COOMe)$_2$)] **2** (0.108 g, 75% yield based on the Ti complex) were obtained after flush column chromatography (Merck Aluminiumoxid 90, activity II–III, 70–230 mesh; eluent, CH_2Cl_2).

Original complex **2**: Mp. 201.0–208.5°C; MS(EI, 70 eV), m/z (relative intensity) 374(56,M$^+$), 343(11, [M–OMe]$^+$), 232(100, [RhCpS$_2$]$^+$), 168(34,[RhCp]$^+$), and 111(3, [DMAD–OMe]$^+$); UV (CH_2Cl_2) 283.2(ϵ, 2700 dm^{3}mol^{-1}cm^{-1}) and 487.2(ϵ, 1400 dm^{3}mol^{-1}cm^{-1}); IR(KBr) 1732(s), 1691(s), 1521(m), 1430(m), and 1243 cm^{-1}(s); ^{1}H-NMR (270 MHz) (in CDCl$_3$) $\delta = 5.70$(5H, s, Cp) and 3.91(6H, s, OC$H_3 \times 2$) and (in DMSO-d_6) 5.98(5H, s, Cp), and 3.80 (6H,s, OC$H_3 \times 2$); ^{13}C-NMR (67.9 MHz, CDCl$_3$) $\delta = 165.2$(s), 134.0(s), 88.5(d, Cp,J(Rh–C) = 4.4Hz), and 53.43(s), Found: C, 34.4; H, 2.9%. Calcd for $C_{11}H_{11}O_4S_2Rh$: C, 35.4; H, 2.9%.

Adduct **3**: Mp. 153–159°C (decomp.); MS(EI, 70 eV), m/z (relative intensity) 516(0, M$^+$), 374(69, [M-DMAD]$^+$), 316(16, [TTME]$^+$), 285(100, [TTME–OMe]$^+$), 232(96, [RhCpS$_2$]$^+$), 168(39, [RhCp]$^+$), and 111(39, [DMAD–OMe]$^+$); UV (CH_2Cl_2) 262.0(ϵ, 14600 dm^{3}mol^{-1}cm^{-1}) and 353.6(ϵ, 5200 dm^{3}mol^{-1}cm^{-1}); IR(KBr) 1735(s), 1727(s), 1710(s), 1691(s), 1595(m), 1490(s) 1430(m), 1261(s), and 1213 cm^{-1}(s); ^{1}H-NMR (270 MHz) $\delta = 5.52$(5H, s, cp), 3.84(6H, s, OC$H_3 \times 2$), 3.77(3H, s, OCH3), and 3.66(3H, s, OCH$_3$) (in CDCl$_3$) and 5.79(5H, s, Cp), 3.75 (3H,s, OCH_3), 3.70(3H, s, OCH_3), 3.68(3H, s, OCH_3), and 3.59(3H, s, OCH_3) (in DMSO-d_6); ^{13}C-NMR (67.9 MHz, CDCl$_3$) $\delta = 178.6$(s), 169.9(s), 166.5(s), 164.3(d, J(Rh–C) = 27.8 Hz), 162.6(s), 157.9(s), 126.1(s), 107.4(s), 88.5(d, Cp, J(Rh–C) = 4.4 Hz), 53.2(s), and 52.4(s). Found: C, 39.43; H, 3.29; S, 12.34%. Calcd for $C_{17}H_{17}O_8S_2Rh$: C, 39.55; H, 3.32; S, 12.42%.

3.5. Preparation of original complex by photodissociation of the adduct

The CH_2Cl_2 solution of the adduct **3** (50 cm^3, [**3**] = 6.0×10^{-5} mol dm^{-3}) was irradiated for 24 h with a high pressure mercury lamp in a Schlenk tube of Pyrex glass. The color of the solution changed from yellow–red to red. The spectral change in UV–vis is shown in Fig. 4. After the reaction, the solution was concentrated to ca. 5 cm^3 at room temperature under reduced pressure. The resulting solution was submitted to flush column chromatography (SiO$_2$: Wakogel C300, eluent: CH_2Cl_2/Et_2O ($v/v = 85/15$)) to afford the red–black crystals of **2** in 60–70% yield.

3.6. X-ray structure analysis

Cell constants were determined from 15 high-order reflections ($26 < 2\theta$ (Mo$K\alpha$) $< 36°$) on a Rigaku automated diffractometer; the crystal was mounted such that the c axis was parallel to the ϕ axis of the diffractometer. Throughout the data collection, the intensities of three standard reflections were measured every 100 reflections to check the stability of the crystal and the instrument; a maximum variation in intensity of < 2% was noted and no decay correction was applied to the data. Intensities were corrected for Lorenz and polarization effects. The anisotropy of absorption was checked for the axial 0 1 1 reflection ($\chi = 90°$) in 15° steps of ϕ, and the crystal showed transmission factors (normalized to an average of unity) varying form 0.93 to 1.16, and no correction was made for absorption.

The space group P$\bar{1}$ was confirmed by successful refinement of the structure. The structure was solved by the Pattersom and Fourier methods and refined by the block-diagonal least-squares method [15]. All non-hydrogen atoms were anisotropically refined with the function $\Sigma w(F_o - |F_c|)$ [16] being minimized. All 17 hydrogen atoms were located from the difference Fourier map and were refined isotropically. The final R and R_{wF}, and the goodness of fit (GOF) were 0.028, 0.035, and 1.03, respectively, with $w = 1/\sigma(F_o)^2$, for 4091 reflections (NO) and 321 variables (NV), from which $NO/NV = 12.7$. No systematic variation was observed in an analysis of $\Sigma w(F_o - |F_c|)^2$ as a function of either F_o or $(\sin\theta)/\lambda$; a final difference Fourier map showed no other features with an absolute value of greater than 0.4 eÅ^{-3} near to the rhodium position.

Neutral atomic scatterring factors were used with Rh and S corrected for anomalous dispersion [16]. The final atomic parameters are listed in Table 3. The anisotropic temperature factors for non-hydrogen atoms are available in Table S1 [17]. Bond distances and angles including atoms are given in Table S2 [17]. A list of final calculated and observed structure amplitude is collected in Table S3 [17].

Acknowledgment

The present study was supported in part by Grants-in-Aid for Scientific Research on Priority Areas on "Molecular Magnetism", nos. 0417120 and 03233102 and by Grants-in-Aid for Scientific Research, nos. 03640464 and 04453028 from the Ministry of Education, Science, and Culture.

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