

Preparation, Properties, and Some Reactions of Novel Ruthenium Thiolate Complexes

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Received September 14, 1988

Treatment of $[\text{Cp}^*\text{RuCl}_2]_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) with excess ArSH ($\text{Ar} = \text{Ph}$, $p\text{-MeC}_6\text{H}_4$, $p\text{-ClC}_6\text{H}_4$) in CH_2Cl_2 at room temperature afforded the diruthenium complexes $[\text{Cp}^*\text{Ru}(\text{SAr})_3\text{RuCp}^*]\text{Cl}$. The X-ray analysis of the complex ($\text{Ar} = \text{Ph}$) showed the existence of a Ru-Ru single bond surrounded by three bridging thiolate ligands. On the other hand, $[\text{Cp}^*\text{RuCl}_2]_2$ reacted with excess PhCH_2SH to give the doubly bridged diruthenium complex $[\text{Cp}^*\text{RuCl}(\text{SCH}_2\text{Ph})_2\text{RuCp}^*]\text{Cl}$. A series of alkanethiolate complexes having the analogous structure $[\text{Cp}^*\text{RuCl}(\text{SR})_2\text{RuCp}^*]\text{Cl}$ were prepared by the reaction of $[\text{Cp}^*\text{RuCl}_2]_2$ with excess Me_3SiSR ($\text{R} = \text{Et}$, $i\text{-Pr}$, $t\text{-Bu}$) in THF at reflux. These alkanethiolate diruthenium complexes reacted with CO in THF or CH_2Cl_2 at room temperature and $t\text{-BuNC}$ in THF at reflux to give monosubstituted complexes $[\text{Cp}^*\text{RuCl}(\text{SR})_2\text{RuCp}^*(\text{L})]\text{Cl}$ ($\text{L} = \text{CO}$, $\text{R} = \text{Et}$, $i\text{-Pr}$; $\text{L} = t\text{-BuNC}$, $\text{R} = \text{Et}$). In contrast, monomeric thiolate complexes $[\text{Cp}^*\text{Ru}(\text{PR}_3)(\text{SPh})_2]$ ($\text{R} = \text{Me}$, Ph) were prepared by the reaction of $[\text{Cp}^*\text{Ru}(\text{PR}_3)\text{Cl}_2]$ with excess NaSPh .

Introduction

Systematic study on the cluster assembly of iron-sulfur compounds has already been extensively carried out, and a great number of iron complexes with sulfide and/or thiolate ligands have been reported.² On the contrary, the chemistry of ruthenium-sulfur compounds has still been poorly advanced³ because in past years the investigation on transition-metal-sulfur compounds mainly stemmed from the biological interest in synthesizing the model compounds of the active sites of natural enzymes, and hence sulfur compounds containing the metals not relating to the biological systems have been left relatively unexplored. Recently we have reported the preliminary result on the synthesis and the X-ray structure of the novel diruthenium complex $[\text{Cp}^*\text{Ru}(\text{SPh})_3\text{RuCp}^*]\text{Cl}$ (**1a**) with three bridging thiolate ligands around its Ru-Ru single bond.⁴ Here we describe in detail the preparation, properties, and the structure of this complex together with those of the relating mono- and diruthenium thiolate complexes.

Experimental Section

General Data. All experiments were carried out under a nitrogen atmosphere. All solvents were dried and distilled under nitrogen. Thiols, $t\text{-BuNC}$, PPh_3 , and PMe_3AgI were commercially obtained and used without further purification. Compounds $[\text{Cp}^*\text{RuCl}_2]_2$ (**2**),⁵ $[\text{Cp}^*\text{Ru}(\text{PR}_3)\text{Cl}_2]$ ($\text{R} = \text{Ph}$, Me),⁶ and Me_3SiSR ($\text{R} = \text{Et}$, $i\text{-Pr}$, $t\text{-Bu}$)⁷ were prepared according to the published methods. ¹H NMR spectra were recorded on a JEOL JNM-GX-400 spectrometer. IR spectra were measured with a Shimadzu IR-408 spectrometer by KBr method. EPR spectra were obtained at X-band frequencies by using a JEOL JEX-FEIX spectrometer. Electrochemical measurements were made with Hokuto Denko instrumentation (HA-501 Potentiostat and HB-105 Function

Generator) using a glassy carbon working electrode; potentials were measured vs a saturated calomel electrode as reference. Elemental analyses were performed at the Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo.

Preparation of $[\text{Cp}^*\text{Ru}(\text{SPh})_3\text{RuCp}^*]\text{Cl}$ (1a**).** Into a degassed solution of PhSH (2.50 mL, 24.4 mmol) in CH_2Cl_2 (40 mL) was added complex **2** (2.23 g, 3.63 mmol), and the solution was stirred for 24 h. After addition of hexane (100 mL) into a dark brown product solution, the mixture was cooled to -18°C . The solid formed was filtered off, washed with hexane (20 mL \times 2), and then recrystallized from CH_2Cl_2 /hexane. Dark brown needles deposited were filtered off, washed with hexane (20 mL \times 2), and then dried in vacuo. The title compound was isolated as mono CH_2Cl_2 solvate (2.69 g, 81%). Anal. Calcd for $\text{C}_{36}\text{H}_{47}\text{Cl}_3\text{S}_3\text{Ru}_2$: C, 50.89; H, 5.17; Cl, 11.55; S, 10.45. Found: C, 50.29; H, 5.19; Cl, 11.58; S, 10.23.

Preparation of $[\text{Cp}^*\text{Ru}(\text{SC}_6\text{H}_4\text{-}p\text{-Me})_3\text{RuCp}^*]\text{Cl}$ (1b**).** This complex was isolated in 67% yield by the same method as that described above using complex **2** (826 mg, 1.34 mmol) and $p\text{-MeC}_6\text{H}_4\text{SH}$ (4.10 g, 33.0 mmol). The crystals for elemental analysis were obtained as $3/2\text{CHCl}_3$ solvate after recrystallization of the product from CHCl_3 /hexane. Anal. Calcd for $\text{C}_{42.5}\text{H}_{52.5}\text{Cl}_{1.5}\text{S}_3\text{Ru}_2$: C, 48.29; H, 5.02; Cl, 18.45; S, 9.10. Found: C, 48.42; H, 5.22; Cl, 16.46; S, 9.12.

