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Addition of $CHSiMe_3$ to the Co–S Bond of 1,2,5,3-cobaltadithiazole. Formation and reactions of stereoisomeric cobaltathiirane complexes

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Abstract

In the reaction between (η^5-cyclopentadienyl) (1-phenylmethanimine-*N*,1-dithiolato)cobalt(III), ($[\mathrm{Cp}\overline{\mathrm{CoSNC(Ph)S}}]$, **1**) and trimethylsilyldiazomethane, trimethylsilylmethylene adds between Co and S adjacent to N. Two geometrical isomers of cobaltathiirane complexes are formed: in the major addition product **2a**, the trimethylsilyl group is located at the *anti*-position with respect to the cobaltadithiazole ring and in the minor product **2b**, at the *syn*-position. These two stereoisomers are in equilibrium. Equilibrium is attained in 10 h at 80°C, when the reaction is started either from **2a** or from **2b**. From the temperature dependence of the equilibrium, ΔG value of the isomerization of the stereoisomers is estimated to be 34 kJ mol^{-1}. These isomeric trimethylsilylmethylene adducts react with HCl to give a common product, chloro(η^5-cyclopentadienyl)[*N*-(trimethylsilylmethylthio)-κS-1-phenylmethanimine-1-thiolato-κS]cobalt(III) (**4**). By treatment with tetrabutylammonium fluoride, **4** undergoes a ring reforming reaction to give a methylene adduct, (η^5-cyclopentadienyl)-[*N*-(methylene-κC)-thio-κS]-1-phenylmethanimine-1-thiolato-κS]cobalt(III).

Keywords: Cobalt; Thiirane; Cobaltadithiazole; Isomerization; Addition-elimination; Alkylidene

1. Introduction

A metalladithiolene ring is a unique metallacycle of conjugated five-membered ring with six π-electrons. Among metalladithiolene complexes, the complexes of the type [M(1,2-ethenedithiolato)$_n$] having only dithiolato as the ligand have been extensively studied and their interesting properties have been revealed[1].

Since the first synthesis of (η^5-cyclopentadienyl)[1,2-bis(trifluoromethyl)-1,2-ethenedithiolato]cobalt(III) by King [2], the new field of the chemistry of metalladithiolene complexes having ligands other than dithiolato has been developed. We have studied the chemistry (synthesis, physical properties and reactivities) of metalladithiolene complexes having both cyclopentadienyl and 1,2-ethenedithiolato as ligands ((η^5-cyclopentadienyl)(1,2-ethenedithiolato)metal(III) (metal = Co and Rh)) and reported their unique properties different from those of [M(1,2-ethenedithiolato)$_n$]-type metalladithiolenes [3]. Whereas the [M(1,2-ethenedithiolato)$_n$]-type metalladithiolenes undergo addition reactions mainly at sulfur atoms [4–9], the [M(Cp)(1,2-ethenedithiolato)]-type metalladithiolenes undergo addition reactions at the metal and sulfur. Diazo compounds react very easily with $[\mathrm{Co(Cp)(S_2C_2XY)}]$-type cobaltadithiolenes and their selenium analogs to give alkylidene adducts in which the alkylidene groups bridge between Co and chalcogen without breaking the cobalt–chalcogen bonds [10,11]. Some azides undergo a similar reaction [12]. The alkylidene adducts of the cobaltadithiolenes react further with a phosphite resulting in the coordination of the phosphorus to the metal and opening of the three-membered ring [13]. Dimethyl acetylenedicarboxylate adds between the rhodium and sulfur of rhodiadithiolene [14]. Quadricyclane adds between cobalt and sulfur of the cobaltadithiolene ring accompanying the skeletal rearrangement of the hydrocarbon [15]. A remarkable feature of these adducts is the elimination of the added moieties by UV irradiation [2b,10,13,16].

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We have recently synthesized a new family of metallacycle, cobaltadithiazole, which consists of one cobalt atom, two coordinated sulfur atoms, one unsaturated carbon and one unsaturated nitrogen atom [17].

The comparison of the physical and chemical properties of metalladithiolene and metalladithiazole is important in order to clarify the features of the new metallacycle. In a comparative study of the metalladithiazole and metalladithiolene rings, we have reported the different behavior of cobaltadithiolene and cobaltadithiazole in the reaction with dimethyl acetylenedicarboxylate [18].

In the previous paper, we reported the addition of a trimethylsilylmethylene group between the Co and S of the cobaltadithiolene ring and the ring opening and reforming reactions of the trimethylsilylmethylene adducts [19]. We describe here the reaction of a cobaltadithiazoles with trimethylsilyldiazomethane.

