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Reactions of dithiolenes with diazo compounds: cycloaddition and dissociation of alkylidene groups

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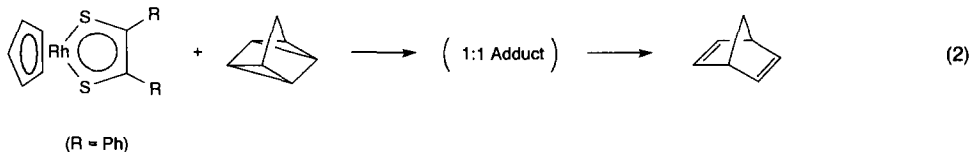
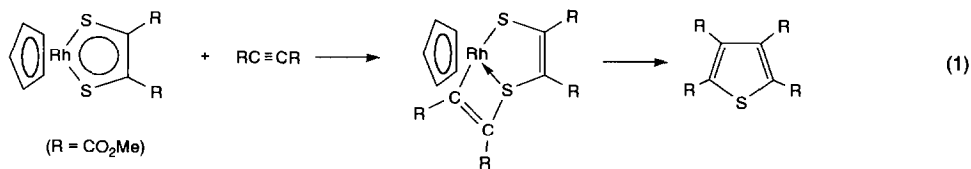
Abstract

1,2-Ethylenedithiolatometal complexes $\text{CpM}(\text{S}_2\text{C}_2\text{R}^1\text{R}^2)$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{M} = \text{Co}, \text{Rh}$; $\text{R}^1, \text{R}^2 = \text{CO}_2\text{Me}, \text{Ph}, \text{H}, \text{CN}$) (**1a–h**) react with diazo compounds $\text{N}_2\text{CR}^3\text{R}^4$ ($\text{R}^3, \text{R}^4 = \text{H}, \text{Ph}, \text{CO}_2\text{Et}, \text{CO}_2\text{Me}$) to yield 1:1 alkylidene-adducts $\text{CpM}(\text{S}_2\text{C}_2\text{R}^1\text{R}^2)(\text{CR}^3\text{R}^4)$ (**2–18**) containing a C–M–S three-membered ring, with the evolution of N_2 . Highly regioselective cycloaddition is observed in the reactions of unsymmetrical complexes **1f** ($\text{M} = \text{Co}, \text{R}^1 = \text{H}, \text{R}^2 = \text{CO}_2\text{Me}$) and **1g** ($\text{M} = \text{Rh}, \text{R}^1 = \text{H}, \text{R}^2 = \text{CO}_2\text{Me}$). The reaction of **1h** ($\text{M} = \text{Co}, \text{R}^1 = \text{H}, \text{R}^2 = \text{Ph}$) with N_2CH_2 gives two stereoisomers in the ratio of 35:22. The reaction of the alkyne-adduct $\text{CpRh}\{\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2\}\{\text{C}_2(\text{CO}_2\text{Me})_2\}$ with N_2CH_2 gives methylene-adduct **6** ($\text{M} = \text{Rh}, \text{R}^1 = \text{R}^2 = \text{CO}_2\text{Me}, \text{R}^3 = \text{R}^4 = \text{H}$). The crystal and molecular structure of adduct **15** ($\text{M} = \text{Co}, \text{R}^1 = \text{R}^3 = \text{H}, \text{R}^2 = \text{CO}_2\text{Me}, \text{R}^4 = \text{CO}_2\text{Et}$) has been determined; the five-membered dithiolene ring is planar, and the plane of the C–Co–S three-membered ring is almost perpendicular to the dithiolene ring. 1,2-Benzenedithiolatometal complexes $\text{CpM}(\text{S}_2\text{C}_6\text{R}^5\text{R}^6)$ ($\text{M} = \text{Co}, \text{Rh}$; $\text{R}^5, \text{R}^6 = \text{H}, \text{Cl}$) (**1i–l**) also react with diazo compounds $\text{N}_2\text{CR}^3\text{R}^4$ ($\text{R}^3, \text{R}^4 = \text{H}, \text{CO}_2\text{Et}, \text{CO}_2\text{Me}$) to yield alkylidene-adducts $\text{CpM}(\text{S}_2\text{C}_6\text{R}^5\text{R}^6)(\text{CR}^3\text{R}^4)$ (**19–23**). Thermal dissociations of adducts **2** ($\text{M} = \text{Co}, \text{R}^1 = \text{R}^2 = \text{CO}_2\text{Me}, \text{R}^3 = \text{R}^4 = \text{H}$) and **3** ($\text{M} = \text{Co}, \text{R}^1 = \text{R}^2 = \text{Ph}, \text{R}^3 = \text{R}^4 = \text{H}$) in cyclohexene give the corresponding parent complexes (**1a**: $\text{M} = \text{Co}, \text{R}^1 = \text{R}^2 = \text{CO}_2\text{Me}$; and **1b**: $\text{M} = \text{Co}, \text{R}^1 = \text{R}^2 = \text{Ph}$) and cyclohexene derivatives. Adduct **3** undergoes photodissociation to give the parent complex **1b**. A possible reaction mechanism for the cycloaddition is suggested and ^1H and ^{13}C NMR data of the alkylidene-adducts are also reported.

Introduction

Metalladithiolenes are stable due to a high degree of electron delocalization in the dithiolene ring systems, which manifests itself in intense electronic transitions at unusually low energies [1]. Although η^5 -cyclopentadienyl cobalt or rhodium complexes with a dithiolato ligand also have electron delocalization in the dithiolene rings, the central metal atoms are coordinatively unsaturated and they undergo addition reactions with some reagents. Henderson et al. reported the addition reactions of these types of cobaltadithiolene with phosphines and phosphites [2]. We have recently reported that dimethyl acetylenedicarboxylate (DMAD)

[3] and quadricyclane [4] add to one of the rhodium–sulfur bonds of dithiolatorhodium complexes to yield isolable 1:1 addition products, which are the intermediates of the catalytic generation of tetrakis(methoxycarbonyl)thiophene and of isomerization into norbornadiene, respectively, as shown in eqs. 1 and 2.



These cycloaddition reactions suggest that a certain degree of multiplicity is present in the Rh–S bonds of these complexes. The multiplicity of the metal–chalcogen bonds of dichalcogenolenes has only been discussed from the results of the X-ray analyses [5].

There has been recent interest in multiple bonds between transition metals (M) and main group elements (E), and a multiplicity of the M–E bonds in some complexes has been studied on the basis of reactions with diazo compounds. Herrmann reported cycloaddition of alkylidene groups to a chromium–chalcogen bond of the organochromium complex [6]. Strecker and Werner reported cycloaddition of diarylcarbene to organocobalt isocyanides [7]. These [2 + 1]-cycloaddition reactions give the three-membered metallacycles. Alkylidene-adducts of cobalt [8] or rhodium [9] porphyrin were also reported.

We have preliminarily reported that the complexes $\text{CpCo}(\text{S}_2\text{C}_2\text{R}^1\text{R}^2)$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{R}^1, \text{R}^2 = \text{CO}_2\text{R}, \text{H}$) react with some diazo compounds to yield 1:1 alkylidene-adducts [10]. During that study, we have found that these adducts undergo thermal- and photodissociation to yield the parent metalladithiolenes. This paper presents full details of the addition reaction, the factors which control the cycloaddition, and the structure and dissociation of the adducts including the rhodium complexes and the benzenedithiolato complexes.

Results and discussion

Reactions of metalladithiolenes with diazo compounds

The 1,2-ethylenedithiolato complexes $\text{CpM}(\text{S}_2\text{C}_2\text{R}^1\text{R}^2)$ (**1a–h**) and the 1,2-benzenedithiolato complexes $\text{CpM}(\text{S}_2\text{C}_6\text{R}^1\text{R}^2)$ (**1i–l**) react with diazomethane and its derivatives to give novel metalla-bicyclic compounds accompanied by the loss of N_2 . The results of the reactions are summarized in Table 1. The data given in Table 1 show that the reaction is dependent on the following factors: electron density on the carbon atom of diazo compounds, character of the central metal of metalladithiolene ring, and substituent on the dithiolato ligand.

The reactions of symmetrical metalladithiolenes **1a–e** with the diazo compounds give alkylidene-adducts **2–12** as shown in eq. 3.

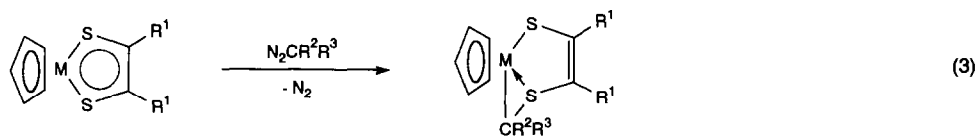
Table 1

Chemical reactivities of dithiolenes with diazo compounds

Dithiolenes	Diazo compound	Condition	Product (%)
1a	N ₂ CH ₂	<i>a</i>	2 (92)
1b	N ₂ CH ₂	<i>a</i>	3 (85)
1c	N ₂ CH ₂	<i>a</i>	4 (50)
1d	N ₂ CH ₂	<i>a</i>	5 (84)
1e	N ₂ CH ₂	<i>a</i>	6 (56)
1a	N ₂ CPh ₂	1 h <i>b</i>	7 (99)
1a	N ₂ CHCO ₂ Et	3 h <i>c</i>	8 (87)
1b	N ₂ CHCO ₂ Et	3 h <i>c</i>	9 (80)
1e	N ₂ CHCO ₂ Et	5 min <i>b</i>	10 (76)
1a	N ₂ C(CO ₂ Me) ₂	24 h <i>c</i>	11 (5)
1a	N ₂ C(CO ₂ Me) ₂	24 h <i>d</i>	11 (40)
1e	N ₂ C(CO ₂ Me) ₂	24 h <i>c</i>	12 (31)
1f	N ₂ CH ₂	<i>a</i>	13 (45)
1g	N ₂ CH ₂	<i>a</i>	14 (28)
1f	N ₂ CHCO ₂ Et	5 h <i>c</i>	15 (59)
1g	N ₂ CHCO ₂ Et	5 min <i>b</i>	16 (63)
1h	N ₂ CH ₂	<i>a</i>	17 (35) + 18 (22)
1i	N ₂ CH ₂	<i>a</i>	19 (70)
1j	N ₂ CH ₂	<i>a</i>	20 (70)
1k	N ₂ CH ₂	<i>a</i>	21 (64)
1l	N ₂ CH ₂	<i>a</i>	22 (65)
1i	N ₂ CHCO ₂ Et	12 h <i>c</i>	23 (15)

a At 0 °C. The reaction occurred immediately after diazomethane was added. *b* At room temperature.*c* Reflux in benzene. *d* Reflux in benzene with CuI-P(OMe)₃.