Preparation of $[\text{Cp}^*\text{Ru}(\text{SC}_6\text{H}_4\text{-}p\text{-Cl})_3\text{RuCp}^*]\text{Cl}$ (1c**).** This complex was also prepared analogously from complex **2** (606 mg, 0.986 mmol) and $p\text{-ClC}_6\text{H}_4\text{SH}$ (3.01 g, 20.8 mmol) in 89% yield as $1/2\text{CH}_2\text{Cl}_2$ solvate. Anal. Calcd for $\text{C}_{38.5}\text{H}_{45}\text{Cl}_3\text{S}_3\text{Ru}_2$: C, 47.11; H, 4.43; Cl, 18.06; S, 9.80. Found: C, 47.01; H, 4.85; Cl, 16.51; S, 9.24.

Preparation of $[\text{Cp}^*\text{RuCl}(\text{SCH}_2\text{Ph})_2\text{RuCp}^*]\text{Cl}$ (3**).** This complex was also isolated as $1/2\text{CH}_2\text{Cl}_2$ solvate according to the same procedure as described above in 17% yield from complex **2** (1.16 g, 1.89 mmol) and PhCH_2SH (5.0 mL, 43 mmol). Anal. Calcd for $\text{C}_{34.5}\text{H}_{45}\text{Cl}_3\text{S}_2\text{Ru}_2$: C, 49.78; H, 5.45; Cl, 12.79; S, 7.70. Found: C, 50.48; H, 5.58; Cl, 12.66; S, 7.33.

Preparation of $[\text{Cp}^*\text{RuCl}(\text{SEt})_2\text{RuCp}^*]\text{Cl}$ (4a**).** To a suspension of complex **2** (488 mg, 0.794 mmol) in THF (10 mL) was added Me_3SiSEt (557 mg, 4.15 mmol), and the mixture was refluxed for 7 h. The product solution was concentrated to about half volume and hexane (10 mL) added. The brown crystalline solid deposited was filtered off and dried in vacuo (430 mg, 41%). The product could be recrystallized from $\text{CH}_2\text{ClCH}_2\text{Cl}$ /hexane. Anal. Calcd for $\text{C}_{24}\text{H}_{40}\text{Cl}_2\text{S}_2\text{Ru}_2$: C, 43.30; H, 6.06; S, 9.63; Cl, 10.65. Found: C, 42.42; H, 6.08; S, 9.93; Cl, 10.65.

Preparation of $[\text{Cp}^*\text{RuCl}(\text{S-}i\text{-Pr})_2\text{RuCp}^*]\text{Cl}$ (4b**).** This complex was obtained as a brown crystalline solid from complex **2** (460 mg, 0.749 mmol) and $\text{Me}_3\text{SiS-}i\text{-Pr}$ (0.55 g, 3.7 mmol) in 41% yield by the analogous method to complex **4a**. This compound could be recrystallized from CH_2Cl_2 /hexane. Anal. Calcd for

(1) (a) The University of Tokyo. (b) The Institute of Physical and Chemical Research.

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(3) Some ruthenium sulfide and thiolate complexes relating to a present study have already been reported: (a) Ogilvy, A. E.; Rauchfuss, T. B. *Organometallics* 1988, 7, 1884. (b) Rauchfuss, T. B.; Rodgers, D. P. S.; Wilson, S. R. *J. Am. Chem. Soc.* 1986, 108, 3114. (c) Killops, S. D.; Knox, S. A. *J. Chem. Soc., Dalton Trans.* 1978, 1260.

(4) Hidai, M.; Imagawa, K.; Cheng, G.; Mizobe, Y.; Wakatsuki, Y.; Yamazaki, H. *Chem. Lett.* 1986, 1299.

(5) Suzuki, H.; Oshima, N.; Narasaka, S.; Moro-oka, Y. 33rd Symposium on Organometallic Chemistry, Japan, 1985.

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(7) Abel, E. W. *J. Chem. Soc.* 1960, 4406.

$C_{26}H_{44}Cl_2S_2Ru_2$: C, 45.01; H, 6.39. Found: C, 44.72; H, 6.26.

Preparation of [Cp*RuCl(S-*t*-Bu)₂RuCp*Cl] (4c). This complex was also obtained in 16% yield by the same procedure as that for complex 4a except for the reaction time of 14 h. Anal. Calcd for $C_{28}H_{48}Cl_2S_2Ru_2$: C, 46.59; H, 6.70; Cl, 9.82; S, 8.88. Found: C, 45.46; H, 6.68; Cl, 9.44; S, 8.58.

Reaction of [Cp*RuCl(SET)₂RuCp*Cl] (4a) with CO. Through a solution of complex 4a (120 mg, 0.18 mmol) in THF (10 mL) was bubbled CO gas for 2 h. During this period the initial brown solution became a yellow suspension. The mixture was continuously stirred under a CO atmosphere overnight. The solid of [Cp*RuCl(SET)₂RuCp*(CO)]Cl (5a) was collected by filtration, washed with hexane, and dried in vacuo (90 mg, 72%). Anal. Calcd for $C_{25}H_{40}OCl_2S_2Ru_2$: C, 43.28; H, 5.81; Cl, 10.22; S, 9.24. Found: C, 42.81; H, 5.87; Cl, 10.20; S, 9.03.

Reaction of [Cp*RuCl(S-*i*-Pr)₂RuCp*Cl] (4b) with CO. The analogous treatment of complex 4b (128 mg, 0.184 mmol) with CO in CH_2Cl_2 provided the dark yellow solid of [Cp*RuCl(S-*i*-Pr)₂RuCp*(CO)]Cl (5b) as $^{3/2}CH_2Cl_2$ solvate (60 mg, 38%). Anal. Calcd for $C_{28.5}H_{47}OCl_2S_2Ru_2$: C, 40.31; H, 5.58. Found: C, 40.52; H, 6.12.

Reaction of [Cp*RuCl(SET)₂RuCp*Cl] (4a) with *t*-BuNC. To a solution of complex 4a (143 mg, 0.214 mmol) in THF (10 mL) was added *t*-BuNC (0.10 g, 1.2 mmol), and the mixture was refluxed for 4 h. The product solution was reduced in volume to about half and hexane (10 mL) added. The yellowish green solid of [Cp*RuCl(SET)₂RuCp*(*t*-BuNC)]Cl (5c) obtained was filtered off and dried in vacuo (80 mg, 50%). Anal. Calcd for $C_{29}H_{49}NCl_2S_2Ru_2$: C, 46.51; H, 6.60; N, 1.87. Found: C, 45.90; H, 6.53; N, 1.94.