2. Results and discussion

2.1. Reaction with trimethylsilyldiazomethane

Similarly to the cobaltadithiolene ring [19], the cobaltadithiazole ring in (η^5-cyclopentadienyl)(1-phenylmethanimine-*N*,1-dithiolato)cobalt(III) ([CpCoSNC(Ph)S], **1**) undergoes addition of a methylene group between Co and S in the reaction with diazo compounds. The reaction of **1** with trimethylsilyldiazomethane gave two trimethylsilylmethylene adducts. The reaction in a dichloromethane solution at 40°C for 6 h gave the two adducts **2a** and **2b** in 52 and 5% yields, respectively.

The structures of these two adducts were determined by X-ray crystal analysis. The ORTEP [20] drawings of **2a** and **2b** are shown in Fig. 1.

The X-ray structures show that these two adducts are a pair of geometrical isomers. In each complex, a trimethylsilyl group bridges between Co and S and a cobaltathiirane ring is formed. In both cases, the sulfur atom adjacent to N is bridged. In the major product, **2a**, the trimethylsilyl group is located at the *anti*-position with respect to the cobaltadithiazole ring, whereas in the minor product, **2b**, the trimethylsilyl group is located at the *syn*-position with respect to the cobaltadithiazole ring.

In a crystal of **2b**, there are two crystallographically independent molecules (**2b-A** and **2b-B**) in which the corresponding bond lengths and bond angles agree well, within experimental error.

Selected bond lengths, bond angles, dihedral angles and torsion angles of the trimethylsilylmethylene adducts **2a**, **2b-A** and **2b-B** are given in Table 1, in which the corresponding values are listed in the same row.

The cobaltadithiazole ring of each trimethylsilylmethylene adduct is almost planar. The three-membered cobaltathiirane ring is nearly perpendicular to the cobaltadithiazole ring. The bond distances between Co and the bridged S of **2a**, **2b-A** and **2b-B** are 2.159(2), 2.157(2) and 2.159(2) Å, respectively. These distances are longer than the Co–S bond of the free cobaltadithiazole (2.107(1) Å in (η^5-pentamethylcyclopentadienyl)-(1-phenylmethanimine-*N*,1-dithiolato)cobalt(III)). These values indicate the bond between Co and S is weakened

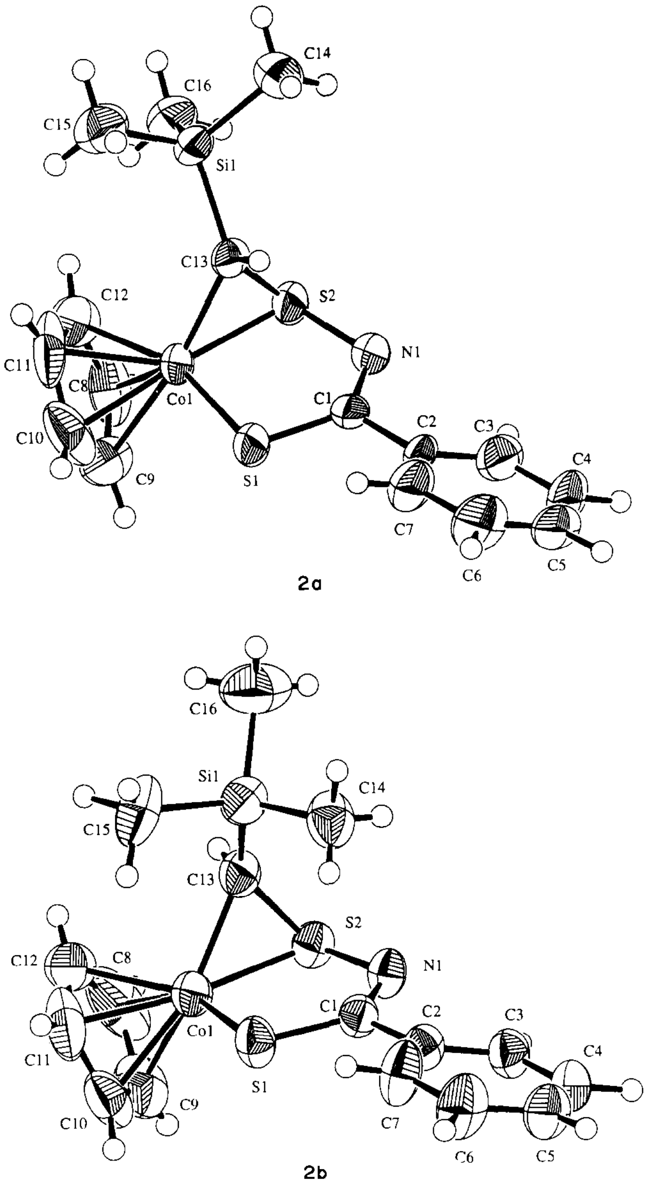


Fig. 1. ORTEP drawings of trimethylsilylmethylene adducts **2a** and **2b**.