The reactions of **1a–e** with N₂CH₂ occur rapidly at 0 °C accompanied with vigorous evolution of N₂ to yield the methylene-adducts **2–6** respectively. Complex **1a** also reacts readily with N₂CPh₂ to give diphenylmethylene-adduct **7** at room

**1a**: M=Co, R¹=CO₂Me**1b**: M=Co, R¹=Ph**1c**: M=Co, R¹=H**1d**: M=Co, R¹=CN**1e**: M=Rh, R¹=CO₂Me**2**: M=Co, R¹=CO₂Me, R²=R³=H**3**: M=Co, R¹=Ph, R²=R³=H**4**: M=Co, R¹=R²=R³=H**5**: M=Co, R¹=CN, R²=R³=H**6**: M=Rh, R¹=CO₂Me, R²=R³=H**7**: M=Co, R¹=CO₂Me, R²=R³=Ph**8**: M=Co, R¹=CO₂Me, R²=H, R³=CO₂Et**9**: M=Co, R¹=Ph, R²=H, R³=CO₂Et**10**: M=Rh, R¹=CO₂Me, R²=H, R³=CO₂Et**11**: M=Co, R¹=R²=R³=CO₂Me**12**: M=Rh, R¹=R²=R³=CO₂Me

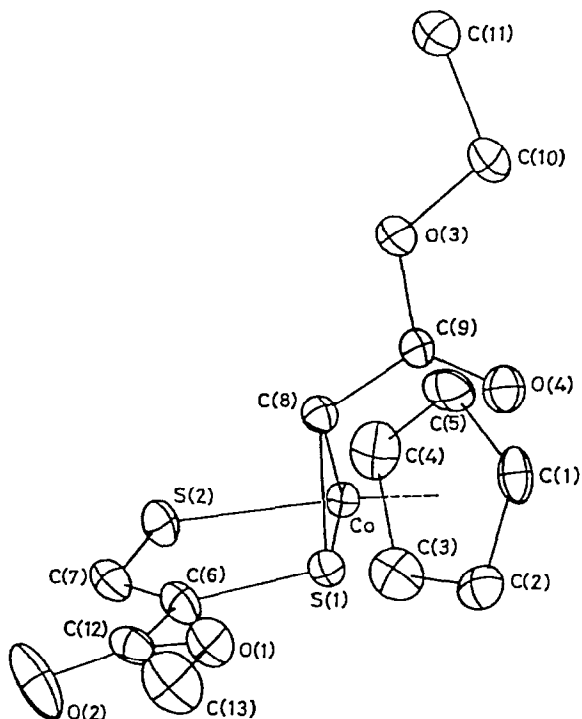
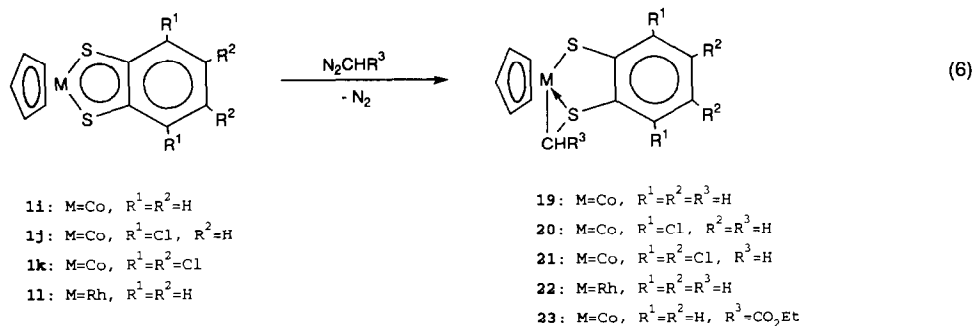
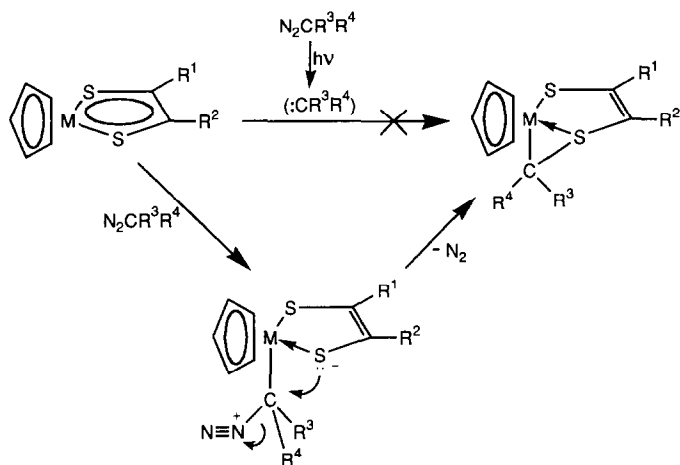


Fig. 1. Molecular structure of $\text{CpCo}(\text{S}_2\text{C}_2\text{H},\text{CO}_2\text{Me})(\text{CHCO}_2\text{Et})$ (**15**) showing the atom labelling.

Benzenedithiolato metal complexes **1i–l** also react with N_2CH_2 and $\text{N}_2\text{CHCO}_2\text{Et}$ to give alkylidene-adducts **19–23**, as shown in eq. 6. Adducts **19–23** were isolated as air-stable microcrystalline solids and were spectroscopically characterized.

We interpret these cycloaddition reactions as indicating that the dithiolenes of cobalt or rhodium are not only coordinatively unsaturated but also have a multiplicity at the metal–sulfur bonds. Analogous dithiolatotitanium complexes $\text{Cp}_2\text{Ti}(\text{S}_2\text{C}_2(\text{CO}_2\text{Et})_2)$ [13] or $\text{Cp}_2\text{Ti}(\text{S}_2\text{C}_6\text{H}_4)$ [14] did not react with N_2CH_2 , and neither did amidothiophenol complex $\text{CpCo}(\text{SNHC}_6\text{H}_4)$ [15].





Scheme 1.

Mechanism for the addition reactions

The diazo compounds do not cause the elimination of N_2 without the complexes in each reaction condition. The reactions of complex **1a** with carbene generated by the photoirradiation of N_2CHCO_2Et or $N_2C(CO_2Me)_2$ did not give the addition product **8** or **11**, but caused fast decomposition of **1a**. Complexes **1a**, **8**, and **11** are stable against the irradiation. These facts indicate that cycloaddition of the metalladithiolenes with diazo compounds does not proceed via the carbene, and that the elimination of N_2 is caused by the interaction with the complexes.

The introduction of electron-attracting substituents to diazo compounds reduces the reactivity of the addition reaction. In contrast with the remarkable substituent effects in the diazo compounds, the substituents in the dithiolenes ring affect the reactivity to a lesser extent. However, we observed a tendency that electron-attracting substituents in dithiolato ligands increase the reactivity of the addition reaction. The reversible half-wave potentials of the one-electron reduction step of $(\eta^5\text{-cyclopentadienyl})(1,2\text{-ethylenedithiolato})\text{cobalt(III)}$ complexes depend linearly on the sum of the field parameters of the substituents in the dithiolato ligand [16]. This linear relationship is interpreted in terms of the variation of the electron density on the metal atom transferred through C–S bonds. These substituent effects indicate that the alkylidene addition reaction should be initiated by the nucleophilic attack of the diazo compounds at the metal atom of the complexes.

One reasonable description for the reaction mechanism is shown in Scheme 1. The cobalt atom of the dithiolato complexes accepts an electron pair from the carbon atom of the diazo compounds. Elimination of N_2 then occurs by nucleophilic attack of sulfur at the alkylidene carbon. In the case of unsymmetrical complexes **1f** and **1g**, the sulfur atom attached to the carbon carrying the ester group is more reactive than the other sulfur atom, because the latter sulfur atom is stabilized by a resonance with the carbonyl of the dithiolate ligand. The reason why complex **1b** does not react with $N_2C(CO_2Me)_2$ is that the electron density at the cobalt atom of **1b** $\{E_{1/2}^r(\text{red}) = -1.16\}$ is too high to accept a lone pair of $N_2C(CO_2Me)_2$.

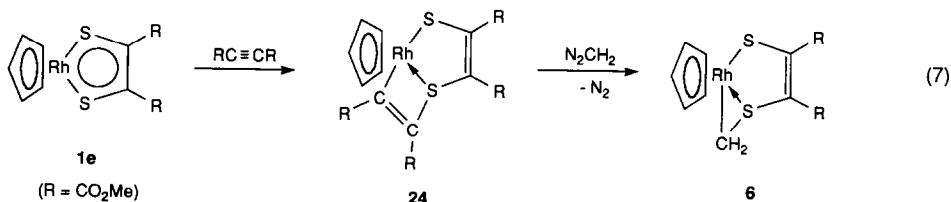
Table 2

Selected bond lengths (Å) and angles (deg) for CpCo(S₂C₂H,CO₂Me)(CHCO₂Et) (**15**) with estimated standard deviations (esd's) in parentheses

Co–S(1)	2.185(2)	Co–S(2)	2.214(3)
Co–C(1)	2.087(10)	Co–C(2)	2.074(10)
Co–C(3)	2.055(10)	Co–C(4)	2.028(11)
Co–C(5)	2.088(11)	Co–C(8)	1.983(8)
C(1)–C(2)	1.418(14)	C(1)–C(5)	1.402(15)
C(2)–C(3)	1.398(14)	C(3)–C(4)	1.482(15)
C(4)–C(5)	1.379(15)	C(6)–C(7)	1.426(12)
C(6)–C(12)	1.436(13)	C(6)–S(1)	1.759(9)
C(7)–S(2)	1.670(9)	C(8)–C(9)	1.489(11)
C(8)–S(1)	1.782(8)	C(9)–O(3)	1.328(10)
C(9)–O(4)	1.212(10)	C(10)–C(11)	1.528(14)
C(10)–O(3)	1.486(11)	C(12)–O(1)	1.379(12)
C(12)–O(2)	1.177(13)	C(13)–O(1)	1.441(13)
Co–S(1)–C(6)	103.9(3)	Co–S(2)–C(7)	103.7(3)
Co–C(8)–S(1)	70.8(3)	S(1)–Co–S(2)	91.7(1)
S(1)–Co–C(8)	50.3(2)	S(2)–Co–C(8)	94.0(2)
S(1)–C(6)–C(7)	117.8(6)	C(6)–C(7)–S(2)	122.8(7)
C(6)–S(1)–C(8)	102.0(4)	C(7)–C(6)–C(12)	119.0(8)
C(6)–C(12)–O(1)	110.8(8)	C(12)–O(1)–C(13)	116.2(8)
C(6)–C(12)–O(2)	127.6(10)	S(1)–C(8)–C(9)	113.1(6)
C(8)–C(9)–O(3)	108.8(7)	C(9)–O(3)–C(10)	115.4(6)
O(3)–C(10)–C(11)	104.2(7)	C(8)–C(9)–O(4)	126.5(8)
O(4)–C(9)–O(3)	124.7(8)	C(1)–C(2)–C(3)	111.7(9)
C(2)–C(3)–C(4)	103.5(9)	C(3)–C(4)–C(5)	108.8(9)
C(4)–C(5)–C(1)	109.7(10)	C(5)–C(1)–C(2)	106.1(9)

Reaction of DMAD-adduct **24** with N₂CH₂

We have reported the [2 + 2] cycloaddition reaction of DMAD with dithiolenone **1e** to give adduct **24** (eq. 1) [3]. Coordinatively saturated complex **24** reacts further with N₂CH₂ to give 49% of alkylidene-adduct **6**, as shown in eq. 7; in this reaction, the bicyclo[3.2.0] ring of **24** is converted into the bicyclo[3.1.0] metallacycle. This reaction proceeds more slowly than that of free complex **1e** with N₂CH₂. By contrast, complex **6** did not react with DMAD.