Preparation of [Cp*Ru(PMe₃)₃(SPh)₂]. To a suspension of [Cp*Ru(PMe₃)₂Cl₂] (0.24 g, 0.62 mmol) in MeOH (5 mL) was added NaSPh (0.24 g, 1.80 mmol), and the mixture was stirred for 4 h at room temperature. After the product solution was cooled to -18 °C, the dark violet solid that precipitated was filtered off and dried in vacuo (0.13 g, 39%). The product could be crystallized from hexane at -18 °C. Anal. Calcd for $C_{25}H_{34}PS_2Ru$: C, 56.35; H, 6.86. Found: C, 56.19; H, 6.61.

Preparation of [Cp*Ru(PPh₃)₃(SPh)₂]. This complex was prepared from [Cp*Ru(PPh₃)₂Cl₂] (194 mg, 0.341 mmol) and NaSPh (287 mg, 2.17 mmol) by the same method as that of the PMe₃ analogue as a black crystalline solid (180 mg, 74%). This compound could be recrystallized from C_6H_6 /MeOH. Anal. Calcd for $C_{40}H_{40}PS_2Ru$: C, 67.01; H, 5.62. Found: C, 67.04; H, 5.62.

X-ray Crystallographic Analysis of 1a. The crystal and refinement data are summarized in Table I. The structure was solved by direct methods using MULTAN 78 which revealed the positions of the two Ru atoms. A subsequent difference Fourier synthesis and refinement by block-diagonal least-squares afforded the positions of most of the non-hydrogen atoms. After several cycles of refinement, disordered positions were found for a set of three SPh groups and the Cl anion. Attempts to resolve these disordered forms by assuming space group *P*1 instead of *P*1̄ were unsuccessful. Elemental analysis data and spectral data indicated crystals of this complex contain one CH_2Cl_2 molecule per molecular unit. This could not be well resolved in the difference map; only six broad peaks were observed around (0.7, 0.7, 0.7) with maximum electron densities of $8.6 e \text{ \AA}^{-3}$, and these were assumed to be Cl atoms of the highly disordered CH_2Cl_2 unit. Many hydrogen atoms were located from the difference Fourier map, and the remaining hydrogen atoms of the complex were placed at the calculated positions. They were included in the final stage of the refinement with fixed positional and thermal parameters. Anomalous dispersion effects for Ru were included in the calculation by using Cromer's values of $\Delta f'$ and $\Delta f''$.⁸ The atomic scattering factors were from ref 9, and final atomic parameters are given in Table II.

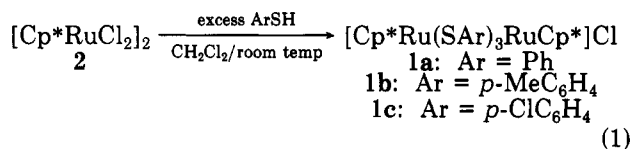
Results and Discussion

Diruthenium Complexes with Three Bridging Thiolate Ligands. When treated with excess benzene-

Table I. Crystallographic Data for [Cp*Ru(SPh)₃RuCp*]Cl (1a)

(A) Crystal Data	
formula	$C_{38}H_{48}ClRu_2S_3 \cdot CH_2Cl_2$
mol wt	919.7
space group (cryst system)	<i>P</i> 1̄ (triclinic)
cryst color	dark brown
<i>a</i> , Å	11.380 (2)
<i>b</i> , Å	17.043 (3)
<i>c</i> , Å	11.116 (2)
α , deg	101.76 (2)
β , deg	105.76 (2)
γ , deg	87.66 (2)
cell vol, Å ³	2031.1 (7)
<i>Z</i>	2
D_{measd} (flotation), g cm ⁻³	1.48 (5)
D_{calcd} , g cm ⁻³	1.504
$F(000)$, electrons	936
μ_{calcd} , cm ⁻¹	11.0
cryst dims, mm	0.15 × 0.14 × 0.11
(B) Data Collection and Reduction	
diffractometer	Rigaku AFC-5
monochromator	graphite
radiatn ($\lambda/\text{Å}$)	Mo K α (0.7107)
temp, °C	18
max 2 θ , deg	55
scan method	ω -2 θ
scan speed, deg s ⁻¹	0.06
reflens measd	$\pm h, \pm k, +l$
unique data	7350
data, $I > 3\sigma(I)$	4392
(C) Solution and Refinement	
no. of parameters refined	614
$R = \sum(F_o - F_c)/\sum F_o $	0.069
$R_w = \sum w(F_o - F_c)^2/\sum w F_o ^2$	0.057
weighting scheme	$w = 1/(\sigma(F_o))$
max residuals, e Å ⁻³	0.9 (in solvent region)

thiol in CH_2Cl_2 at room temperature for 24 h, [Cp*RuCl₂]₂ (2) gave a diruthenium complex, [Cp*Ru(SPh)₃RuCp*]Cl (1a), in 81% yield. Analogous treatment of complex 2 with *p*-MeC₆H₄SH and *p*-ClC₆H₄SH also resulted in the formation of the corresponding diruthenium complexes 1b and 1c (eq 1). These complexes show sharp resonances



in their ¹H NMR spectra despite the presence of Ru(III) centers, indicating the existence of the spin-spin pairing between the two ruthenium atoms. The diamagnetic character of complex 1a is also demonstrated by the measurements of the magnetic moment by the Faraday method ($\mu_{eff} = 0$) and the EPR spectrum (EPR silent). The solutions of these complexes in DMF-0.1 M [*n*-Bu₄N][BF₄] show two successive reversible reduction waves under cyclic voltammetric conditions. These potentials shift to the negative direction as the electron-donating ability of the para substituent becomes stronger (Table III).

The structure of complex 1a determined by the X-ray analysis is depicted in Figure 1. Singly primed atoms connected by solid lines relate to the disordered SPh ligands in 17% abundance. Bond distances and angles summarized in Table IV clearly disclose the existence of a metal-metal single bond; the Ru-Ru distance of 2.630 (1) Å is significantly shorter than those of the triply bridged diruthenium complexes without a Ru-Ru bond, [(Ru(μ -S-2-CH₂-3,5,6-Me₃C₆H)(S-2,3,5,6-Me₄C₆H)(NO))₂(μ -S-2,3,5,6-Me₄C₆H)]⁻ (3.347 (1) Å)¹⁰ and

(8) Cromer, D. T. *Acta Crystallogr.* 1965, 18, 17.

