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Reactions of Cobaltadithiolenes with Germanorbornadiene—Formation and Structure of Unique Binuclear Cobalt Complexes Containing a Bridging Dimethylgermylene Moiety

Masatsugu Kajitani,*,† Sachiyo Adachi,† Chikako Takayama,†
Masami Sakurada,† Mikio Yamazaki,‡ Takeo Akiyama,† and Akira Sugimori†

Department of Chemistry, Faculty of Science and Technology, Sophia University, 7-1 Kioicho, Chiyoda-ku, Tokyo 102, Japan, and X-Ray Research Laboratory, Rigaku Corporation, Matsubara-cho 3-9-12, Akishima-shi, Tokyo 196, Japan

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*Summary: The reactions of cobaltadithiolene complexes $CpCo(S_2C_2Z_2)$ (**2a**, Z = CN; **2b**, COOMe) with 1,4,5,6-tetraphenyl-2,3-benzo-7,7-dimethyl-7-germanorborna-2,5-diene (**1**) gave binuclear cobalt complexes (**3a**, Z = CN; **3b**, Z = COOMe). The structure of **3a** was determined by X-ray structure analysis.*

Introduction

Recently, much attention has been focused on divalent species (R_2E groups) such as carbenes,[1] silylenes,[2] germylenes,[3] and stannylenes.[3] The chemistry of germylenes has been studied extensively over the last two decades. Ando and co-workers recently reported that the reactions of germylenes with olefins give germacyclopropanes[4] and 1,2-digermacyclobutanes.[5,6] Although the reactions of divalent group 14 species with organic compounds have received much attention, those with organometallic compounds have been less well-explored: Complexes with multiple bonds between transition metals and substituent-free ("bare") main group elements, such as C, Si, Ge, Sn, and chalcogens, have been reviewed.[7] As an example, a μ-Se complex (μ-Se)-$\{CpCr(CO)_2\}_2$ reacts smoothly with diazomethane at one of the Cr≡Se bonds to give an adduct containing a Cr−Se−C three-membered ring.[8] Diazo compounds are versatile reagents for the synthesis of μ-methylene complexes in reactions with organometallics.[9] However, only a few organometallic compounds containing a bridging germylene moiety between two metal atoms, such as bis(germylene)-bridged diiron complexes, have been described.[10−12] No report has appeared concerning a direct reaction between an organometallic compound and a germylene to form a complex containing a germylene moiety.

A metalladithiolene ring is a unique metallacycle which exhibits both aromaticity and unsaturation. It undergoes substitution reactions due to aromaticity.[13] On the other hand, it also behaves as an unsaturated molecule. Diazo compounds,[14] azides,[15] alkynes,[16] and quadricyclane[17] insert between the metal and sulfur atoms in the metalladithiolene ring. In the reactions of the diazo compounds and azides, N_2 is eliminated forming a cobaltathiirane ring or a cobaltathiaaziridine ring (Scheme 1).

In an extension of the study on the reaction of the cobaltadithiolene complexes with diazo compounds, our interests have been focused on the reactivities of germylenes, R_2Ge, toward cobaltadithiolenes. We report here the reactions of $CpCo(S_2C_2Z_2)$ (Z = CN, COOMe, and Ph) with Me_2Ge, formed by thermolysis of 1,4,5,6-tetraphenyl-2,3-benzo-7,7-dimethyl-7-germanorborna-2,5-diene,[18] to give germanium-containing products.

Results and Discussion

A mixture of dithiolene complexes $CpCo(S_2C_2Z_2)$ (**2a**, Z = CN; **2b**, Z = COOMe) and 1,4,5,6-tetraphenyl-2,3-benzo-7,7-dimethyl-7-germanorborna-2,5-diene (about twice as much as **2a** or **2b**) was heated in refluxing benzene for 4 h. In each case, novel binuclear cobalt complexes (**3a** and **3b**) having a $GeMe_2$ unit were obtained in 30% and 26% yields, respectively (Scheme 2). An analogous product was not obtained with CpCo-$(S_2C_2Ph_2)$.