Molecular structure of CpCo(S₂C₂H,CO₂Me)(CHCO₂Et) (**15**)

An ORTEP drawing of complex **15** is shown in Fig. 1, and the important crystallographic parameters are listed in Tables 2 and 3. The five-membered CoS₂C₂ [Co, S(1), S(2), C(6), C(7)] ring is almost planar; the centers of the five atoms of the CoS₂C₂ moiety [Co, S(1), S(2), C(6), C(7)] lie within 0.038 Å of a plane. The plane of the C–Co–S three-membered ring is almost perpendicular to

Table 3

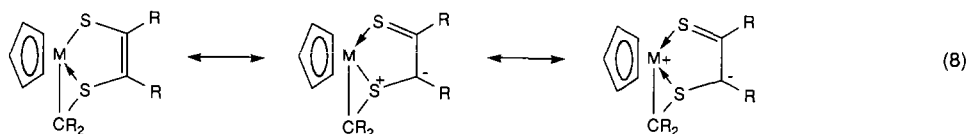
Atomic coordinates and thermal parameters^a for CpCo(S₂C₂H,CO₂Me)(CHCO₂Et) (**15**) with the esd's in parentheses^b

Atom	x	y	z	B _{eq} (Å ²)
Co	0.0694(1)	0.2426(1)	0.1064(1)	1.9
S(1)	0.1417(2)	0.3557(2)	-0.0546(3)	2.4
S(2)	0.2802(2)	0.1354(2)	0.1619(3)	3.2
O(1)	0.3285(6)	0.4256(6)	-0.2506(8)	4.0
O(2)	0.5333(7)	0.3235(8)	-0.1230(10)	6.6
O(3)	-0.1630(6)	0.1334(5)	-0.3844(7)	3.0
O(4)	-0.1650(6)	0.3453(5)	-0.2964(8)	3.3
C(1)	-0.0195(10)	0.3737(9)	0.2941(12)	3.5
C(2)	-0.1309(9)	0.3170(9)	0.1370(12)	3.5
C(3)	-0.1249(9)	0.1856(9)	0.1161(13)	3.5
C(4)	-0.0031(11)	0.1614(9)	0.2790(15)	4.4
C(5)	0.0532(10)	0.2753(10)	0.3827(12)	3.9
C(6)	0.3220(8)	0.3011(8)	-0.0398(11)	2.8
C(7)	0.3770(9)	0.1993(8)	0.0562(11)	3.2
C(8)	0.0438(8)	0.2161(7)	-0.1693(9)	2.2
C(9)	-0.1054(8)	0.2422(8)	-0.2865(10)	2.3
C(10)	-0.3149(9)	0.1429(9)	-0.5036(12)	4.0
C(11)	-0.3456(9)	0.0090(9)	-0.6174(13)	4.1
C(12)	0.4084(10)	0.3437(9)	-0.1392(12)	3.4
C(13)	0.4024(11)	0.4734(11)	-0.3610(14)	5.8

^a The equivalent isotropic thermal parameters for non-hydrogen atoms were computed using the following expression: $B_{eq} = (4/3) \times (a^2 B_{1,1} + b^2 B_{2,2} + c^2 B_{3,3})$. ^b Final atomic parameters of hydrogen atoms are deposited.

the plane of the dithiolene ring. The angle between planes Cp and CoS₂C₂ is 71.15°.

The alkylidene group bonds to Co and S(1); the length of Co and S(1) is 2.185(2) Å which indicates the existence of a Co–S(1) bond. The central cobalt atom of **15**, therefore, is coordinatively saturated and satisfies the eighteen electron rule. The ethoxycarbonyl substituent of alkylidene group is oriented *exo* to the dithiolene ring. The bond lengths of the bicyclo[3.1.0] ring are Co–S(1) 2.185(2), Co–S(2) 2.214(3), S(1)–C(6) 1.759(9), S(2)–C(7) 1.670(9), C(6)–C(7) 1.426(12), Co–C(8) 1.983(8), and S(1)–C(8) 1.782(8) Å. The bond length of Co–S(1) is shorter than that of Co–S(2) owing to the strain of the three-membered ring. The bond length of S(2)–C(7) is considerably shorter than that of S(1)–C(6); S(2)–C(7) has double-bond character, which is presumably due to the importance of the resonance structures shown in eq. 8.



NMR data

Particular spectroscopic features of the alkylidene-adducts appear in the ¹³C NMR signals for the two vicinal carbon atoms of the dithiolato moieties; the

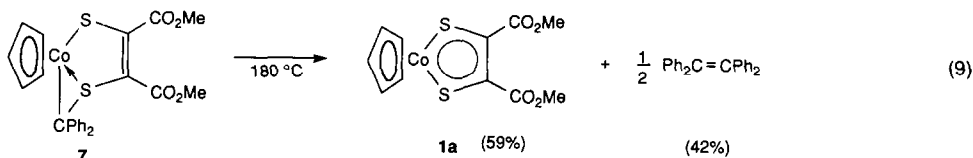
resonances for the carbon atom adjacent to the alkylidene-bridges appear approximately 50 ppm upfield of that for the other ring carbons. This large splitting of the resonances for two ring carbons is also presumably due to the importance of the resonance structures shown in eq. 8. A similar explanation is possible for the large splitting of the two carbon resonances for the analogous metalladithiolene ring of the quadricyclane-adduct $\text{CpRh}(\text{C}_7\text{H}_8)(\text{S}_2\text{C}_2\text{Ph}_2)$ (δ 117.9 and 163.8) in which the quadricyclane bridges Rh and sulfur (eq. 2) [4].

The large coupling constants for ^{103}Rh and bridging ^{13}C of adducts **6** ($J(\text{RhC}) = 20.8$ Hz), **10** (19.5), **12** (21.9), **14** (20.8), **16** (19.6), and **22** (20.8) show the bonds between rhodium and the carbon. The ^{13}C - ^1H spin-spin coupling constants of alkylidene C-H in adducts **2-6**, **8-10**, and **13-23** are in the range of $J(\text{CH}) = 164$ -177 Hz. It is known that the ^{13}C - ^1H coupling increases markedly with increasing s character of the carbon hybridization, i.e., 125 Hz for sp^3 and 155-170 Hz for sp^2 , and in the small rings the J values increase significantly owing to the effects of ring strain, i.e., 160.5 Hz for cyclopropane [17].

An important feature in the ^1H NMR spectra of adducts **4**, **13-17** is long range spin-spin couplings for the alkylidene proton and a dithiolene ring proton. The $^5J(\text{HH})$ between the dithiolene ring proton and the alkylidene proton oriented *endo* to the dithiolene ring in structure-analyzed **15** is 0.74 Hz. Similar spin-spin couplings are observed in **4** ($^5J(\text{HH})$ 1.46 Hz), **13** (0.86), **14** (0.98), **16** (0.75), and **17** (1.28).

Thermal dissociation of alkylidene-adducts

All alkylidene-adducts dissociate thermally to give quantitatively the parent complex **1**. Thermal dissociation of diphenylmethylene-adduct **7** in the solid phase at 180°C for 5 min gave 59% of **1a** and 42% of tetraphenylethylene, which is the dimerized product of diphenylmethylene shown in eq. 9.



Thermal dissociation of methylene-adducts **2** and **3** in cyclohexene gave the parent metalladithiolenes (**1a** and **1b**, respectively) and a product mixture shown in Table 6. The product ratios are similar to those resulting from thermal decomposition or direct photolysis of N_2CH_2 in benzene solution [18]. These results give the evidence for the generation of methylene from the adducts; the alkylidene-adducts are regarded as precursors for carbenes. Carbene chemistry appears to have now been established with considerable thoroughness and the field has matured [19], but new synthetic methods may still be expected to be explored. The generation of carbenes from this type of organometallic complexes is rare [20].

Compared with the obvious generation of methylene from the adducts above, thermal reactions of ethoxycarbonylmethylene-adduct **8** and bis(methoxycarbonyl)methylene-adduct **11** in cyclohexene gave neither insertion, addition, nor dimerization products of the respective carbene, but yielded small amounts of hydrogen-abstracted products (ethyl acetate and dimethyl malonate, respectively). A thermal dissociation of **11** in the presence of Me_2S , which reacts with singlet bis(methoxy-

Table 4

¹H NMR data of complexes 2–23, in CDCl₃ (270 MHz; δ in ppm, TMS int; *J* in Hz)