(9) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1976; Vol. 3.

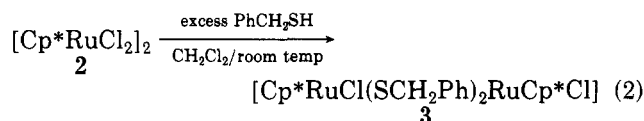
Table II. Atomic Coordinates ($\times 10^4$) for Complex 1a with Estimated Standard Deviations in Parentheses

atom	x	y	z	multiplicity
Ru(1)	2609 (1)	7455 (1)	3401 (1)	1.0
Ru(2)	697 (1)	7564 (1)	1484 (1)	1.0
S(1)	2718 (3)	7712 (2)	1431 (3)	0.83333
S(2)	1156 (3)	6427 (2)	2412 (3)	0.83333
S(3)	1062 (3)	8413 (2)	3480 (3)	0.83333
C(11)	4641 (10)	7501 (9)	4146 (11)	1.0
C(12)	4121 (10)	8069 (7)	4983 (11)	1.0
C(13)	3424 (10)	7629 (8)	5485 (10)	1.0
C(14)	3489 (11)	6818 (8)	4968 (12)	1.0
C(15)	4221 (10)	6728 (8)	4124 (12)	1.0
C(16)	5529 (11)	7680 (12)	3454 (14)	1.0
C(17)	4440 (13)	8935 (8)	5313 (15)	1.0
C(18)	2845 (13)	8019 (11)	6525 (12)	1.0
C(19)	2967 (15)	6154 (10)	5364 (16)	1.0
C(20)	4644 (15)	5957 (10)	3478 (16)	1.0
C(21)	-98 (11)	8071 (8)	-237 (12)	1.0
C(22)	-827 (12)	8284 (8)	596 (12)	1.0
C(23)	-1311 (10)	7593 (8)	787 (11)	1.0
C(24)	-894 (10)	6937 (7)	8 (11)	1.0
C(25)	-121 (11)	7223 (8)	-614 (11)	1.0
C(26)	506 (15)	8638 (11)	-754 (16)	1.0
C(27)	-1136 (15)	9106 (9)	1136 (17)	1.0
C(28)	-2232 (12)	7512 (13)	1482 (15)	1.0
C(29)	-1229 (16)	6069 (10)	-196 (16)	1.0
C(30)	418 (14)	6784 (10)	-1619 (12)	1.0
C(31)	3261 (11)	6882 (8)	462 (11)	0.83333
C(32)	4059 (12)	7104 (9)	-169 (13)	0.83333
C(33)	4520 (14)	6528 (10)	-942 (14)	0.83333
C(34)	4259 (15)	5760 (10)	-1105 (16)	0.83333
C(35)	3495 (15)	5508 (9)	-491 (15)	0.83333
C(36)	3012 (13)	6076 (9)	340 (14)	0.83333
C(41)	100 (11)	6261 (8)	3275 (11)	0.83333
C(42)	-294 (13)	6826 (9)	4109 (15)	0.83333
C(43)	-1111 (15)	6640 (9)	4774 (15)	0.83333
C(44)	-1542 (13)	5870 (10)	4480 (14)	0.83333
C(45)	-1165 (18)	5358 (11)	3674 (17)	0.83333
C(46)	-376 (16)	5525 (9)	3084 (15)	0.83333
C(51)	1552 (12)	9401 (8)	3524 (13)	0.83333
C(52)	2056 (13)	9631 (8)	2669 (14)	0.83333
C(53)	2379 (12)	10393 (8)	2745 (13)	0.83333
C(54)	2163 (12)	10995 (8)	3683 (15)	0.83333
C(55)	1741 (12)	10803 (9)	4603 (16)	0.83333
C(56)	1435 (14)	9989 (10)	4546 (16)	0.83333
S(1')	1984 (15)	6508 (9)	1560 (15)	0.16667
S(2')	629 (14)	7691 (9)	3644 (14)	0.16667
S(3')	2389 (13)	8537 (9)	2325 (14)	0.16667
C(31')	2959 (44)	6417 (29)	510 (50)	0.16667
C(32')	3523 (51)	7134 (37)	375 (58)	0.16667
C(33')	4293 (59)	7062 (41)	-464 (56)	0.16667
C(34')	4509 (58)	6300 (39)	-1160 (56)	0.16667
C(35')	3960 (51)	5599 (35)	-1028 (56)	0.16667
C(36')	3192 (55)	5666 (37)	-190 (62)	0.16667
C(41')	91 (42)	6902 (34)	4194 (55)	0.16667
C(42')	-900 (53)	6950 (35)	4726 (56)	0.16667
C(43')	-1258 (59)	6266 (41)	5113 (58)	0.16667
C(44')	-623 (82)	5549 (46)	4963 (95)	0.16667
C(45')	396 (83)	5485 (49)	4446 (100)	0.16667
C(46')	721 (88)	6169 (56)	3985 (98)	0.16667
C(51')	1885 (69)	9448 (41)	3188 (64)	0.16667
C(52')	1849 (56)	10101 (42)	2480 (60)	0.16667
C(53')	1475 (87)	10871 (51)	3035 (82)	0.16667
C(54')	1141 (61)	10965 (42)	4186 (62)	0.16667
C(55')	1193 (58)	10322 (42)	4822 (60)	0.16667
C(56')	1585 (74)	9556 (50)	4289 (78)	0.16667
Cl(A)	3854 (15)	9488 (10)	-81 (16)	0.32467
Cl(B)	5482 (19)	9540 (13)	1597 (20)	0.32221
Cl(C)	4873 (30)	9729 (19)	572 (28)	0.35312
Cl(1)	6208 (8)	8094 (6)	8295 (9)	0.34133
Cl(2)	6493 (11)	6075 (8)	6798 (12)	0.32431
Cl(3)	6821 (11)	6807 (7)	6863 (11)	0.34839
Cl(4)	6678 (10)	6421 (7)	6819 (10)	0.32690
Cl(5)	6494 (13)	7834 (9)	7876 (14)	0.32143
Cl(6)	6014 (11)	8272 (7)	8547 (12)	0.33763

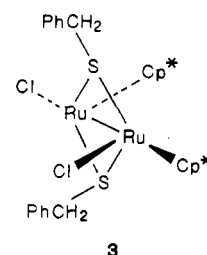
^aCl(A), Cl(B), and Cl(C) are disordered Cl anions with ca. $1/3$ atom multiplicity. Cl(1)–Cl(6) are Cl atoms of the disordered CH_2Cl_2 molecule. All Cl atoms were refined with isotropic thermal parameters.