The structure of complex **3a** was determined by X-ray structure analysis; its ORTEP drawing is shown in Figure 1. Important crystallographic parameters are listed in Table 1. Table 2 shows the selected bond lengths and angles of **3a**.

As shown in Figure 1, the structure of **3a** can be characterized as follows: (1) it is a novel binuclear cobalt complex and consists of a $GeMe_2$, a NC−C≡C−CN, and

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* To whom correspondence should be addressed. E-mail: kajitam@hoffman.cc.sophia.ac.jp.

† Sophia University.

‡ Rigaku Corporation.

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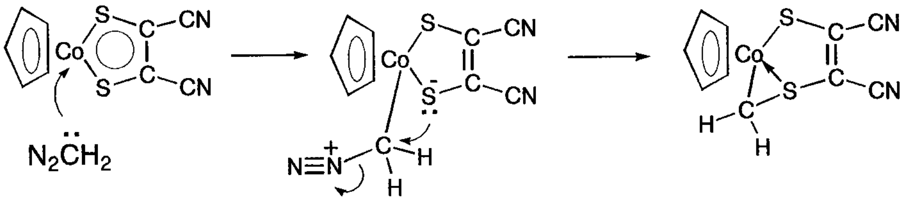
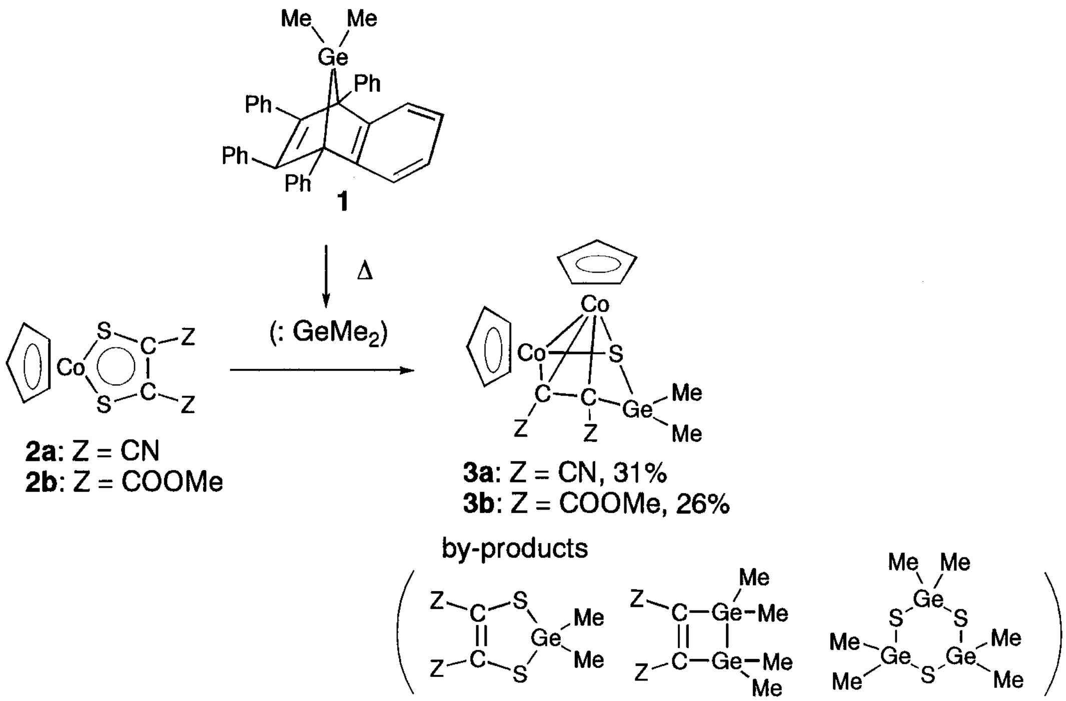
Scheme 1