Complex	δ
2	1.74 (1H, d, <i>J</i> (HH) 2.93, CH ₂), 3.62 (1H, d, <i>J</i> (HH) 2.93, CH ₂), 3.72 (3H, s, OCH ₃), 3.79 (3H, s, OCH ₃), 5.12 (5H, s, C ₅ H ₅)
3	1.81 (1H, d, <i>J</i> (HH) 2.65, CH ₂), 3.46 (1H, d, <i>J</i> (HH) 2.65, CH ₂) 5.12 (5H, s, C ₅ H ₅), 7.05–7.10 (10H, m, Ph)
4	1.52 (1H, dd, <i>J</i> (HH) 2.56 and 1.46, CH ₂), 3.41 (1H, d, <i>J</i> (HH) 2.56, CH ₂), 5.08 (5H, s, C ₅ H ₅), 5.11 (1H, d, <i>J</i> (HH) 5.49, dithiolene ring proton), 6.61 (1H, dd, <i>J</i> (HH) 5.49 and 1.46, dithiolene ring proton)
5	1.63 (1H, d, <i>J</i> (HH) 3.67, CH ₂), 3.74 (1H, d, <i>J</i> (HH) 3.67, CH ₂), 5.25 (5H, s, C ₅ H ₅)
6	2.18 (1H, dd, <i>J</i> (RhH) 0.76 and <i>J</i> (HH) 3.03, CH ₂), 3.55 (1H, dd, <i>J</i> (RhH) 2.27 and <i>J</i> (HH) 3.03, CH ₂), 3.74 (3H, s, OCH ₃), 3.83 (3H, s, OCH ₃), 5.46 (5H, d, <i>J</i> (RhH) 0.75, C ₅ H ₅)
7	3.55 (3H, s, OCH ₃), 3.74 (3H, s, OCH ₃), 4.80 (5H, s, C ₅ H ₅), 7.1–7.8 (10H, m, Ph)
8	1.35 (3H, t, <i>J</i> (HH) 7, CH ₂ CH ₃), 2.17 (1H, s, CH), 3.73 (3H, s, OCH ₃), 3.80 (3H, s, OCH ₃), 4.23 (2H, m, <i>J</i> (HH) 7, CH ₂ CH ₃), 5.15 (5H, s, C ₅ H ₅)
9	1.37 (3H, t, <i>J</i> (HH) 7.20, OCH ₂ CH ₃), 2.21 (1H, s, carbene proton), 4.26 (2H, q, <i>J</i> (HH) 7.20, OCH ₂ CH ₃), 5.13 (5H, s, C ₅ H ₅), 7.03–7.17 (10H, m, Ph)
10	1.30 (3H, t, <i>J</i> (HH) 7, CH ₂ CH ₃), 2.84 (1H, d, <i>J</i> (RhH) 1.47, CH), 3.75 (3H, s, OCH ₃), 3.84 (3H, s, OCH ₃), 4.16 (2H, m, <i>J</i> (RhH) 4.6 and <i>J</i> (HH) 7, CH ₂ CH ₃), 5.43 (5H, d, <i>J</i> (RhH) 0.73, C ₅ H ₅)
11	3.56 (3H, s, OCH ₃), 3.76 (3H, s, OCH ₃), 3.81 (3H, s, OCH ₃), 3.83 (3H, s, OCH ₃), 5.22 (5H, s, C ₅ H ₅)
12	3.63 (3H, s, OCH ₃), 3.76 (3H, s, OCH ₃), 3.78 (3H, s, OCH ₃), 3.84 (3H, s, CH ₃), 5.48 (5H, d, <i>J</i> (RhH) 0.74, C ₅ H ₅)
13	1.62 (1H, dd, <i>J</i> (HH) 3.0 and 0.86, CH ₂), 3.55 (1H, d, <i>J</i> (HH) 3.0, CH ₂), 3.71 (3H, s, OCH ₃), 5.09 (5H, s, C ₅ H ₅), 8.00 (1H, d, <i>J</i> (HH) 0.86, dithiolene ring proton)
14	2.07 (1H, dt, <i>J</i> (RhH) 0.98, <i>J</i> (HH) 2.93 and 0.98, CH ₂), 3.55 (1H, dd, <i>J</i> (RhH) 2.93 and <i>J</i> (HH) 2.93, CH ₂), 3.73 (3H, s, OCH ₃), 5.45 (5H, d, <i>J</i> (RhH) 0.98, C ₅ H ₅), 8.31 (1H, dd, <i>J</i> (RhH) 3.91 and <i>J</i> (HH) 0.98, CH ₂)
15	1.34 (3H, t, <i>J</i> (HH) 7.0, CH ₂ CH ₃), 2.02 (1H, d, <i>J</i> (HH) 0.74, CH), 3.72 (3H, s, OCH ₃), 4.22 (2H, q, <i>J</i> (HH) 7.0, CH ₂ CH ₃), 5.12 (5H, s, C ₅ H ₅), 8.10 (1H, d, <i>J</i> (HH) 0.74, dithiolene ring proton)
16	1.29 (3H, t, <i>J</i> (HH) 7.19, CH ₂ CH ₃), 2.70 (1H, dd, <i>J</i> (RhH) 1.56 and <i>J</i> (HH) 0.76, alkylidene proton), 3.75 (3H, s, OCH ₃), 4.15 (2H, qd, <i>J</i> (RhH) 2.65 and <i>J</i> (HH) 7.19, CH ₂ CH ₃), 5.41 (5H, d, <i>J</i> (RhH) 0.75, C ₅ H ₅), 8.42 (1H, dd, <i>J</i> (RhH) 4.16 and <i>J</i> (HH) 0.76, dithiolene ring proton)
17	1.72 (1H, dd, <i>J</i> (HH) 2.55 and 1.28, CH ₂), 3.54 (1H, d, <i>J</i> (HH) 2.55, CH ₂), 5.12 (5H, s, C ₅ H ₅), 6.86 (1H, d, <i>J</i> (HH) 1.28, dithiolene ring proton), 7.10–7.50 (5H, m, Ph)
18	1.77 (1H, d, <i>J</i> (HH) 2.56, CH ₂), 3.46 (1H, d, <i>J</i> (HH) 2.56, CH ₂), 5.09 (5H, s, C ₅ H ₅), 5.39 (1H, s, dithiolene ring proton), 7.20–7.55 (5H, m, Ph)
19	1.96 (1H, d, <i>J</i> (HH) 3.03, CH ₂), 3.61 (1H, d, <i>J</i> (HH) 3.03, CH ₂), 5.09 (5H, s, C ₅ H ₅), 6.7–7.5 (4H, m, aromatic)
20	2.03 (1H, d, <i>J</i> (HH) 3.03, CH ₂), 3.68 (1H, d, <i>J</i> (HH) 3.03, CH ₂), 5.13 (5H, s, C ₅ H ₅), 6.71 (1H, d, <i>J</i> (HH) 8.33, aromatic), 7.00 (1H, d, <i>J</i> (HH) 8.33, aromatic)

Table 4 (continued)

	Complex δ
21	2.04 (1H, d, $J(\text{HH})$ 3.41, CH_2), 3.71 (1H, d, $J(\text{HH})$ 3.41, CH_2), 5.15 (5H, s, C_5H_5)
22	2.46 (1H, dd, $J(\text{HH})$ 3.03 and $J(\text{RhH})$ 0.76, CH_2), 3.67 (1H, dd, $J(\text{HH})$ 3.03 and $J(\text{RhH})$ 2.27, CH_2), 5.48 (5H, d, $J(\text{RhH})$ 0.76, C_5H_5), 6.7–7.6 (4H, m, aromatic)
23	1.34 (3H, t, $J(\text{HH})$ 7, CH_2CH_3), 2.40 (1H, s, alkylidene proton), 4.23 (1H, q, $J(\text{HH})$ 7, CH_2CH_3), 5.11 (5H, s, C_5H_5), 6.7–7.5 (4H, m, aromatic)

carbonyl)carbene to yield stable dimethylsulfonium bis(methoxycarbonyl)methylide [21], did not give the sulfonium-ylide but gave 71% of complex **1a** and 14% of dimethyl malonate. These facts indicate that thermal dissociation of alkoxy-carbonylmethylene-adducts does not afford carbene species. The thermal dissociations of **11** in toluene- d_8 yielded only deuterium-free dimethyl malonate $\{\text{CH}_2(\text{CO}_2\text{CH}_3)_2\}$. This shows that the hydrogen source of this hydrogen-abstraction reaction is not the solvent but the adduct. Although 3,3'-bis(cyclohexenyl), which is produced by the hydrogen-abstraction from cyclohexene [22], was just yielded by the thermal dissociation of **11** in cyclohexene, the quantity was small enough to disregard it.

Photodissociation of alkylidene-adducts

Some alkylidene adducts undergo photodissociation to give the parent complexes **1**. UV-vis spectral change of adduct **3** during irradiation is shown in Fig. 2. The absorption at 600 nm, which is assigned to **1b**, was increased up to 80% yield. The photodissociation of adduct **3** was promoted by the addition of benzophenone as a triplet sensitizer, and was inhibited by the addition of 1,3-cyclohexadiene.

The efficiency of the photodissociation was influenced by the metal atom and the substituents of the dithiolato ligand. The irradiation of the rhodium adducts caused photodissociation more easily than that of the cobalt adducts. The adducts which have phenyl substituents at the dithiolato ligand dissociated most smoothly. The cobalt adducts which have ester or cyano substituents at the dithiolato ligand were stable against the irradiation.

Adduct **11**, which is stable against irradiation, causes photodissociation only in the presence of benzophenone. Irradiation of the solution of adduct **11** in CDCl_3 in the presence of benzophenone and Me_2S gave 73% of complex **1a** and 52% of dimethyl malonate, which is the hydrogen-abstracted product of the alkylidene group, but did not yield the sulfonium-ylide, which is expected to be a singlet carbene-trapping product. These results prove that the photodissociation of alkylidene-adducts proceeds via the triplet state of the adducts and does not generate singlet carbenes. The irradiation of adducts **3** or **9** in cyclohexene was also carried out, but it caused decomposition of the adducts; photodissociation was inhibited in this olefin.

Experimental

General

All reactions were conducted under a pure argon atmosphere using standard Schlenk techniques. All NMR spectra were recorded on a JEOL JNM-GX270 spectrometer. Mass spectra were recorded on a JEOL JMS-D300 spectrometer.