$[(\text{Me}_2\text{PhP})_3\text{Ru}(\mu\text{-SH})_3\text{Ru}(\text{SH})(\text{PMe}_2\text{Ph})_2]$ (3.371 (3) Å).¹¹ Three thiolate ligands coordinate to two Ru atoms almost symmetrically so that the Ru–Ru bond is on a pseudo threefold axis. The Ru–S–Ru angles of about 68° are much smaller than those reported for $[(\text{Me}_2\text{PhP})_3\text{Ru}(\mu\text{-SH})_3\text{Ru}(\text{SH})(\text{PMe}_2\text{Ph})_2]$ ($86\text{--}87^\circ$), which may result from the shorter Ru–Ru distance in complex 1a. Two Cp* ligands coordinate to the Ru atoms perpendicularly to the Ru–Ru single bond in a staggered conformation. The three S atoms and phenyl groups are arranged approximately in a plane which is parallel to the Cp* ligands and bisects the Ru–Ru bond. Thus S(1)–S(2)–S(3)–C(31)–C(41)–C(51) define a plane with the largest deviation being 0.08 Å; the largest deviation of the 18 phenyl C atoms from this plane is 0.45 Å. Apparently there must exist considerable steric repulsion between the Cp* ligands and the phenyl groups of the bridging thiolate ligands.

Diruthenium Complexes with Two Bridging Thiolate Ligands. Although alkanethiols such as EtSH and *t*-BuSH did not react with complex 2 in CH_2Cl_2 at room temperature, PhCH_2SH reacted smoothly to give a doubly bridged diruthenium complex $[\text{Cp}^*\text{RuCl}(\text{SCH}_2\text{Ph})_2\text{RuCp}^*\text{Cl}]$ (3) in 17% yield (eq 2). The ^1H



NMR spectrum of complex 3 also exhibits sharp resonances at expected positions, indicating diamagnetic nature; i.e. the presence of the Ru–Ru single bond. Since the molar conductivity of complex 3 in CH_2Cl_2 is about 800 times smaller than that of complex 1a which is a one to one electrolyte, the neutral structure is plausible for complex 3. Since crystals suitable for X-ray analysis were not



obtained, we examined the EXAFS of complex 3 in the solid form;¹² this demonstrated the existence of one Ru (2.58 (4) Å), two bridging S or Cl (2.32 (3) Å), and one terminal S or Cl atom (2.45 (3) Å) around the Ru atom. Although S and Cl atoms are not distinguishable from each other by an EXAFS study, we have concluded that the structure with two bridging thiolate ligands is much more plausible because the bond length between Ru and the bridging atoms observed in complex 3 corresponds well to those observed in complex 1a (2.33 (3) and 2.35 (2) Å by EXAFS and X-ray crystallography, respectively) and is too short to be assigned as the Ru–Cl_{bridging} bond;¹³ moreover, the absorption band assignable to $\nu(\text{Ru}\text{--}\text{S}_{\text{bridging}})$ appeared

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(13) The Ir–S_{bridging} and Ir–Cl_{terminal} bond distances in $[\text{IrCl}_2(\mu^2\text{-SPh})_2(\text{COD})_2]$ are reported to be 2.356 (14) and 2.44 (2) Å, respectively, which are in good agreement with those in complex 3: Cotton, F. A.; Lahuerta, P.; Latorre, J.; Sanau, M.; Solana, I.; Schwotzer, W. *Inorg. Chem.* **1988**, *27*, 2131.

Table III. Properties of Diruthenium Complexes with Bridging Thiolate Ligands

complex	¹ H NMR, ^a ppm	redox potentials ^b		molar conductivity, cm ² mol ⁻¹ Ω ⁻¹
		E ^{red} , V	E ^{ox} , V	
[Cp*Ru(SPh) ₃ RuCp*]Cl (1a)	1.39 (s, 30 H, Cp*) 7.28–7.38 (m, 15 H, SPh)	-0.48 (r) -1.02 (r)	no. ^d	811
[Cp*Ru(SC ₆ H ₄ - <i>p</i> -Me) ₃ RuCp*]Cl (1b)	1.37 (s, 30 H, Cp*) 2.29 (s, 9 H, <i>p</i> -Me) 7.08, 7.22 (d, 6 H each, SC ₆ H ₄)	-0.52 (r) -1.07 (r)	no. ^d	736
[Cp*Ru(SC ₆ H ₄ - <i>p</i> -Cl) ₃ RuCp*]Cl (1c)	1.49 (s, 30 H, Cp*) 7.28 (s, 12 H, SC ₆ H ₄)	-0.38 (r) -0.90 (r)	no. ^d	584
[Cp*RuCl(SCH ₂ Ph) ₂ RuCp*]Cl (3)	1.48 (s, 30 H, Cp*) 4.38 (s, 4 H, CH ₂) 7.26–7.50 (m, 10 H, Ph)	-1.25 (ir) -2.00 (ir)	+0.52 (r)	1.01
[Cp*RuCl(SEt) ₂ RuCp*]Cl (4a)	1.56 (s, 30 H, Cp*) 1.37 (t, 6 H, CH ₂ Me) 3.09 (qua, 4 H, CH ₂ Me)	-1.36 (ir) -2.13 (r)	+0.49 (r)	20.6
[Cp*RuCl(S- <i>i</i> -Pr) ₂ RuCp*]Cl (4b)	1.52 (s, 30 H, Cp*) 1.29 (d, 12 H, CHMe ₂) 4.34 (sep, 2 H, CHMe ₂)	-1.38 (ir) -2.01 (ir)	+0.51 (r)	11.5
[Cp*RuCl(S- <i>t</i> -Bu) ₂ RuCp*]Cl (4c)	1.57 (s, 22 H, Cp*) 1.65 (s, 8 H, Cp*) 1.51 (s, 13 H, CMe ₃) 1.70 (s, 5 H, CMe ₃)	-0.69 (ir) -1.32 (ir) -2.09 (ir)	+0.50 (r)	163

^aIn CD₂Cl₂. Relative to Me₃SiOSiMe₃. ^bIn DMF-0.1 M [*n*-Bu₄N][BF₄]. V vs SCE; (r) = reversible where $E = E_{1/2}$ and (ir) = irreversible where $E = E_p$. Scan rate = 200 mV s⁻¹. ^cAbout 0.6 mM solution in CH₂Cl₂. ^dNot observed.