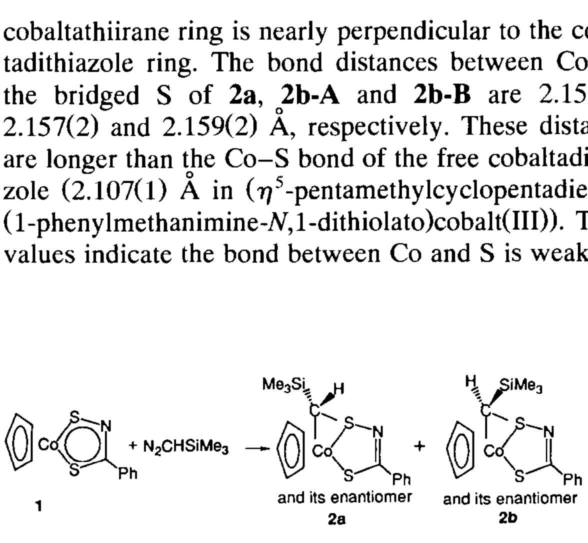


Table 1
Selected geometrical data of trimethylsilylmethylene adducts **2a** and **2b**

	2a	**2b**	
		A	**B**
Bond lengths (Å)			
Co–S(1)	2.210(2)	2.198(2)	2.195(2)
Co–S(2)	2.159(2)	2.157(2)	2.159(2)
Co–C(13)	1.994(6)	2.007(6)	1.990(5)
S(2)–C(13)	1.750(7)	1.753(6)	1.738(5)
S(2)–N(1)	1.689(6)	1.694(4)	1.680(4)
S(1)–C(1)	1.717(7)	1.714(5)	1.722(5)
C(1)–N(1)	1.310(10)	1.312(6)	1.309(6)
C(13)–Si(1)	1.869(6)	1.850(6)	1.875(5)
Si(1)–C(14)	1.852(8)	1.840(7)	1.833(6)
Si(1)–C(15)	1.85(1)	1.841(7)	1.857(7)
Si(1)–C(16)	1.861(10)	1.872(8)	1.861(7)
Co–C(8)	2.081(8)	2.049(8)	2.062(6)
C(1)–C(2)	1.491(8)	1.483(7)	1.481(6)
Bond angles (°)			
S(1)–Co–S(2)	88.07(7)	88.35(6)	88.14(6)
Co–S(2)–C(13)	60.3(2)	60.7(2)	60.3(2)
S(1)–Co–C(13)	92.2(2)	96.3(2)	95.5(2)
S(2)–Co–C(13)	49.6(2)	49.6(2)	49.3(2)
Co–C(13)–S(2)	70.1(2)	69.7(2)	70.4(2)
Co–S(1)–C(1)	102.1(3)	102.4(2)	102.6(2)
S(2)–N–C(1)	115.5(5)	115.6(4)	116.4(4)
N–C(1)–S(1)	125.4(5)	125.2(4)	124.3(4)
Co–S(2)–N	108.5(2)	108.3(2)	108.4(2)
Co–C(13)–S(2)	70.1(2)	69.7(2)	70.4(2)
Co–C(13)–Si(1)	128.2(3)	127.2(3)	128.0(3)
S(2)–C(13)–H(13)	111.8	100.7	110.0
Co–C(13)–Si(1)	128.2(3)	127.2(3)	128.0(3)
S(2)–C(13)–Si(1)	118.8(4)	132.7(3)	132.9(3)
C(13)–Si(1)–C(14)	106.8(3)	116.5(3)	117.9(3)
C(13)–Si(1)–C(15)	109.0(4)	106.6(3)	103.5(3)
C(13)–Si(1)–C(16)	111.8(4)	105.2(3)	106.1(3)
S(1)–C(1)–C(2)	117.8(6)	118.4(4)	118.5(4)
N(1)–C(1)–C(2)	116.7(6)	116.4(5)	117.2(4)
Dihedral angles (°)			
S(1)–CoS(2) –CoS(2)C(13)	94.5(2)	99.7(2)	98.9(2)
S(1)CoS(2) –Cp ring	108.9(9)	108.9(9)	107.7(6)
S(1)CoS(2)–Ph	149.0(9)	157.7(6)	151.8(6)
CoS(2)C(13) –Cp ring	125.6(9)	127.8(9)	128.5(6)
CoS(2)C(13)–Ph	85.64(9)	101.4(6)	94.6(6)
Cp ring–Ph	54.9(9)	52.5(9)	54.0(6)
Torsion angles (°)			
Co–S(1)–C(1)–N	−1.1(7)	3.8(5)	1.4(5)
Co–S(2)–N–C(1)	−7.2(6)	−2.2(4)	−3.4(4)
Co–C(13)–S(2)–N	−101.9(2)	−100.3(2)	100.6(2)
Co–S(1)–C(1) –C(2)	−179.8(5)	−173.4(4)	−176.5(4)
Co–S(2)–C(13)–Si	−123.5(4)	122.4(5)	124.2(4)
S(1)–Co–S(2) –C(13)	−94.5(2)	−99.7(2)	−98.9(2)
S(1)–Co–S(2)–N	5.2(2)	3.4(2)	3.3(2)
S(1)–Co–C(13) –S(2)	85.6(2)	82.4(1)	82.8(1)
S(1)–Co–C(13)–Si	−162.9(4)	−46.5(3)	−46.9(3)
S(2)–Co–C(13)–Si	111.5(5)	−128.9(4)	−129.7(4)
N–S(2)–Co–C(13)	99.7(3)	103.2(3)	102.2(3)
S(1)–C(1)–N–S(2)	5.7(9)	−1.2(6)	1.3(6)
S(2)–Co–S(1) –C(1)	−2.7(3)	−3.6(2)	−2.6(2)
S(2)–N–C(1)–C(2)	−175.7(5)	176.0(4)	179.3(4)