Table 5

^{13}C NMR data of alkylidene-adducts **2–23**, in CDCl_3 (270 MHz; δ in ppm, TMS int; J in Hz)

Complex	δ
2	24.6 ($J(\text{CH})$ 167.3, C^3), 52.2 (CH_3), 53.1 (CH_3), 83.9 (C_5H_5), 114.6 (C^2), 162.4, 167.3, 176.2
3	24.1 ($J(\text{CH})$ 166.0, C^3), 83.6 (C_5H_5), 118.9 (C^2), 126.1, 127.5, 127.7, 127.9, 128.7, 129.4, 137.8, 140.9, 162.4 (C^1)
4	25.2 ($J(\text{CH})$ 164.8, C^3), 83.3 (C_5H_5), 108.1 (C^2), 155.0 (C^1)
5	22.7 ($J(\text{CH})$ 169.1, C^3), 84.9 (C_5H_5), 101.8, 113.0, 114.8, and 152.7 (C^1)
6	28.7 ($J(\text{RhC})$ 20.8 and $J(\text{CH})$ 169.1, C^3), 52.3 (OCH_3), 53.1 (OCH_3), 86.6 ($J(\text{RhC})$ 4.9, C_5H_5), 113.0 (C^2), 162.7, 167.8 ($J(\text{RhC})$ 2.4, C^1), 173.1
7	52.3 (OCH_3), 52.7 (OCH_3), 58.6 (C^3), 86.6 (C_5H_5), 112.7 (C^2), 126.5, 127.1, 127.6, 128.3, 128.4, 128.5, 132.4, 141.1, 163.0, 166.6, 180.8 (C^1)
8	14.5 (CH_2CH_3), 34.1 ($J(\text{CH})$ 175.7, C^3), 52.3 (OCH_3), 53.1 (OCH_3), 61.3 (CH_2CH_3), 85.1 (C_5H_5), 113.3 (C^2), 161.9, 166.7, 177.7, 177.9
9	14.7 (OCH_2CH_3), 32.0 ($J(\text{CH})$ 174.6, C^3), 61.1 (OCH_2CH_3), 84.7 (C_5H_5), 111.7 (C^2), 126.4, 127.8, 127.9, 128.7, 129.6, 137.2, 140.4, 165.2, 179.2
10	14.5 (CH_2CH_3), 40.3 ($J(\text{RhC})$ 19.5, $J(\text{CH})$ 177.0, C^3), 52.4 (OCH_3), 53.3 (OCH_3), 61.2 (CH_2CH_3), 87.9 ($J(\text{RhC})$ 4.9, C_5H_5), 112.5 (C^2), 162.4, 167.3 ($J(\text{RhC})$ 2.4), 174.9, 175.8 ($J(\text{RhC})$ 2.4)
11	37.8 (C^3), 52.5 (OCH_3), 53.1, 53.2, 86.0 (C_5H_5), 113.6 (C^2), 162.1, 166.2, 166.5, 175.5, 180.8
12	45.1 ($J(\text{RhC})$ 21.9, C^3), 52.5 (OCH_3), 53.0 (OCH_3), 53.2 (OCH_3), 53.3 (OCH_3), 88.6 ($J(\text{RhC})$ 6.1, C_5H_5), 112.8 (C^2), 162.5, 165.7, 167.1 ($J(\text{RhC})$ 2.4), 173.4 ($J(\text{RhC})$ 2.4), 177.9
13	25.2 ($J(\text{CH})$ 166.6, C^3), 51.9 (OCH_3), 83.6 (C_5H_5), 117.6 (C^2), 163.7 (CO), and 172.3 ($J(\text{CH})$ 170.9, C^1)
14	29.3 ($J(\text{RhC})$ 20.8 and $J(\text{CH})$ 167.9, C^3), 52.0 (OCH_3), 86.2 ($J(\text{RhC})$ 6.1, C_5H_5), 116.0 (C^2), 164.0 (CO), 168.8 ($J(\text{RhC})$ 2.4, C^1)
15	14.6 (CH_2CH_3), 34.2 ($J(\text{CH})$ 175.8, C^3), 52.0 (OCH_3), 61.1 (CH_2CH_3), 84.8 (C_5H_5), 116.2 (C^2), 163.3, 174.0 (C^1), 178.4
16	14.5 (CH_2CH_3), 40.5 ($J(\text{RhC})$ 19.6, $J(\text{CH})$ 177.0, C^3), 52.1 (OCH_3), 61.0 (CH_2CH_3), 87.5 ($J(\text{RhC})$ 4.9, C_5H_5), 115.4 (C^2), 163.7, 170.7 (C^1), 176.1 ($J(\text{RhH})$ 2.4)
17	25.2 ($J(\text{CH})$ 166.6, C^3), 83.5 (C_5H_5), 125.0 (C^2), 125.9 (Ph), 126.0 (Ph), 128.5 (Ph), 136.5, 148.7 (C^1)
18	25.1 ($J(\text{CH})$ 166.0, C^3), 83.4 (C_5H_5), 103.5 (C^2), 126.8 (Ph), 127.8 (Ph), 128.4 (Ph), 138.7, 170.5 (C^1)
19	27.3 ($J(\text{CH})$ 166.0, C^3), 83.6 (C_5H_5), 120.7 (CH), 128.4 (CH), 130.3 (CH), 130.4 (CH), 131.3 (C^2), 154.0 (C^1)
20	27.7 ($J(\text{CH})$ 167.2, C^3), 84.1 (C_5H_5), 122.2 (CH), 130.0 (CH), 132.1, 133.1, 133.6, 155.7 (C^1)
21	28.0 ($J(\text{CH})$ 167.3, C^3), 84.3 (C_5H_5), 131.2, 132.2, 133.2, 155.3
22	31.3 ($J(\text{CH})$ 167.3 and $J(\text{RhC})$ 20.8, C^3), 86.1 ($J(\text{RhC})$ 6.1, C_5H_5), 121.1 (CH), 128.9 (CH), 129.3 (C^2), 130.2 (CH), 131.0 (CH), 150.8 (C^1)
23	14.2 (CH_3), 35.5 ($J(\text{CH})$ 175.8, C^3), 61.2 (CH_3), 84.6 (C_5H_5), 121.3 (CH), 128.9 (CH), 129.4 (C^2), 130.0 (CH), 131.1 (CH), 154.7 (C^1), 178.5 (CO)

Table 6

Yields of products from decomposition in cyclohexene

Compound	Conditions					Total yield (%)
2	180 °C, 40 min	1	0.4	0.5		34
3	170 °C, 10 min	1	0.8	1.7		44
N ₂ CH ₂	Thermal decomposition at 265 °C	1	0.43	1.7 ^a		
N ₂ CH ₂	Thermal decomposition catalyzed by copper powder	1	0	0 ^a		
N ₂ CH ₂	Neat photolysis	1	0.24	1.3 ^a		
N ₂ CH ₂	Photolysis, sensitized by benzophenone	1	Trace	0.42 ^a		

^a Ref. 18.

UV-vis spectra were measured on a Hitachi Spectrometer Model 228. IR spectra were recorded on a JEOL JIR-RFX3001 spectrophotometer operated in the absorbance mode. Preparative HPLC was carried out on an LC-08 (Japan Analytical Ind. Co., Ltd.). Elemental analyses were carried out with a Perkin-Elmer Model 240C apparatus. GLC analysis was performed on a Shimadzu GC-6A chromatograph equipped with a flame-ionization detector in a stream of N₂, in a

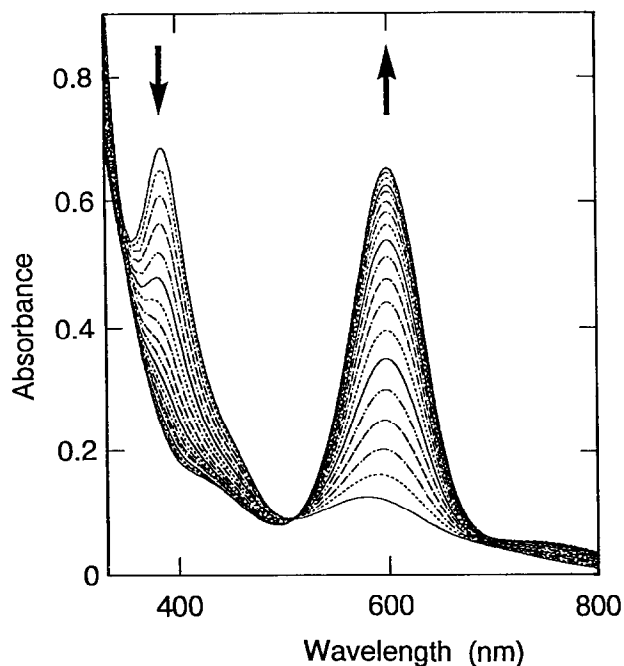


Fig. 2. UV-vis spectral change of CpCo(S₂C₂Ph₂)(CH₂) (**3**) (1.00×10^{-4} mol dm⁻³) in benzene under an argon atmosphere with a high pressure mercury lamp. The spectra were measured every 10 min.

glass 2 m × 3 mm column using 10% PEG-20M as a liquid phase on Uniport B of 80–100 mesh. Wakogel C-300 silica gel (200–300 mesh) was used for flush chromatography. Merck silica gel 60 GF-254 was used for preparative TLC. All melting points are uncorrected.

The dithiolatometal complexes were synthesized according to the literature methods [23]. The diazo compounds N_2CH_2 [24], N_2CPh_2 [25], N_2CHCO_2Et [26], and $N_2C(CO_2Me)_2$ [11a] were prepared by the literature methods. Norcarane [27] and 3,3'-biscyclohexenyl [22] used for standard samples were prepared by the literature methods. Other solvents and reagents were dried prior to use when necessary with appropriate drying agents.

$CpCo\{S_2C_2(CO_2Me)_2\}(CH_2)$ (**2**)

A solution of N_2CH_2 (0.12 g, 3.0 mmol) in ether was added dropwise to a solution of complex $CpCo\{S_2C_2(CO_2Me)_2\}$ (**1a**) (99.7 mg, 0.302 mmol) in ether (20 cm³) at 0 °C. The color changed from purple to brown immediately and the reaction mixture was stirred for 1 h. The solvent was removed at reduced pressure and the residue was chromatographed on a silica-gel column. Elution with CH_2Cl_2 gave a brown band which afforded **2** as a brown crystalline solid in 92% yield (95.5 mg, 0.278 mmol); m.p. 98–101 °C. Anal. Found: C, 41.86; H, 3.81. $C_{12}H_{13}O_4S_2Co$ calc.: C, 41.77; H, 3.80%. UV-vis (CH_2Cl_2): λ_{max} (ϵ) 250 (20900), 307 (9950), 396 (4040), 488 nm (2600). IR (KBr): 1725s, 1692s, 1480s, 1250s, 1090w, 1030m cm⁻¹. MS (EI, 70 eV): m/z (relative intensity) 344 (100, M^+), 330 (9, $M - CH_2$), 226 (15), 188 (29, $CpCoS_2$).

$CpCo(S_2C_2Ph_2)(CH_2)$ (**3**)

Complex $CpCo(S_2C_2Ph_2)$ (**1b**) (49.1 mg, 0.134 mmol) was treated with a 10-fold excess of N_2CH_2 , exactly as outlined for complex **1a**. Chromatography on silica-gel gave **3** as a brown crystalline solid in 85% yield (43.2 mg, 0.114 mmol). Decomp. 166–170 °C. Anal. Found: C, 63.19; H, 4.77. $C_{20}H_{17}S_2Co$ calc.: C, 63.15; H, 4.50%. UV-vis (CH_2Cl_2): λ_{max} (ϵ) 240 (20100), 398 (4430), 518 nm (1230). IR (KBr): 1520m, 870m, 770m, 760m, 750s, 700s cm⁻¹. MS (EI, 70 eV): m/z (relative intensity) 380 (4, M^+), 366 (46, $M - CH_2$), 188 (100, $CpCoS_2$), 178 (31, Ph_2C_2), 124 (24, $CpCo$).