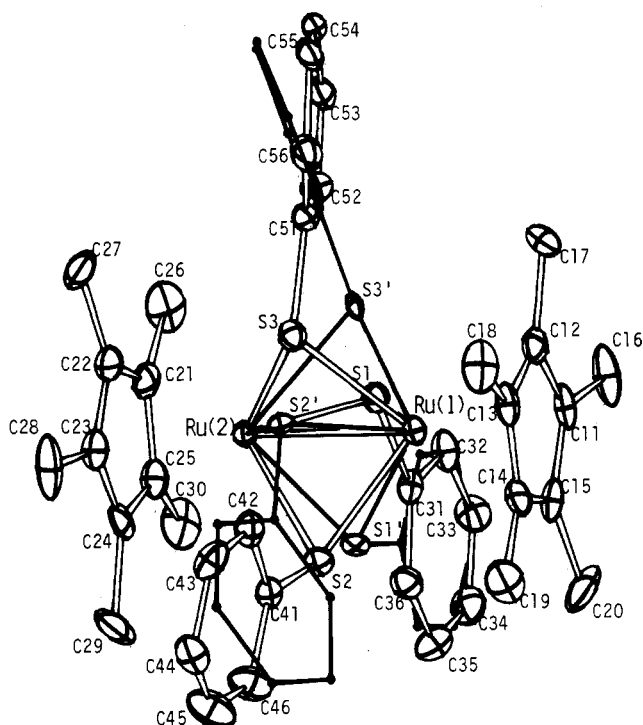


Figure 1. The ORTEP view and atom numbering scheme of complex 1a.

at 394 cm⁻¹ in its far-IR spectrum.¹² Two isomeric configurations, *cis* and *trans*, are possible for this structure, but the *cis* configuration that has a mirror plane bisecting the Ru–Ru bond seems more appropriate because the methylene protons of the benzyl groups appear as one singlet resonance in the ¹H NMR spectrum, indicating that these two protons are enantiotopic to each other. The steric repulsion between two Cp* rings may be present substantially for the *cis* structure in comparison with the *trans* configuration. However, that between the Cp* rings and the thiolate groups, which is observed even in complex 1a between the Cp* rings and the phenyl groups as described above, is much smaller in the *cis* structure, which may result in the preferential formation of the *cis* compound for complex 3. Dissolved in DMF, complex 3 shows one reversible oxidation wave and two successive irre-

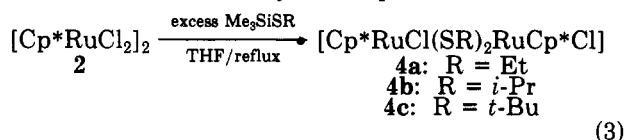
Table IV. Selected Bond Distances and Angles^a

Distances (Å)			
Ru(1)–Ru(2)	2.630 (1)	Ru(2)–S(1)	2.341 (4)
Ru(1)–S(1)	2.355 (4)	Ru(2)–S(2)	2.352 (4)
Ru(1)–S(2)	2.340 (4)	Ru(2)–S(3)	2.330 (4)
Ru(1)–S(3)	2.358 (4)	Ru(2)–C(21)	2.215 (14)
Ru(1)–C(11)	2.234 (11)	Ru(2)–C(22)	2.213 (13)
Ru(1)–C(12)	2.216 (10)	Ru(2)–C(23)	2.210 (12)
Ru(1)–C(13)	2.213 (10)	Ru(2)–C(24)	2.226 (10)
Ru(1)–C(14)	2.228 (14)	Ru(2)–C(25)	2.228 (11)
Ru(1)–C(15)	2.231 (13)	Ru(2)–S(1')	2.28 (2)
Ru(1)–S(1')	2.29 (1)	Ru(2)–S(2')	2.39 (2)
Ru(1)–S(2')	2.35 (2)	Ru(2)–S(3')	2.45 (1)
Ru(1)–S(3')	2.37 (2)	S(1')–C(31')	1.80 (6)
S(1)–C(31)	1.794 (14)	S(2')–C(41')	1.77 (7)
S(2)–C(41)	1.796 (16)	S(3')–C(51')	1.81 (7)
S(3)–C(51)	1.783 (15)		
Angles (deg)			
Ru(1)–S(1)–Ru(2)	68.1 (1)	Ru(1)–S(1')–Ru(2)	70.3 (4)
Ru(1)–S(2)–Ru(2)	68.2 (1)	Ru(1)–S(2')–Ru(2)	67.3 (5)
Ru(1)–S(3)–Ru(2)	68.3 (1)	Ru(1)–S(3')–Ru(2)	66.2 (5)
Ru(2)–Ru(1)–S(1)	55.7 (1)	Ru(2)–Ru(1)–S(1')	54.5 (4)
Ru(2)–Ru(1)–S(2)	56.1 (1)	Ru(2)–Ru(1)–S(2')	57.0 (4)
Ru(2)–Ru(1)–S(3)	55.4 (1)	Ru(2)–Ru(1)–S(3')	58.4 (3)
Ru(1)–Ru(2)–S(1)	56.2 (1)	Ru(1)–Ru(2)–S(1')	55.2 (4)
Ru(1)–Ru(2)–S(2)	55.7 (1)	Ru(1)–Ru(2)–S(2')	55.7 (4)
Ru(1)–Ru(2)–S(3)	56.4 (1)	Ru(1)–Ru(2)–S(3')	55.4 (4)
Ru(1)–S(1)–C(31)	113.5 (5)	Ru(1)–S(1')–C(31')	115 (2)
Ru(2)–S(1)–C(31)	114.2 (5)	Ru(2)–S(1')–C(31')	115 (2)
Ru(1)–S(2)–C(41)	116.7 (4)	Ru(1)–S(2')–C(41')	112 (2)
Ru(2)–S(2)–C(41)	112.9 (5)	Ru(2)–S(2')–C(41')	122 (2)
Ru(1)–S(3)–C(51)	113.1 (5)	Ru(1)–S(3')–C(51')	113 (3)
Ru(2)–S(3)–C(51)	114.6 (5)	Ru(2)–S(3')–C(51')	109 (3)

^aNumbers in parentheses are estimated standard deviations.

versible reduction waves in its cyclic voltammogram (Table III).