by the bridging by the trimethylsilylmethylene group, presumably due to the decrease in the double bond character of the Co–S bond, i.e. the loss of aromaticity of the ring caused by the bridging.

The dihedral angle between the cobaltathiirane ring and the S(1)–Co–S(2) plane of **2a** (94.5(2)°) is smaller than those of **2b-A** and **2b-B** (99.7(2) and 98.9 (2)°, respectively). The bond angle of S(1)–Co–C(13) = 92.2(2)° in **2a** is also smaller than those of 96.3(2) and 95.5(2)° in **2b-A** and **2b-B**, respectively. These values indicate that the *anti*-form **2a** in which a bulky trimethylsilyl group is directed away from the cobaltadithiolene ring is less sterically hindered than the *syn*-form **2b**.

2.2. Equilibrium of the two isomers of the trimethylsilylmethylene adduct

The stereoisomers **2a** and **2b** are equilibrated at moderate temperatures. When we heat pure **2a** or **2b** in benzene at 80°C, we obtain a mixture of **2a** and **2b** in the ratio $\approx 2:1$. As shown in Fig. 2, the equilibrium is attained in 10 h.

The equilibrium is temperature dependent. The plot of $\ln K$ versus $1/T$ (Fig. 3) gives ΔG (difference in

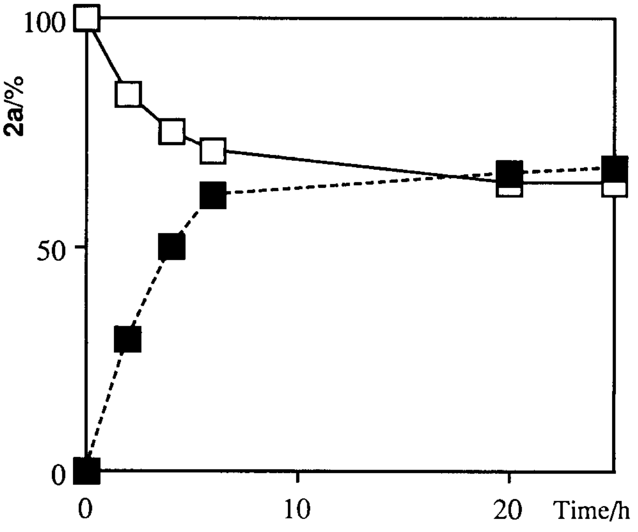
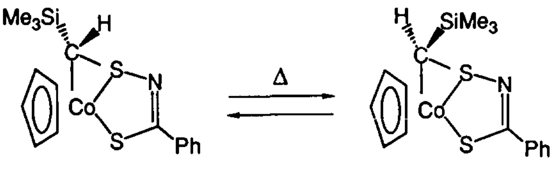