$CpCo(S_2C_2H_2)(CH_2)$ (**4**)

Complex $CpCo(S_2C_2H_2)$ (**1c**) (0.211 mg, 0.986 mmol) was treated with a 10-fold excess of N_2CH_2 , exactly as outlined for complex **1a**. Chromatography on an alumina column gave **4** as a brown crystalline solid in 50% yield (0.112 g, 0.491 mmol); m.p. 92 °C. Anal. Found: C, 41.90; H, 4.10. $C_8H_9S_2Co$ calc.: C, 42.10; H, 3.98%. UV-vis (C_6H_6): λ_{max} (ϵ) 280 (8876), 310 (6792), 430 (1104), 517 nm (1106). IR (KBr): 1500s, 1414m, 1350w, 1053m, 995w, 916w, 841s, 814s, 698m, 687s, 669s, 640m, 611w cm⁻¹. MS (EI, 70 eV): m/z (relative intensity) 228 (100, M^+), 214 (67, $M - CH_2$), 188 (74, $CpCoS_2$), 124 (67, $CpCo$).

$CpCo\{S_2C_2(CN)_2\}(CH_2)$ (**5**)

Complex $CpCo\{S_2C_2(CN)_2\}$ (**1d**) (0.115 mg, 0.436 mmol) was treated with a 10-fold excess of N_2CH_2 , exactly as outlined for complex **1a**. Chromatography on silica-gel gave **5** as a red crystalline solid in 87% yield (0.105 g, 0.378 mmol).

Decomp. 142–143 °C. Anal. Found: C, 43.01; H, 2.35; N, 9.87. $C_{10}H_7N_2S_2Co$ calc.: C, 43.17; H, 2.54; N, 10.07%. UV-vis (CH_2Cl_2): λ_{max} (ϵ) 252 (15700), 308 (7280), 524(3200), 676.8 nm (427). IR (KBr): 2180s, 1450s, 1400m, 1160m, 840m, 820s, 500m cm^{-1} . MS (EI, 70 eV): m/z (relative intensity) 278 (33, M^+), 264 (49, $M - CH_2$), 188 (66, $CpCoS_2$), 124 (100, $CpCo$).

CpRh{ $S_2C_2(CO_2Me)_2$ }(CH_2) (**6**)

Complex $CpRh\{S_2C_2(CO_2Me)_2\}$ (**1e**) (97.0 mg, 0.259 mmol) was treated with a 10-fold excess of N_2CH_2 , exactly as outlined for complex **1a**. Chromatography on silica-gel gave **6** as a red crystalline solid in 56% yield (56.0 mg, 0.144 mmol); m.p. 85 °C. Anal. Found: C, 37.12; H, 3.37. $C_{12}H_{13}O_4S_2Rh$ calc.: C, 37.44; H, 3.48%. UV-vis (CH_2Cl_2): λ_{max} (ϵ) 236 (17800), 313 (5140), 408 nm (5000). IR (KBr): 1727s, 1690s, 1480s, 1430m, 1245s, 1090w, 1025m, 760w cm^{-1} . MS (EI, 70 eV): m/z (relative intensity) 388 (37, M^+), 374 (64, $M - CH_2$), 232 (100, $CpRhS_2$), 168 (61, $CpRh$).

CpCo{ $S_2C_2(CO_2Me)_2$ }(CPh_2) (**7**)

A solution of N_2CPh_2 (0.400 g, 2.06 mmol) in benzene (10 cm^3) was added dropwise to a solution of **1a** (0.205 g, 0.621 mmol) in benzene (100 cm^3) at room temperature. The color of the solution changed from purple to brown immediately. The solution was stirred for 1 h at room temperature. Removal of solvent at reduced pressure and chromatography of the residue on silica-gel gave **7** as a brown crystalline solid in 99% yield (0.306 g, 0.617 mmol). Decomp. 162–164 °C. Anal. Found: C, 57.88; H, 4.26. $C_{24}H_{21}S_2Co$ calc.: C, 58.06; H, 4.26%. UV-vis (CH_2Cl_2): λ_{max} (ϵ) 241.6 (20357), 302.0 (14856), 369.6 (5454), 540.8 nm (1958). IR (KBr): 1730s, 1687s, 1481s, 1439m, 1433m, 1263s, 1244s, 1080w, 1030m, 1018sh, 849w, 760m, 698m cm^{-1} . MS (EI, 70 eV): m/z (relative intensity) 496 (20, M^+), 188 (100, $CpCoS_2$), 124 (33, $CpCo$).

CpCo{ $S_2C_2(CO_2Me)_2$ }($CHCO_2Et$) (**8**)

A solution of complex **1a** (0.201 g, 0.609 mmol) and N_2CHCO_2Et (0.287 g, 2.52 mmol) in benzene (30 cm^3) was refluxed for 3 h, during which time the color changed from purple to dark purple. Removal of solvent at reduced pressure and chromatography of the residue on silica-gel gave a dark purple band on elution with CH_2Cl_2 /ether (19:1), which afforded **8** as a black crystalline solid in 87% yield (0.220 g, 0.529 mmol); m.p. 155–157 °C. Anal. Found: C, 43.04; H, 4.01. $C_{15}H_{17}O_6S_2Co$ calc.: C, 43.27; H, 4.09%. UV-vis (CH_2Cl_2): λ_{max} (ϵ) 243 (14500), 283 (18000), 376 (4580), 543 nm (1440). IR (KBr): 1736s, 1703s, 1695s, 1496s, 1300m, 1254s, 1240s, 1159m, 1151m, 1022m cm^{-1} . MS (EI, 70 eV): m/z (relative intensity) 416 (19, M^+), 352 (31), 343 (19, $M - CO_2Et$), 330 (16, $M - CHCO_2Et$), 188 (100, $CpCoS_2$), 124 (31, $CpCo$).

CpCo($S_2C_2Ph_2$)($CHCO_2Et$) (**9**)

A solution of complex **1b** (29.9 mg, 0.082 mmol) and N_2CHCO_2Et (53.0 mg, 0.465 mmol) in benzene (70 cm^3) was refluxed for 3 h, during which time the color changed from blue to green. Removal of solvent at reduced pressure and chromatography of the residue on silica-gel gave **9** as a green crystalline solid in 80% yield (28.7 mg, 0.063 mmol); m.p. 134–135 °C. Anal. Found: C, 60.90; H, 4.74.

$C_{23}H_{21}O_2S_2Co$ calc.: C, 61.1; H, 4.65%. UV-vis (CH_2Cl_2): λ_{max} (ϵ) 291 (22800), 385 (6780), 583 nm (1260). IR (KBr): 1674s, 1529m, 1252s, 1043m, 837w, 829w, 764w, 742m, 694m cm^{-1} . MS (EI, 70 eV): m/z (relative intensity) 452 (53, M^+), 366 (34, $M - CHCO_2Et$), 188 (77, $CpCoS_2$), 178 (56, Ph_2C_2), 124 (56, $CpCo$).

$CpRh\{S_2C_2(CO_2Me)_2\}(CHCO_2Et)$ (**10**)

A solution of complex **1e** (36.4 mg, 0.0973 mmol) and N_2CHCO_2Et (70.0 mg, 0.614 mmol) in benzene (40 cm^3) was stirred at room temperature for 5 min, during which time the color changed from red to orange. Chromatography on silica-gel gave **10** as a red crystalline solid in 76% yield (33.8 mg, 0.0735 mmol); m.p. 172–174 °C. Anal. Found: C, 38.84; H, 3.72. $C_{15}H_{17}O_6S_2Rh$ calc.: C, 39.13; H, 3.70%. UV-vis (CH_2Cl_2): λ_{max} (ϵ) 250 (16700), 319 nm (6320). IR (KBr): 1734s, 1705s, 1695s, 1496s, 1431w, 1300m, 1251s, 1240s, 1151m, 1020m cm^{-1} . MS (EI, 70 eV): m/z (relative intensity) 460 (25, M^+), 387 (61, $M - CO_2Et$), 374 (14, $M - CHCO_2Et$), 232 (100, $CpRhS_2$), 200 (47, $CpRhS$), 168 (45, $CpRh$).

$CpCo\{S_2C_2(CO_2Me)_2\}\{C(CO_2Me)\}$ (**11**)

Method A. A solution of complex **1a** (0.100 g, 0.303 mmol) and $N_2C(CO_2Me)_2$ (0.500 g, 3.16 mmol) in benzene (20 cm^3) was refluxed for 24 h. Removal of solvent at reduced pressure and chromatography of the residue on silica-gel gave two bands. The first, purple band was eluted with CH_2Cl_2 and found to contain starting material. The second, black band was eluted with CH_2Cl_2 /ether (7:3); this yielded **11** as a black crystalline solid in 5% yield (7.4 mg, 0.016 mmol); m.p. 148 °C. Anal. Found: C, 41.74; H, 3.66. $C_{16}H_{17}O_8S_2Co$ calc.: C, 41.74; H, 3.70%. UV-vis (CH_2Cl_2): λ_{max} (ϵ) 288 (12100), 380 (2080), 568 nm (573). IR (KBr): 1732s, 1697s, 1495m, 1431m, 1286m, 1265m, 1236s, 1217m, 1053w, 1028w cm^{-1} . MS (EI, 70 eV): m/z (relative intensity) 460 (1.3, M^+), 330 [51, $M - C(CO_2Me)_2$], 188 [100, $CpCoS_2$], 124 (24, $CpCo$).

Method B. A solution of complex **1a** (0.100 g, 0.303 mmol), $N_2C(CO_2Me)_2$ (0.500 g, 3.16 mmol), and $CuI-P(OMe)_3$ (62.0 mg, 0.175 mmol) in benzene (20 cm^3) was refluxed for 24 h. The color changed from purple to black. Chromatography gave one major black band which afforded 55.8 mg (0.121 mmol, 40%) of **11**. A minor colorless band included a trace amount of tetramethyl ethylenetetra-carboxylate which gave the parent peak (M^+ 260) in EI-MS.