As described above, common alkanethiols did not react with complex 2. However, when Me₃SiSR (R = Et, *i*-Pr, *t*-Bu) were chosen as the thiolate source, a series of diruthenium complexes, [Cp*RuCl(SR)₂RuCp*]Cl (4), could be obtained in moderate yields (eq 3). Thus treatment



of complex 2 with excess Me₃SiSR in THF at reflux for

Table V. Properties of Diruthenium Complexes with CO and *t*-BuNC Ligands

complex	IR, ^a cm ⁻¹	¹ H NMR, ^b ppm	molar conductivity, cm ² mol ⁻¹ Ω ⁻¹
[Cp*RuCl(SEt) ₂ RuCp*(CO)]Cl (5a)	1983	1.67 (s, 15 H, Cp*) 1.96 (s, 15 H, Cp*) 1.45 (t, 6 H, CH ₂ Me, ³ J = 12.5 Hz) 2.96, 3.81 (dq, 2 H each, CH ₂ Me, ² J = 7.3, ³ J = 12.5 Hz)	921
[Cp*RuCl(S- <i>i</i> -Pr) ₂ RuCp*(CO)]Cl (5b)	1985	1.66 (s, 15 H, Cp*) 1.99 (s, 15 H, Cp*) 1.38, 1.53 (d, 6 H each, CHMe ₂ , ³ J = 6.7 Hz) 4.42 (sep, 2 H, CHMe ₂ , ³ J = 6.7 Hz)	605
[Cp*RuCl(SEt) ₂ RuCp*(<i>t</i> -BuNC)]Cl (5c)	2150	1.60 (s, 15 H, Cp*) 1.80 (s, 15 H, Cp*) 1.25 (s, 9 H, CMe ₃) 1.41 (t, 6 H, CH ₂ Me, ³ J = 12.8 Hz) 2.93, 3.89 (dq, 2 H each, CH ₂ Me, ² J = 7.3, ³ J = 12.8 Hz)	578

^a KBr disks. $\nu(\text{C}\equiv\text{O})$ or $\nu(\text{N}\equiv\text{C})$. ^b CDCl₃ solution. Relative to Me₃SiOSiMe₃. dq = doublet of quartets. ^c About 0.6 mM solution in CH₂Cl₂.

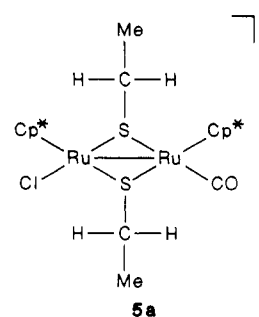
about 7 h gave complexes **4**, which were isolated as dark brown microcrystals. Spectroscopic data shown in Table III as well as the results of elemental analyses of complexes **4a** and **4b** correspond well with the doubly bridged diruthenium structure established for complex **3**. In the case of complex **4c**, the ¹H NMR spectrum shows two singlet peaks assignable to the Cp* ligands together with two singlet peaks of the *t*-Bu groups, indicating the presence of two different species in solution. Since the molar conductivity of complex **4c** in CH₂Cl₂ is significantly larger than those of complexes **3**, **4a**, and **4b**, a cationic complex might exist as a minor component in about 27% abundance. This cationic complex also shows only two singlet resonances assignable to Cp* and S-*t*-Bu ligands in its ¹H NMR spectrum, and thus a symmetrical structure [Cp*Ru(S-*t*-Bu)₂(μ-Cl)RuCp*]Cl may be plausible for this minor component. Dissociation of one Cl anion to the outer sphere may result from the steric crowding of the S-*t*-Bu groups.

As shown in Table III, the cyclic voltammograms of complexes **4a** and **4b** exhibit two successive reduction and one oxidation waves as observed for complex **3**, whereas complex **4c** shows three reduction waves. Presumably the reduction wave observed at -0.69 V can be assigned to the one-electron reduction process of the cationic species existing in solution described above.

It is interesting to note that the structures of the produced thiolate complexes sharply depend upon the nature of the thiolate sources. As described above, even when treated with excess amount of PhCH₂SH or Me₃SiSR, only two chlorides in complex **2** were replaced by thiolates to give complexes **3** and **4**, whereas the reaction of complex **2** with aromatic thiols afforded the complexes with three thiolate ligands. Moreover, treatment of complex **2** with NaSR (R = Et, PhCH₂, Ph) gave another series of thiolate complexes [Cp*₂Ru₂(SR)₃]_n. Characterization of these paramagnetic ruthenium complexes is in progress and will be reported in a subsequent paper.

Reactions of Doubly Bridged Diruthenium Complexes with Carbon Monoxide and Isocyanide. When CO was bubbled through a solution of complex **1a** in CH₂Cl₂ and the mixture was stirred overnight under CO atmosphere, a yellow solid was obtained which showed $\nu(\text{C}\equiv\text{O})$ band at 1995 cm⁻¹ in its IR spectrum. However, in spite of repeated purification trials, isolation of the characterizable pure complex was unsuccessful. On the other hand, analogous treatment of complexes **4a** and **4b** with CO in THF or CH₂Cl₂ gave the diruthenium complexes [Cp*RuCl(SR)₂RuCp*(CO)]Cl (**5a**, R = Et; **5b**, R = *i*-Pr) in moderate yields. Complexes **5a** and **5b** show strong $\nu(\text{C}\equiv\text{O})$ bands at 1983 and 1985 cm⁻¹, respectively.

Molar conductivities observed for these complexes are consistent with the monocationic structure. The ¹H NMR spectrum of complex **5a** exhibits two singlet peaks with



the same intensities assignable to two Cp* ligands, which are now inequivalent because of the coordination of CO to only one Ru atom. As shown below, the methylene protons of thiolate ligands become diastereotopic to each other and each proton appear as a doublet of quartets with the coupling constants of ²J = 7.3 and ³J = 12.5 Hz. In the case of complex **5b**, two methyl groups of S-*i*-Pr ligands become diastereotopic and appear as two double peaks in its ¹H NMR spectrum. These spectroscopic data are summarized in Table V. Presumably due to the strong electron-donating ability of thiolate ligands, the high valent Ru(III) atoms in these complexes can bind such π acidic molecules as CO. This interesting feature of sulfur ligands is also observed in [Ru(CO)(S-2,3,5,6-Me₄C₆H₄)₄]¹⁴ and [(η^5 -C₅Me₄Et)₂Ru₂S₂(CO)₂]¹⁵, the former of which is quite a rare example that has a CO ligand coordinating to the Ru(IV) atom as well as [(η^5 -C₅H₄Et)RuBr₃(CO)].¹⁶ Treatment of complex **4a** with excess *t*-BuNC in THF at reflux also gives the monosubstituted diruthenium complex [Cp*RuCl(SEt)₂RuCp*(*t*-BuNC)]Cl (**5c**) in 50% yield. The $\nu(\text{N}\equiv\text{C})$ band appears at 2150 cm⁻¹ in its IR spectrum, which is slightly higher than that of free *t*-BuNC. The ¹H NMR spectrum of complex **5c** corresponds very well to that of the CO analogue **5a** except for the resonance due to the *t*-Bu group.