Scheme 2



two CpCo moieties. Co(1) is bonded to Co(2) (Co(1)−Co(2) = 2.452(3) Å). The Co atoms are coordinatively unsaturated; Co(1) is six-coordinate, and Co(2) is seven-coordinate. (2) A GeMe$_2$ group is inserted into the S−C bond of **3a**, not into the Co−S bond. (3) In **3a**, two sp^2-dithiolene carbons (bond length = 1.404(7) Å) in the original complex CpCo(S$_2$C$_2$(CN)$_2$)[14] are converted into two sp^3-carbons, which constitute a three-membered ring of Co(2), C(1), and C(2) (Co(2)−C(1) = 1.99 Å. Co(2)−C(2) = 2.05 Å, C(1)−C(2) = 1.46 Å). This is supported by the bond angles around C(1) and C(2), as seen in Table 2. This change can be seen in the ^{13}C NMR spectra: the signal of the dithiolene carbons (δ 143.1) in the original complex is replaced by the signals of two unsymmetrical sp^3-carbons (δ 82.2 and 38.7) of **3a**. (4) The binuclear cobalt complex, **3a**, has only one sulfur atom. This may be a result of desulfurization by the GeMe$_2$ species.

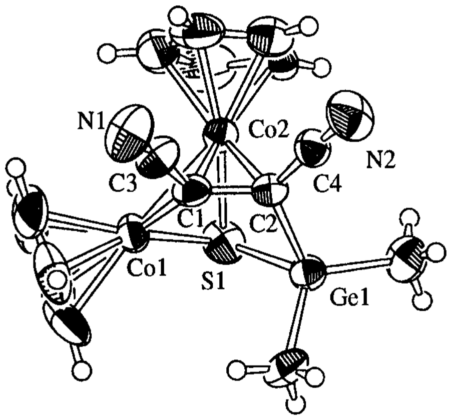


Figure 1. ORTEP drawing of **3a**.

Table 1. Crystal Data for 3a

empirical formula	C$_{16}$H$_{16}$N$_2$SCo$_2$Ge
fw	458.83
temp	23(1) °C
wavelength	0.710 69 Å
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell dimens	a = 9.945(5) Å b = 15.576(7) Å c = 11.14(1) Å β = 94.49(6)°
V, Z	1724(1) Å^3, 4
D (calcd)	1.767 g/cm^3
abs coeff, μ(Mo Kα)	37.50 cm^{-1}
F(000)	912.00
cryst size	0.30 × 0.30 × 0.30 mm
radiation	Mo Kα (λ = 0.710 69 Å)
scan type	$\omega-2\theta$
$2\theta_{\max}$ for data collection	55.0°
reflns collected	4316
no. of independent reflns	4116
refinement method	full-matrix least-squares
data/parameter	1931/199
goodness-of-fit on F	1.72
final R indices [$I > 3\sigma(I)$]	R = 0.054, R_w = 0.078
maximum peak in final diff. map	0.69 e$^-$/Å^3
minimum peak in final diff. map	−0.36 e$^-$/Å^3

As minor byproducts, (Me$_2$Ge)(S$_2$C$_2$(COOMe)$_2$), (Me$_2$Ge)$_2$(C$_2$(COOMe)$_2$),[19] and (S-GeMe$_2$)$_3$[20] were detected by MS. The formation of these byproducts suggests that

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Table 2. Selected Bond Lengths and Angles of 3a