$CpRh\{S_2C_2(CO_2Me)_2\}\{C(CO_2Me)\}$ (**12**)

A solution of complex **1e** (50.1 mg, 0.134 mmol) and $N_2C(CO_2Me)_2$ (0.200 g, 1.27 mmol) in benzene (20 cm^3) was refluxed for 24 h. The color changed from red to orange. Chromatography on silica-gel on elution with CH_2Cl_2 /ether (9:1) gave an orange band which afforded **12** as an orange crystalline solid in 31% yield (20.7 mg, 0.041 mmol); m.p. 168–170 °C. Anal. Found: C, 37.99; H, 3.41. $C_{16}H_{17}O_8S_2Rh$ calc.: C, 38.10; H, 3.37%. UV-vis (CH_2Cl_2): λ_{max} (ϵ) 252 (17700), 325 nm (6550). IR (KBr): 1732s, 1697s, 1495m, 1431m, 1286m, 1265m, 1238s, 1221m, 1055m, 1026m, 843w, 762w cm^{-1} . MS (EI, 70 eV): m/z (relative intensity) 504 (4, M^+), 374 [10, $M - C(CO_2Et)_2$], 232 (100, $CpRhS_2$), 200 (14, $CpRhS$) 168 (17, $CpRh$).

$CpCo(S_2C_2H,CO_2Me)(CH_2)$ (**13**)

Complex $CpCo(S_2C_2H,CO_2Me)$ (**1f**) (60.0 mg, 0.221 mmol) was treated with a 10-fold excess of N_2CH_2 . Chromatography on silica-gel gave **13** as a brown

crystalline solid in 45% yield (28.5 mg, 0.100 mmol); m.p. 118–120 °C. Anal. Found: C, 41.83; H, 3.84. $C_{10}H_{11}O_2S_2Co$ calc.: C, 41.96; H, 3.87%. UV-vis (CH_2Cl_2): λ_{max} (ϵ) 250 (20700), 306 (9950), 380 (5080), 486 nm (1870). IR (KBr): 1678s, 1485s, 1255s, 1220sh, 1050m, 860w, 840w, 820w, 740w cm^{-1} . MS (EI, 70 eV): m/z (relative intensity) 286 (100, M^+), 272 (18, $M - CH_2$), 226 (75, $M - HCO_2Me$), 188 (43, $CpCoS_2$), 124 (53, $CpCo$).

CpRh(S₂C₂H,CO₂Me)(CH₂) (14)

Complex $CpRh(S_2C_2H,CO_2Me)$ (**1g**) (94.8 mg, 0.300 mmol) was treated with a 10-fold excess of N_2CH_2 . Chromatography on silica-gel and preparative HPLC (GPC) gave **14** as a brown crystalline solid in 28% yield (28.2 mg, 0.085 mmol); m.p. 152–155 °C. Anal. Found: C, 36.37; H, 3.36. $C_{10}H_{11}O_2S_2Rh$ calc.: C, 36.40; H, 3.19%. UV-vis (CH_2Cl_2): λ_{max} (ϵ) 240 (18500), 265 (21200), 399 nm (6120). IR (KBr): 1675s, 1484s, 1250s, 1220sh, 1044m, 860w, 830w, 810w, 740w cm^{-1} . MS (EI, 70 eV): m/z (relative intensity) 330 (74, M^+), 316 (12, $M - CH_2$), 271 (45, $M - CO_2Me$), 270 (100, $M - HCO_2Me$), 200 (82, $CpRhS$), 168 (77, $CpRh$).

CpCo(S₂C₂H,CO₂Me)(CHCO₂Et) (15)

A solution of complex **1f** (0.272 g, 1.00 mmol) and N_2CHCO_2Et (0.680 g, 5.96 mmol) in benzene (30 cm^3) was refluxed for 5 h. Chromatography on silica-gel on elution with CH_2Cl_2 gave a brown band which afforded **15** as a brown crystalline solid in 59% yield (0.212 g, 0.592 mmol); m.p. 112 °C. Anal. Found: C, 43.63; H, 4.21. $C_{13}H_{15}O_4S_2Co$ calc.: C, 43.58; H, 4.22%. UV-vis (CH_2Cl_2): λ_{max} (ϵ) 235 (14000), 302 (18400), 370 (5400), 545 nm (1200). IR (KBr): 1705s, 1699s, 1483s, 1286m, 1242m, 1222sh, 1142m, 1041m, 860m, 839w, 829w, 746w cm^{-1} . MS (EI, 70 eV): m/z (relative intensity) 358 (34, M^+), 285 (79, $M - CO_2Et$), 272 (20, $M - CHCO_2Et$), 188 (100, $CpCoS_2$), 124 (34, $CpCo$).

CpRh(S₂C₂H,CO₂Me)(CHCO₂Et) (16)

A solution of complex **1g** (0.128 g, 0.405 mmol) and N_2CHCO_2Et (0.140 g, 1.23 mmol) in benzene (30 cm^3) was stirred at room temperature for 5 min. Chromatography on silica-gel gave **16** as an orange-crystalline solid in 63% yield (102.5 mg, 0.255 mmol); m.p. 110 °C. Anal. Found: C, 38.64; H, 3.78. $C_{13}H_{15}O_4S_2Rh$ calc.: C, 38.81; H, 3.76%. UV-vis (CH_2Cl_2): λ_{max} (ϵ) 250 (16100), 320 nm (6970). IR (KBr): 1695s, 1685s, 1480s, 1295m, 1260s, 1210m, 1140s, 1040m, 900w, 830w, 750w cm^{-1} . MS (EI, 70 eV): m/z (relative intensity) 402 (18, M^+), 329 (100, $M - CO_2Et$), 316 (17, $M - CHCO_2Et$), 232 (41, $CpRhS_2$), 200 (26, $CpRhS$), 168 (32, $CpRh$).

CpCo(S₂C₂H,Ph)(CH₂) (17, 18)

Complex $CpCo(S_2C_2H,Ph)$ (**1h**) (205.8 mg, 0.710 mmol) was treated with a 10-fold excess of N_2CH_2 . Chromatography on silica-gel on elution with CH_2Cl_2 /hexane (1:3) gave a brown band which afforded a brown crystalline solid. Mass spectra of this solid showed that it contains the 1:1 methylene-adduct, but the NMR data showed a mixture of two sets of the adducts. MS (EI, 70 eV; mixture sample): m/z (relative intensity) 304 (2, M^+), 303 (11, $M - H$), 290 (69, $M - CH_2$), 188 (100, $CpCoS_2$), 124 (32, $CpCo$). Preparative HPLC of this mixture gave two brown bands, which yielded 75.5 mg (0.25 mmol, 35%) of $CpCo\{\eta^3(S,S',C)-SC(H)C(Ph)S'CH_2\}$ (**17**) and 47.4 mg (0.16 mmol, 22%) of $CpCo\{\eta^3(S,S',C)-$

SC(Ph)C(H)S'(CH₃) (**18**) as air-sensitive brown solids that did not provide satisfactory analyses.

CpCo(S₂C₆H₄)(CH₂) (19)

Complex CpCo(S₂C₆H₄) (**1i**) (492.5 mg, 1.860 mmol) was treated with a 10-fold excess of N₂CH₂. Chromatography on silica-gel gave **19** as a red crystalline solid in 45% yield (231.7 mg, 0.833 mmol). Decomp. 171 °C. Anal. Found: C, 51.66; H, 3.93. C₁₂H₁₁S₂Co calc.: C, 51.80; H, 3.96%. UV-vis (CH₂Cl₂): λ_{max} (ε) 254 (19600), 310 (7200), 330 (7000), 420 nm (700), 525 (1000). IR (KBr): 1570w, 1440s, 1410w, 1240s, 1100w, 820m, 760s cm⁻¹. MS (EI, 70 eV): *m/z* (relative intensity) 278 (100, M⁺), 264 (36, M - CH₂), 212 (63, M - CpH), 153 (39, M - CpCoH).

CpCo(S₂C₆H₂Cl₂)(CH₂) (20)

Complex CpCo(S₂C₆H₂Cl₂) (**1j**) (66.0 mg, 0.198 mmol) was treated with a 10-fold excess of N₂CH₂. Chromatography on silica-gel gave **20** as a red crystalline solid in 67% yield (46.0 mg, 0.133 mmol); m.p. 133–135 °C. Anal. Found: C, 41.34; H, 2.34. C₁₂H₉S₂Cl₂Co calc.: C, 41.52; H, 2.61%. UV-vis (CH₂Cl₂): λ_{max} (ε) 253 (14761), 309 (7266), 523 (1050), 721 nm (181). IR (KBr): 1550w, 1410s, 1330m, 1170s, 1070m, 1060m, 820s, 780m cm⁻¹. MS (EI, 70 eV): *m/z* (relative intensity) 348 [66, M⁺(³⁵Cl³⁷Cl)], 346 [93, M⁺(³⁵Cl₂)], 332 [85, M⁺(³⁵Cl₂) - CH₂], 310 [75, CpCoS₂C₆H(³⁵Cl)(CH₂)], 274 [75, CpCoS₂C₆(CH₂)], 124 (100, CpCo).

CpCo(S₂C₆Cl₄)(CH₂) (21)

Complex CpCo(S₂C₆Cl₄) (**1k**) 34.2 mg, 0.085 mmol) was treated with a 10-fold excess of N₂CH₂. Chromatography on silica-gel gave **21** as a red crystalline solid in 65% yield (22.7 mg, 0.055 mmol). **21**: Decomp. 170–172 °C. Anal. Found: C, 34.53; H, 1.77. C₁₂H₇S₂Cl₄Co calc.: C, 34.64; H, 1.70%. UV-vis (CH₂Cl₂): λ_{max} (ε) 255 (20900), 310 (9110), 350 (6890), 515 nm (1110). IR (KBr): 1330s, 1295m, 1250m, 840w, 820s, 675m cm⁻¹. MS (EI, 70 eV): *m/z* (relative intensity) 416 [23, M⁺(³⁵Cl₃³⁷Cl)], 402 [89, M⁺(³⁵Cl₃³⁷Cl)CH₂], 380 [34, M⁺(³⁵Cl₃³⁷Cl)H(³⁵Cl)], 124 (100, CpCo).

CpRh(S₂C₆H₄)(CH₂) (22)

Complex CpRh(S₂C₆H₄) (**1l**) (68.3 mg, 0.222 mmol) was treated with a 10-fold excess of N₂CH₂. Chromatography on silica-gel gave **22** as a brown crystalline solid in 23% yield (16.0 mg, 0.050 mmol). Decomp. 170 °C. UV-vis (CH₂Cl₂): λ_{max} (ε) 240 (19400), 320 (8610), 400 (2420). IR (KBr): 1570w, 1440s, 1400w, 1240m, 1100w, 830m, 810m, 760s cm⁻¹. MS (EI, 70 eV): *m/z* (relative intensity) 322 (100, M⁺), 308 (47, M - CH₂), 289 (52, M - HS), 256 (26, M - CpH), 168 (38, M - CpRh).