Fig. 2. Isomerization of **2a** and **2b** at 80°C, (□) Start from **2a**; (■), start from **2b**. Initial concentration, 2.7×10^{-2} mol dm^{-3} in $CD_3C_6D_5$.



and its enantiomer
2a

and its enantiomer
2b

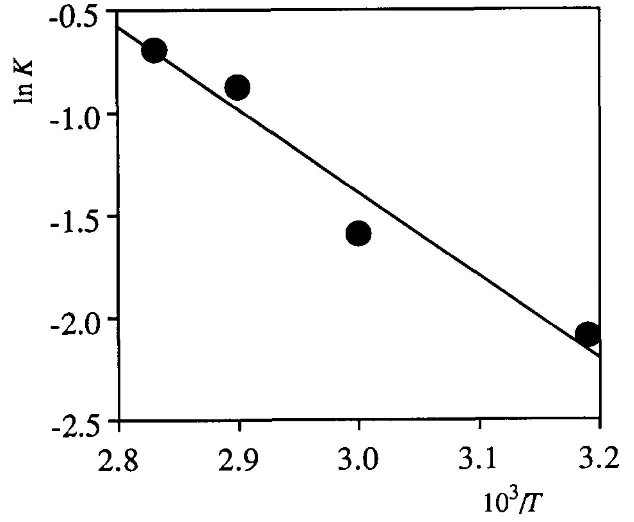


Fig. 3. Plot of $\ln K$ ($K = [\mathbf{2b}]/[\mathbf{2a}]$) against $1/T$ (T = temperature/K).

Gibbs energy) for the isomerization as 34 kJ mol^{-1}. The structure **2a** is more stable than that of **2b**.

Table 2
Yield and composition of the trimethylsilylmethylene adduct

Reaction conditions			Yield of adducts: sum of **2a** and **2b** (%)	Ratio of isomers (**2a**:**2b**)
Solvent	Temperature (°C)	Reaction time (h)		
CH_2Cl_2	40	6	57	92:8
	40	24	58	89:11
C_6H_6	80	2	60	80:20
	80	6	55	76:24
	80	24	56	66:33

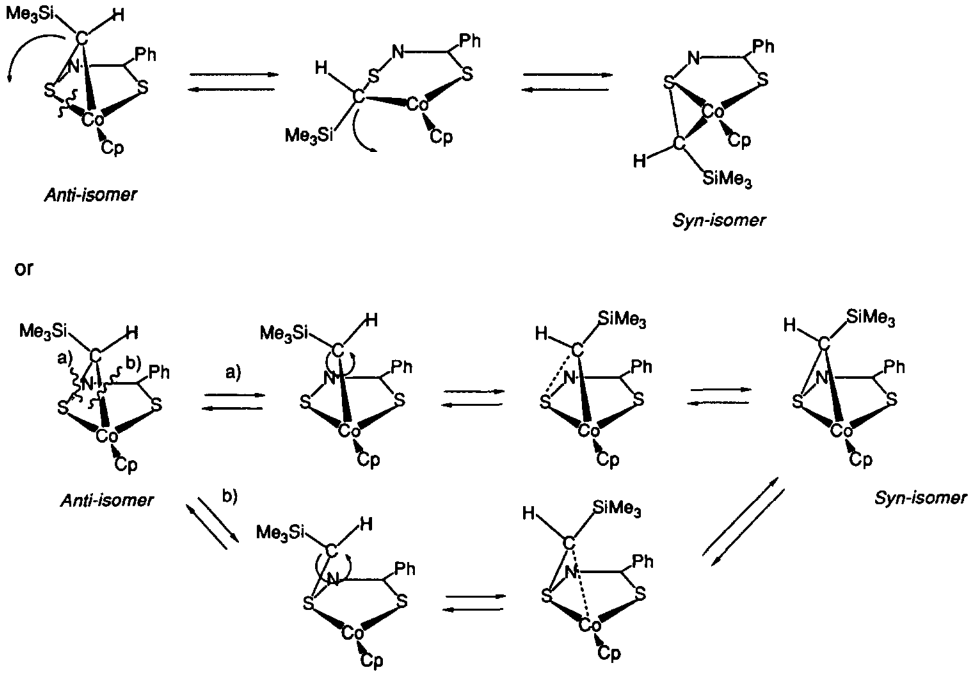
Amount of **1**, 15 μmol; amount of trimethylsilyldiazomethane, 60 μmol.

The isomerization would occur either via the cleavage of the Co–S bond and the inversion of the resulting six-membered ring or via the partial dissociation of either the Co–C or S–C bond (Scheme 1), but we have no evidence for the mechanism.