Bond Lengths (Å)			
Ge(1)−S(1)	2.313(4)	Ge(1)−C(2)	1.954(9)
Ge(1)−C(5)	1.94(1)	Ge(1)−C(6)	1.92(1)
Co(1)−Co(2)	2.452(3)	Co(1)−S(1)	2.184(3)
Co(1)−C(1)	1.88(1)	Co(2)−S(1)	2.234(3)
Co(2)−C(1)	1.989(10)	Co(2)−C(2)	2.047(9)
N(1)−C(3)	1.12(1)	N(2)−C(4)	1.12(1)
C(1)−C(2)	1.46(1)	C(1)−C(3)	1.45(1)
C(2)−C(4)	1.46(1)		
Bond Angles (deg)			
S(1)−Ge(1)−C(2)	85.1(3)	S(1)−Ge(1)−C(5)	109.6(4)
S(1)−Ge(1)−C(6)	114.3(4)	C(2)−Ge(1)−C(5)	116.4(4)
C(2)−Ge(1)−C(6)	112.8(5)	C(5)−Ge(1)−C(6)	115.1(5)
Co(2)−Co(1)−S(1)	57.26(10)	Co(2)−Co(1)−C(1)	52.7(3)
Co(1)−Co(2)−C(2)	55.33(10)	Co(1)−Co(2)−C(1)	48.8(3)
Co(1)−Co(2)−C(2)	81.0(3)	S(1)−Co(2)−C(1)	87.0(3)
S(1)−Co(2)−C(2)	85.1(3)	C(1)−Co(2)−C(2)	42.4(4)
Ge(1)−S(1)−Co(1)	96.2(1)	Ge(1)−S(1)−Co(2)	84.4(1)
Co(1)−C(1)−C(2)	122.6(7)	Co(1)−C(1)−C(3)	78.5(4)
Co(2)−C(1)−C(3)	119.0(9)	Ge(1)−C(2)−Co(2)	99.5(4)
Ge(1)−C(2)−C(1)	112.9(7)	Ge(1)−C(2)−C(4)	122.7(7)
Co(2)−C(2)−C(1)	66.7(5)	Co(2)−C(2)−C(4)	117.2(7)
C(1)−C(2)−C(4)	121.3(8)	N(1)−C(3)−C(1)	177(1)
N(2)−C(4)−C(2)	175(1)		

1 is a $GeMe_2$ source. All the germanium-containing products may be thought to be generated by the electrophilic attack of dimethylgermylene at sulfur.[21] The existence of dimethylgermathione, $Me_2Ge{=}S$, as a transient species has been reported by Michl according to matrix isolation and IR spectroscopy.[22] Kinetic and labeling studies of the formation and trapping reactions of dimethylgermylene were reported by Shusterman et al.[23] Ando's[21] and Okazaki's[24] groups also independently reported the formation of germanethione in the reactions of germylenes with thioketones or elemental sulfur. Although the mechanism of formation for complex **3a** is too complicated to be elucidated, it is almost certain that complex **3a** was formed by the reaction of **2a** with some $GeMe_2$ species which were generated by thermolysis of **1**.

Experimental Section

All experiments were carried out under an atmosphere of argon by using Schlenk tube techniques. The starting complexes ($CpCo(S_2C_2(CN)_2)$),[25] $CpCo(S_2C_2(COOMe)_2)$,[26] and $CpCo(S_2C_2Ph_2)$[27]) were prepared as described in the literature. A precursor of the germylene, 1,4,5,6-tetraphenyl-2,3-benzo-7,7-dimethyl-7-germanorborna-2,5-diene, **1**, was prepared as described in the literature.[11]