Monomeric Thiolate Complexes with Tertiary Phosphine Ligands. It has already been reported that the dimeric complex **2** reacts with equimolar tertiary phosphines to give monomeric phosphine adducts

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[Cp*Ru(PR₃)Cl₂].⁵ Now we have found that treatment of these phosphine adducts with excess NaSPh in MeOH gives monomeric thiolate complexes [Cp*Ru(PR₃)(SPh)₂] (R = Me, Ph) in 39 and 74% yields, respectively. Solutions of these complexes are EPR-active, and both show broad singlet resonances at $g = 2.08$. In the cyclic voltammograms of these complexes appear two reversible waves corresponding to reversible one-electron oxidation and reduction processes (R = Me, +0.14, -0.82 V; R = Ph, +0.50, -0.73 V). Especially in the case of the PMe₃ adduct the complex is susceptible to oxidation at a less positive potential of +0.14 V due to the strong electron-donating ability of the phosphine ligand.

Further investigations of the reactions of complex 2 and its phosphine adducts with a variety of sulfur compounds are in progress to prepare highly aggregated ruthenium-sulfur clusters.

Acknowledgment. We thank Junichi Tsuchiya for recording EPR spectra. The financial support by the Ministry of Education of Japan and Ajinomoto Co. is greatly appreciated.

Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen coordinates (2 pages); a listing of observed and calculated structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

Reaction of Chloro(chloromethyl)dimethylsilane and -germane with Group 14 Element Nucleophiles

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Received September 15, 1988

Reaction of chloro(chloromethyl)dimethylsilane (1) or -germane (2) with group 14 element nucleophiles, R₃M'Li (3, M' = Si, Ge, and Sn), was examined to prepare R₃M'-MMe₂-CH₂-Cl compounds (4, M = Si; 5, M = Ge). However, disubstituted compounds R₃M'-MMe₂-CH₂-M'R₃ (6 or 7) were mainly produced because the carbon-chlorine bonds in 4 or 5 are activated by the β-effect of the R₃M' groups.

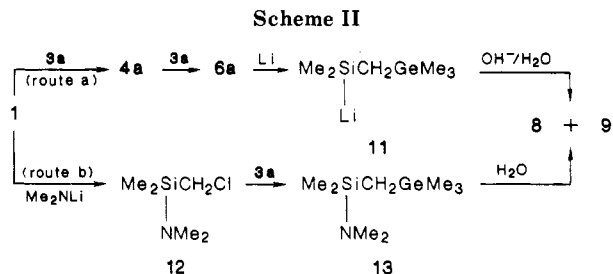
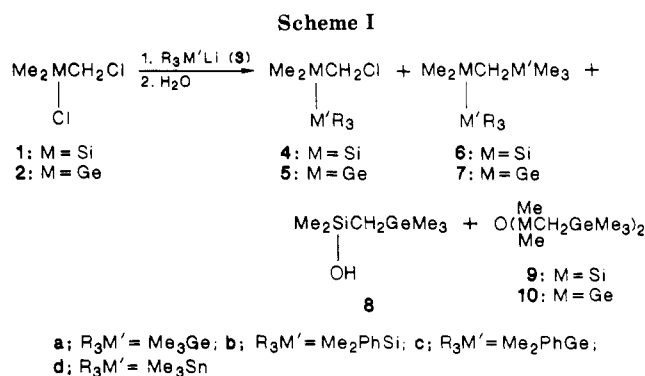
There are few reports on the syntheses of hexaorganodigermanes containing functional group(s) on the alkyl substituents. Although (chloromethyl)pentaalkyldigermane is a key compound for the preparation of such compounds, no appropriate preparation method has been reported.¹

Organo(chloromethyl)dimethylsilane or -germane is easily prepared by treatment of chloro(chloromethyl)dimethylsilane (1) or -germane (2)² with organolithium compounds³ or Grignard reagents⁴ because the Si-Cl or Ge-Cl bond is more reactive than the respective C-Cl bond toward ordinary carbon nucleophiles.

We examined the reaction of 1 and 2 with group 14 element nucleophiles such as R₃Si⁻, R₃Ge⁻, and R₃Sn⁻ (3) in order to prepare periodic group 14 element-element bonded compounds containing a chloromethyl substituent.

Results and Discussion

When a solution of 1 in tetrahydrofuran (THF) was treated at -78 °C with (trimethylgermyl)lithium (3a), prepared from chlorotrimethylgermane and lithium in hexamethylphosphoric triamide (HMPA),⁵ the product was not 1-chloro-2,2,3,3-tetramethyl-2-sila-3-germabutane (4a)



(1) For a review of organogermanium compounds, see: Riviere, P.; Riviere-Baudet, M.; Satge, J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 2, p 399.

(2) Wieber, M.; Frohning, C.-D.; Schwarzmann, G. *Z. Anorg. Allg. Chem.* 1967, 355, 79.

(3) Reaction of 1 or 2 with *n*-butyllithium gave a 93% yield of *n*-butyl(chloromethyl)dimethylsilane or a 94% yield of *n*-butyl(chloromethyl)dimethylgermane, respectively.

(4) Fritz, G.; Burdt, H. *Z. Anorg. Allg. Chem.* 1962, 314, 35.

(5) Wickham, G.; Young, D.; Kitching, W. *J. Org. Chem.* 1982, 47, 4884.

as expected but was a mixture of 2,2,3,3,5,5-hexamethyl-3-sila-2,5-digermahexane (6a), 2,4,4-trimethyl-2-sila-4-germa-2-pentanol (8), and 1,1,3,3-tetramethyl-1,3-bis-[(trimethylgermyl)methyl]disiloxane (9) (entry 1 in Table I). A similar result was obtained even at -100 °C (entry 2). This result indicates that the C-Cl bond is attacked more quickly than the Si-Cl bond by 3a. However, the formation of 8 and 9 was not suppressed by the use of 3a in excess (entries 3 and 4).