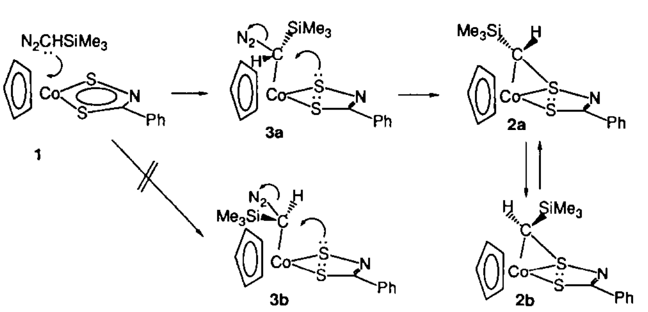
The equilibrium explains the variation of the product yields depending on the reaction time. The reaction of **1** and trimethylsilyldiazomethane in dichloromethane at 40°C for 6 h gives a mixture of **2a** and **2b** in the ratio 92:8 (Table 2). However, after a reaction time of 20 min at the low conversion of the reactants, only **2a** was detected. In the reaction in benzene solution at 80°C, the isomer ratio changes with the reaction time: with increasing reaction time, the yield of **2b** increases. This fact can be explained by the isomerization of the adducts.

2.3. Mechanism for the formation of trimethylsilylmethylene adduct

The results described in the preceding sections indicate that in the initial stage the more stable **2a** is preferentially formed and then **2a** isomerizes to **2b**.



Scheme 1. Proposed mechanisms for isomerization.



Scheme 2. Mechanism for the formation of the trimethylsilylmethylene adduct.

For the addition of methylene to cobaltadithiolenes by diazo compounds, we proposed a mechanism in which the nucleophilic C atom of the diazo compounds attacks the positively charged cobalt atom of the dithiolene complex and then the nucleophilic attack of sulfur on the carbon atom occurs with elimination of N_2 [10].

A similar mechanism can be applied to the formation of the alkylidene adduct of the cobaltadithiazole. The first step is the attack of C of the diazo compound on Co. The sulfur atom adjacent to N is more negatively charged than the other sulfur atom, because the lone-pair electrons at the latter S are attracted by N through conjugation.

The preferable conformation of the intermediate would be **3a**, which is less sterically hindered than **3b**. The intermediate **3a** results in the formation of **2a** (Scheme 2).

2.4. *Cleavage of cobaltathiirane ring with hydrogen chloride and ring reforming in the reaction with tetrabutylammonium fluoride*

Similarly to the trimethylsilylmethylene adducts of the cobaltadithiolene complexes [10], the trimethylsilylmethylene adducts **2a** and **2b** react with HCl in dichloromethane at room temperature to give the same product, chloro(η^5-cyclopentadienyl)[*N*-(trimethylsilylmethylthio-κS)-1-phenylmethanimine-1-thiolato-κS]cobalt(III) (**4**). Its structure was determined on the basis of the comparison of its spectral data with those of a similar adduct from cobaltadithiolene complex, the X-ray structure of which has been determined [19].

The three-component adduct **4**, consisting of cobaltadithiazole, trimethylsilylmethylene and HCl, reacts with tetrabutylammonium fluoride to afford the methylene-bridged complex **2c** with the elimination of tetrabutylammonium chloride and trimethylsilyl fluoride.

The treatment of **2a** with tetrabutylammonium fluoride affords **2c** with the replacement of trimethylsilyl group by hydrogen.

The ring opening by hydrogen chloride and the ring reforming by tetrabutylammonium fluoride also occur in a cobaltadithiolene complex [19].

3. Experimental details

3.1. *Materials*

(η^5-Pentamethylcyclopentadienyl)(1-phenylmethanimine-*N*,1-dithiolato)cobalt(III) was prepared by the method described in a previous paper [17].

3.2. *Reaction of 1 with $N_2CHSiMe_3$*

A dichloromethane solution (150 cm^3) of **1** (44 mg, 0.15 mmol) and trimethylsilyldiazomethane (0.6 mmol, 0.3 cm^3 of 2.0 mol dm^{-3} in hexane solution) was refluxed for 2 h. After evaporation of the solvent, the reaction mixture was submitted to silica gel column chromatography using Wako gel C200 as the stationary phase and dichloromethane as the eluent.