Reaction of $CpCo(S_2C_2(CN)_2)$ (2a) with 1. Under an atmosphere of argon, a solution of $CpCo(S_2C_2(CN)_2)$ (0.25 g, 0.95 mmol) and the germanorbornadiene **1** (1.00 g, 1.86 mmol) in benzene (12 mL) was heated at reflux for 4 h. The solvent was removed at reduced pressure. Chromatography of the residue on silica gel (Wako-gel C-300) (eluent: *n*-hexane/CH_2Cl_2) gave one major and several minor products. The starting complex (0.062 g, 52%) was recovered, and the major product was isolated as a dark red crystalline solid: yield 0.066 g, 0.143 mmol (30% based on **2a**); mp 183 °C (decomposition). Anal. Calcd for $C_{16}H_{16}N_2SGeCo_2$: C, 41.75; H, 3.51. Found: C, 41.80; H, 3.46. ^1H NMR ($CDCl_3$): δ 5.14 (s, 5H, Cp), 5.12 (s, 5H, Cp), 0.981 (s, 3H, $GeCH_3$), 0.0655 (s, 3H, $GeCH_3$). ^{13}C NMR ($CDCl_3$): δ 127.4 (s, CN), 121.8 (s, CN), 84.4 (s, Cp), 82.2 (s, *C*−CN), 80.7 (s, Cp), 38.7 (s, *C*−CN), 9.1 (s, $GeCH_3$), 2.2 (s, $GeCH_3$). IR (KBr, cm^{-1}): 832 (s), 2185 (m), 2529 (m), 2928 (m), 3105 (m). UV−vis (λ_{max} (ϵ), CH_2Cl_2): 194 (4420), 241 (16 070), 280 (19 180), 450 (2660), 456 nm (2660). MS (EI, 70 eV): *m/z* 460 (100, M^+), 458 (74.5, M^+), 445 (22.9, $M^+ - CH_3$), 430 (10.1, $M^+ - (CH_3)_2$), 264 (22.6, $CpCo(S_2C_2(CN)_2{}^+)$, 189 (82.9, $CpCoCp^+$), 124 (35.3, $CpCo^+$).

Reaction of $CpCo(S_2C_2(COOMe)_2)$ (2b) with 1. The same procedure was used in the reaction of $CpCo(S_2C_2(COOMe)_2)$ (0.68 g, 2.06 mmol) and the germanorbornadiene (2.14 g, 4.00 mmol) in benzene (5 mL). Chromatography of the residue after solvent removal on silica gel (Wako-gel C-300) (eluent: *n*-hexane/CH_2Cl_2) gave one major and several minor products. The major product was isolated as a dark red crystalline solid and was purified by preparative HPLC (yield 0.14 g, 0.27 mmol; 26% based on **2b**). The high-resolution mass spectrum of the product showed the composition of $C_{18}H_{22}O_4SCo_2Ge$: mp 118 °C. HRMS (EI, 70 eV): *m/z* found 525.9113; calcd for $C_{18}H_{22}O_4SCo_2Ge$, 525.9115. MS (EI, 70 eV): *m/z* 526 (32, M^+), 496 (5.5), 341 (4.0), 304 (17.5), 280 (27.0, $(CpCo)_2S^+$), 189 (100, Cp_2Co^+). IR (KBr, cm^{-1}): 1703 (s), 1689(s), 1429 (m), 1333 (s), 1200 (s), 1153 (s), 1059 (m), 1001 (m), 833 (m), 818 (m), 580 (m). ^1H NMR ($CDCl_3$): δ −0.023 (3H, s, $GeCH_3$), 0.85 (3H, s, $GeCH_3$), 3.57 (3H, s, OCH_3), 3.94 (3H, s, OCH_3), 4.92 (5H, s, Cp), 4.99 (5H, s, Cp). ^{13}C NMR ($CDCl_3$): δ 4.71 (s, $GeCH_3$), 8.50(s, $GeCH_3$), 51.54 (s, OCH_3), 51.61 (s, OCH_3), 79.62 (s, Cp), 82.21 (s, Cp), 82.62 (s, *C*−COO), 83.85 (s, *C*−COO), 171.66 (s, CO), 171.70 (s, CO).

X-ray Diffraction Study of $(CpCo)_2(NC{-}C{\equiv}C{-}CN)(GeMe_2)S$ (3a). All measurements were made on a Rigaku AFC5S diffractometer with graphite-monochromated Mo Kα radiation. The structure was solved by heavy-atom Patterson methods (DIRDIF PATTY)[28] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Idealized positions were used for the hydrogen atoms. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp.[29] Table 1 presents crystal data, data collection parameters, and least-squares refinement parameters. Tables of atomic coordinates for non-hydrogen atoms, complete lists of bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters are available as Supporting Information.

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Supporting Information Available: Text of X-ray experimental details, tables of crystal data and structure refinement details, positional and thermal parameters, bond distances and angles, torsion angles, and least-squares planes, and ORTEP diagram for **3a** (28 pages). Ordering information is given on any current masthead page.

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