CpCo(S₂C₆H₄)(CHCO₂Et) (23)

A solution of complex **1i** (0.101 g, 0.383 mmol) and N₂CHCO₂Et (0.152 g, 1.33 mmol) in benzene (100 cm³) was refluxed for 12 h, during which time the color changed from purple to green. Removal of solvent at reduced pressure and chromatography of the residue on silica-gel on elution with CH₂Cl₂ gave a green band which afforded **23** as a green crystalline solid in 15% yield (0.020 g, 0.057 mmol); m.p. 167 °C. Anal. Found: C, 51.41; H, 4.32. C₁₅H₁₅O₂S₂Co calc.: C, 51.43; H, 4.29%. UV-vis (CH₂Cl₂): λ_{max} (ε) 245 (7560), 290 (11500), 437 (480), 600

nm (480). IR (KBr): 1690s, 1445m, 1300s, 1170s, 1050w, 835m, 755m cm^{-1} . MS (EI, 70 eV): m/z (relative intensity) 350 (38, M^+), 264 (100, $M - \text{CHCO}_2\text{Et}$), 153 (65, $M - \text{CpCoCO}_2\text{Et}$).

Reaction of $\text{CpRh}\{S_2C_2(\text{CO}_2\text{Me})_2\}\{C_2(\text{CO}_2\text{Me})_2\}$ (24) with N_2CH_2

Complex **24** was prepared by the literature method [3]. A solution of complex **24** (0.208 g, 0.403 mmol) in ether (100 ml) was treated with a 20-fold excess of N_2CH_2 . Chromatography on silica-gel gave two bands. The first, orange band was eluted with CH_2Cl_2 and yielded 75.0 mg (0.193 mmol, 48%) of methylene-adduct **6**. The second, orange band was eluted with $\text{CH}_2\text{Cl}_2/\text{ether}$ (9:1) and was identified by MS as unreacted **24**.

Thermal dissociation of adduct 7

Adduct **7** (21.5 mg, 0.043 mmol) was packed in an aluminum vessel and heated at 180°C for 5 min, during which time the adduct melted and the color changed from brown to purple immediately. After cooling, the products were extracted with CH_2Cl_2 . Preparative TLC of the products gave 59% (8.4 mg, 0.0255 mmol) of the parent complex **1a** and 42% (3.0 mg, 0.009 mmol) of tetraphenyl ethylene.

Thermal dissociation of adduct 2 in cyclohexene

A solution of adduct **2** (36.0 mg, 0.105 mmol) in cyclohexene (1 ml) was sealed in a Pyrex glass tube and heated at 180°C for 40 min. The solution was filtered and the products were analyzed by GC-MS and GLC. The parent peak ($M^+ = 96$), which is assigned to composition C_7H_{12} , was observed by means of GC-MS (EI, 70 eV). The assignment of the products was carried out by means of GLC and the quantitative analysis was measured using standard samples.

Thermal dissociation of adduct 3 in cyclohexene

A solution of adduct **3** (11.1 mg, 0.0292 mmol) in cyclohexene (1 ml) was sealed in a Pyrex glass tube and heated at 170°C for 10 min. The products were analyzed by GLC as above for adduct **2**.

Thermal dissociation of adduct 11 in cyclohexene

A solution of adduct **11** (48.0 mg, 0.104 mmol) in cyclohexene (1 ml) was sealed in a Pyrex glass tube and heated at 220°C for 20 min. GC-MS and GLC could not confirm the formation of cyclopropane derivatives or insertion products, but dimethyl malonate (3.0%) and 3,3'-bis(cyclohexenyl) (0.4%) were detected.

Thermal dissociation of adduct 11 in the presence of dimethyl sulfide

A solution of adduct **11** (13.0 mg, 0.028 mmol) and dimethyl sulfide (8.5 mg, 0.137 mmol) in CDCl_3 (0.5 ml) was sealed in an NMR sample tube and heated at 220°C for 2 h. ^1H NMR showed the formation of **1a** (71%) and dimethyl malonate (14%).

Photoreactions of alkylidene-adducts; general procedure

A solution of adducts **2-23** (approximately 10^{-4} mol cm^{-3}) in benzene or CH_2Cl_2 was sealed in a Pyrex glass tube and irradiated with a high pressure mercury lamp through Pyrex glass. UV-vis spectral changes of the solution were observed at regular intervals.

Photodissociation of adduct 11 in the presence of dimethyl sulfide and benzophenone

A solution of adduct **11** (0.5 mg, 0.001 mmol), dimethyl sulfide (0.42 mg, 0.001 mmol), and benzophenone (1.0 mg, 0.006 mmol) in CDCl_3 (0.5 ml) was sealed in an NMR sample tube and irradiated with a high pressure mercury lamp for 5 h. ^1H NMR showed the formation of **1a** (73%) and dimethyl malonate (52%).

Structure determination for adduct 15

The reflection intensities were collected by the ω -scan technique ($2\theta < 60^\circ$) on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$). The 3321 intensities ($|F_o| > 3\sigma(|F_o|)$) were corrected for Lorentz and polarization factors, but not for absorption, because of the low magnitude of μ_r (< 1.0).

Crystal data. $\text{C}_{13}\text{H}_{15}\text{CoS}_2\text{O}_4$, MW = 358.30, triclinic, space group $P\bar{1}$, $a = 9.637(3)$, $b = 10.852(2)$, $c = 7.551(3) \text{ \AA}$, $\alpha = 102.51(2)$, $\beta = 106.92(4)$, $\gamma = 84.31(2)^\circ$, $V = 736.92 \text{ \AA}^3$, $Z = 2$, $D_c = 1.615 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}_\alpha) = 14.41 \text{ cm}^{-1}$.

The structure was solved by the heavy-atom method. The position of the cobalt atom was obtained from the three-dimensional Patterson function, while the positions of all other non-hydrogen atoms were successively located by Fourier syntheses and were refined by a block-diagonal least-squares method and only in the last cycle by a full-matrix least-squares method. In the last cycle of the full matrix least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms, all the parameter shifts were less than one-third of the corresponding standard deviations. The weighting scale was $w = 1/(\sigma^2 F)$. The final R value was 0.070 ($R_w = 0.082$).

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References

- 1 For reviews, see (a) U.T. Mueller-Westerhoff and B. Vance, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (Eds.), *Comprehensive Coordination Chemistry*, Vol. 2, Pergamon, Oxford, 1987, p. 595; (b) R.P. Burns and C.A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 22 (1979) 303; (c) R. Eisenberg, *Prog. Inorg. Chem.*, 12 (1970) 295; (d) G.N. Schrauzer, *Acc. Chem. Res.*, 2 (1969) 72. (e) J.A. McCleverty, *Prog. Inorg. Chem.*, 10 (1968) 49.
- 2 S.D. Henderson, T.A. Stephenson and E.J. Wharton, *J. Organomet. Chem.*, 179 (1979) 43.
- 3 M. Kajitani, T. Suetsugu, R. Wakabayashi, A. Igarashi, T. Akiyama and A. Sugimori, *J. Organomet. Chem.*, 293 (1985) C15.
- 4 M. Kajitani, Y. Eguchi, R. Abe, T. Akiyama and A. Sugimori, *Chem. Lett.*, (1990) 359.
- 5 See for example: W.B. Heuer, A.E. True, P.N. Swepston and B.M. Hoffman, *Inorg. Chem.*, 27 (1988) 1474.
- 6 W.A. Herrmann, *Angew. Chem. Int. Ed. Engl.*, 25 (1986) 56.
- 7 B. Strecker and H. Werner, *Angew. Chem. Int. Ed. Engl.*, 29 (1990) 275.
- 8 J.-I. Setsune and D. Dolphin, *Organometallics*, 3 (1984) 440.

- 9 J. Maxwell and T. Kodadek, *Organometallics*, 10 (1991) 4.
- 10 M. Kajitani, M. Sakurada, K. Dohki, T. Suetsugu, T. Akiyama and A. Sugimori, *J. Chem. Soc., Chem. Commun.*, (1990) 19.
- 11 B.W. Peace, F. Carman and D.S. Wulfman, *Synthesis*, (1971) 658.
- 12 For a general discussion, see W.R. Moser, *J. Am. Chem. Soc.*, 91 (1969) 1135.
- 13 C.M. Bolinger and T.B. Rauchfuss, *Inorg. Chem.*, 21 (1982) 3947.
- 14 H. Köpf and M. Schmidt, *J. Organomet. Chem.*, 4 (1965) 426.
- 15 R.F. Heck, *Inorg. Chem.*, 7 (1968) 1513.
- 16 H. Ushijima, M. Kajitani, K. Shimizu, G.P. Satô, T. Akiyama and A. Sugimori, *J. Electroanal. Chem.*, 303 (1991) 199.
- 17 For a general discussion, see J.B. Stothers, *Carbon-13 NMR Spectroscopy*, Academic Press, New York, 1972, p. 333.
- 18 K.R. Kopecky, G.S. Hammond and P.A. Leermakers, *J. Am. Chem. Soc.*, 84 (1962) 1015.
- 19 For reviews, see (a) M. Regitz (Ed.), *Methoden der Organischen Chemie*, Vol. E19b, Georg Thieme Verlag, Stuttgart, New York, 1989; (b) M. Jones Jr. and R.A. Moss, *Carbenes*, Vols. 1 and 2, Wiley-Interscience, New York, 1973.
- 20 For example, a generation of methylene derivatives on the thermolysis of an organochromium-methylene-adduct was reported. See W.A. Herrmann and J. Rohrmann, *J. Organomet. Chem.*, 284 (1985) 189.
- 21 W. Ando, T. Yagihara, S. Tozune and T. Migita, *J. Am. Chem. Soc.*, 91 (1969) 2786.
- 22 W. Lwowski and T.W. Mattingly Jr., *J. Am. Chem. Soc.*, 87 (1965) 1947.
- 23 (a) H. Bönnemann, B. Bogdanović, W. Brijoux, R. Brinkmann, M. Kajitani, R. Mynott, G.S. Natarajan and M.G.Y. Samson, in J.R. Kosak (Ed.), *Catalysis of Organic Reactions*, Marcel Dekker, New York, 1987, p. 31; (b) J. Locke and J.A. McCleverty, *Inorg. Chem.*, 5 (1966) 1157; (c) R.B. King and C.A. Eggers, *Inorg. Chem.*, 7 (1968) 340.
- 24 T.J. De Boer, H.J. Backer, *Rec. Trav. Chim.*, 73 (1954) 229.
- 25 L.I. Smith and K.L. Howard, *Org. Synth., Coll.*, 3 (1955) 351.
- 26 N.E. Searle, *Org. Synth., Coll.*, 4, (1963) 424.
- 27 H.E. Simmons and R.D. Smith, *J. Am. Chem. Soc.*, 81 (1959) 4256.