Trimethylsilylmethylene adduct (**2a**): black crystals, m.p. 103°C; UV (CH_2Cl_2), 258 (ε, 25 700) and 515 nm (1380); IR (KBr), 3093, 2955, 1727, 1454, 1415, 1245, 953, 871, 838, 813, 774, 759 and 690 cm^{-1}; ^1H NMR ($CDCl_3$), $\delta = 0.19$ (9H, s, Me_3), 1.48 (1H, s, SCH), 5.09 (5H, s, C_5H_5), 7.28 (3H, m, Ph) and 7.88 (2H, d, $J = 7.3$ Hz, Ph); ^{13}C NMR ($CDCl_3$), $\delta = 0.3$ (Me_3), 33.1 (SCH, $J_{CH} = 143$ Hz), 82.6 (C_5H_5), 127.7 (Ph), 127.8 (Ph), 130.4 (Ph), 136.8 (Ph), 198.2 (SCN); MS (70 eV), *m/z* (relative intensity, %) 377 (M^+, 53), 274 ($M^+ - C_6H_5CN$, 31), 168 (CpCoSC, 36) and 73 ($SiMe_3$, 100). Found: C, 49.56; H, 4.91; N, 4.47%. Calculated for $C_{16}H_{20}NS_2SiCo$: C, 50.91; H, 5.34; N, 4.15%.

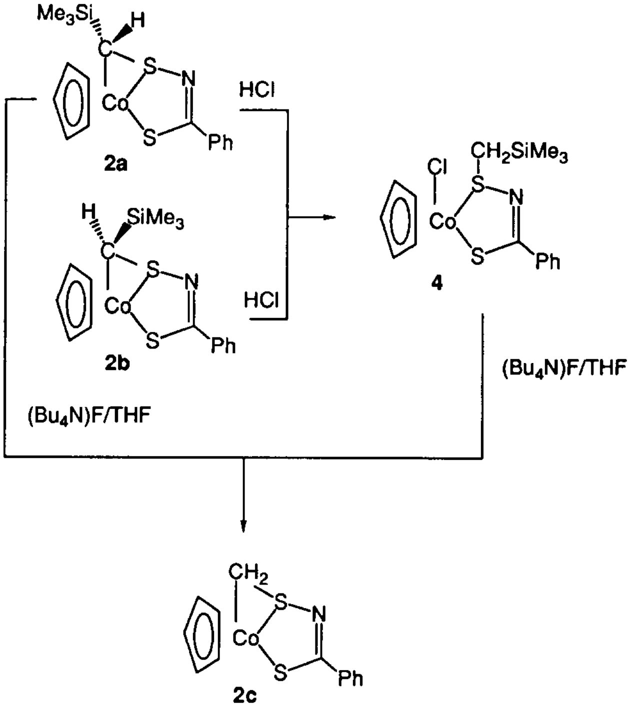


Table 3
Crystallographic data for **2a** and **2b**

	2a	**2b**
Formula	$C_{16}H_{20}CoS_2NSi$	$C_{16}H_{20}CoS_2NSi$
Crystal color	Black	Black
Crystal size (mm)	0.26 × 0.18 × 0.18	0.22 × 0.20 × 0.18
Formula weight	377.48	377.48
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$	$P2_1/c$
a(Å)	12.278(3)	11.448(3)
b(Å)	13.731(3)	27.961(2)
c(Å)	10.483(6)	12.290(3)
β(°)		114.68(2)
V(Å^3)	1767(1)	3574(1)
Z	4	8
d (g cm^{-3})	1.42	1.42
μ (cm^{-1})	104.0	102.8
λ (Cu Kα) (Å)	1.54178	1.54178
T (°C)	25	25
Number of unique reflections	1542	5453
Number of observed reflections	1128	3030
Trans. factors (max.; min.)	1.00; 0.75	1.00; 0.66
R	0.033	0.037
R_w	0.042	0.041

[a] ($I > 3\sigma(I)$)

Trimethylsilylmethylene adduct (**2b**): black crystals, m.p. 101°C; UV (CH_2Cl_2), 263 (ε 25 000) and 526 nm (1750); IR (KBr), 3084, 2955, 1742, 1454, 1415, 1403, 1248, 1227, 959, 892, 831, 762 and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$), $\delta = 0.045$ (9H, s, Me$_3$), 2.34(1H, s, SC*H*), 5.00(5H, s, C_5H_5), 7.29 (3H, m, Ph) and 7.90 (2H, d, $J = 8.5$ Hz, Ph); ^{13}C NMR ($CDCl_3$), $\delta = 0.9$ (Me$_3$), 23.8 (*S*CH, $J_{CH} = 138$ Hz), 82.9 (C_5H_5), 127.8 (Ph), 127.9 (Ph), 130.4 (Ph), 136.9 (Ph), 202.2 (S*C*N); MS (70 eV), m/z (relative intensity, %), 377 (M$^+$, 32), 274 (M$^+ - C_6H_5CN$, 28), 168 (CpCoSC, 33) and 73 (SiMe$_3$, 100).

3.3. X-ray structural analysis

The crystallographic data for **2a** and **2b** are summarized in Table 3. Intensities were collected on a Rigaku AFC-7R diffractomer with graphite monochromatized Cu Kα radiation using an $\omega - 2\theta$ scan technique up to $2\theta = 120°$.

An empirical absorption correction based on azimuthal scans of several reflections was applied [21].

The structures were solved by a direct method using the program SHELXS-86 [22] and refined by a full-matrix least-squares technique.

The hydrogen atoms were located on a difference electron density map and fixed at their positions.

All the calculations were carried out using the program package texan [23].

3.4. Thermal equilibrium

In a sample tube for NMR measurement was placed a toluene-d_8 solution of **2a** or **2b** (2.7×10^{-2} mol dm^{-3}). The solution was heated at 40, 60, 70 and 80°C and the composition ([**2a**]/[**2b**]) was determined by the signals of Cp in the ^{1}H NMR spectrum. Tetramethyl thiophenetetracarboxylate was used as an internal standard.

3.5. Reaction of 2a and 2b with HCl

A suspension between a dichloromethane solution (30 cm^3) of trimethylsilylmethylene adduct **2a** or **2b** (3.8 mg) and hydrochloric acid (0.1 cm^3) was reacted under stirring for 1 h at room temperature. After the reaction, the dichloromethane layer was washed with aqueous sodium hydrogencarbonate. The reaction mixture was submitted to silica gel column chromatography using Wako gel C300 as the stationary phase and ethyl acetate as eluent.

Chloro(η^5-cyclopentadienyl)(trimethylsilylmethyl-κC-1-phenylmethanimine-N,1-dithiolato-κS)cobalt(III) (**4**): black crystals, m.p. 149°C (decomp.); UV (CH_2Cl_2), 238 (ε 19 300), 329 (9300) and 578 nm (900); IR (KBr), 3063, 2943, 2942, 1497, 1485, 1415, 1247, 946, 841, 829, 753 and 691 cm^{-1}; ^{1}H NMR ($CDCl_3$), $\delta = 0.31$ (9H, s, Me$_3$), 2.16 (1H, d, $J = 14$ Hz, SC*H*), 3.02 (1H, d, $J = 14$ Hz, SC*H*), 5.39 (5H, s, C_5H_5), 7.34 (3H, m, Ph), 8.07 (2H, d, $J = 7.3$ Hz, Ph); ^{13}C NMR ($CDCl_3$), $\delta = -0.4$ (Me$_3$), 29.5 (*S*CH, $J_{CH} = 263$ Hz), 87.0(C_5H_5), 127.8(Ph), 128.7(Ph), 130.6(Ph), 135.2(Ph), 186.5(S*C*N); MS (70 eV), m/z (relative intensity%), 378 (M$^+ -$ Cl, 48), 275 (M$^+ - C_6H_5CN$, 11) and 103 (C_6H_5CN, 100). Found: C, 46.46; H, 5.02; N, 3.95%. Calculated for $C_{16}H_{21}NS_2SiCoCl$: C, 46.43; H, 5.11; N, 3.38%.

Methylene adduct (**2c**): black crystals, m.p. 106–107°C; UV (CH_2Cl_2), 255 (ε 27 300) and 499 nm (1880); ^{1}H NMR ($CDCl_3$), $\delta = 1.58$ (1H, d, $J = 4$ Hz, SC*H*), 3.35 (1H, d, $J = 4$ Hz, SC*H*), 5.08 (5H, s, C_5H_5), 7.29 (3H, m, Ph), 7.89 (2H, d, $J = 7.8$ Hz, Ph); ^{13}C NMR ($CDCl_3$), $\delta = 28.0$, 83.4, 127.9, 128.3, 130.4, 136.7, 198.8; MS (70 eV), m/z (relative intensity, %), 305 (M$^+$, 100), 168 (M$^+ -$ CpCoSC, 88) and 156 (CpCoS, 78).

3.6. Reaction of 4 with tetrabutylammonium fluoride

A THF solution (50 cm^3) of **4** (2 mg, 5 μmol) and (Bu$_4$N)F (70 μmol) was kept at room temperature for 1 h. After removal of the solvent, the products were separated by column chromatography using a Wako gel C300 column and dichloromethane as eluent. The formation of **2c** was confirmed by ^{1}H NMR and MS.

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