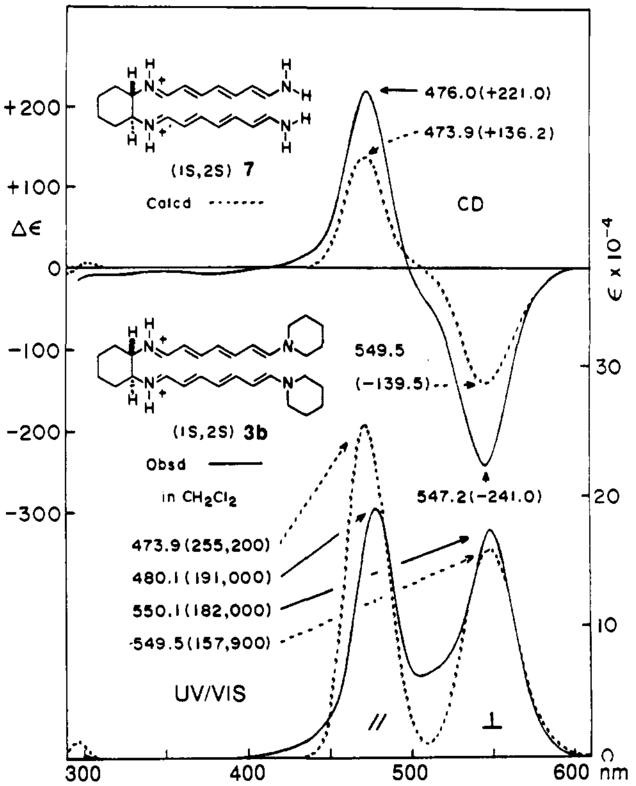
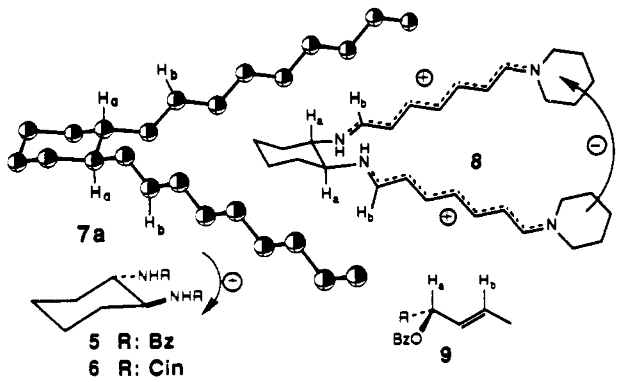


Figure 2. (—) Observed CD and vis spectra of biscation **3b** in CH_2Cl_2, $c = 3 \times 10^{-6}$ M. (···) Calculated CD and vis spectra of model biscation **7**.

MMP2[9] to rationalize these results. In its most stable conformation **7a**, protons H_a and H_b are almost syn; this leads to a *counterclockwise* twist for the two chromophores (**8**), and hence the negative exciton coupling. In acyclic allylic benzoates, the signs of the benzoate CE's were also governed by conformation **9** where H_a/H_b are syn.[10] The CD and UV-vis spectra of (1*S*,2*S*)-**7** were calculated by the π-electron SCF-CI-DV MO method[1,11,12] and the atomic coordinates obtained above. For evaluation of MO parameters, the four N atoms were treated as being the same, and doubly charged cores were assigned to them. Although the calculated CE's are weaker than the observed ones (Figure 2), the latter are in good agreement with conformation **7a**, where the angle between the two long-axis-polarized cyanine transitions is ca. 70°. The following points are responsible for the strong exciton splitting in the UV-vis spectrum of biscation **3** (Figure 2): (i) the energy gap between two bands is as large as 2890 cm^{-1}, and the bands are located in a long wavelength region; the energy splitting is thus emphasized on the wavelength scale; (ii) typically for cyanine dyes,[13] the UV-vis bands have very narrow 1/e band widths of $2\Delta\sigma = 1524$ cm^{-1}; this is much smaller than ordinary UV bands (ca. 5000 cm^{-1}).[1]

The CD and UV curves of the neutral compound **4** were similarly calculated: UV λ_{max} 357 nm (ε 122200); CD 377 nm (Δε −85.6) and 339 nm (+49.7); obsd UV λ_{max} 383 nm (ε 80000), CD 412 nm (Δε −73.2) and 362 nm (+63.4). The calculated bands are at shorter wavelengths, but the overall shapes of the UV and CD bands, as well as the CE signs, are well-reproduced. The fact that in both the biscation and neutral molecule the sign of the exciton split CD couplet is opposite to that expected indicates that this sign reversal is not a consequence of charge repulsion in biscation **3** but results from the unique conformations of **3** and **4**. This example demonstrates the importance in knowing the spatial dispositions of interacting electric transition moments in the exciton chirality method. The vis spectrum of **3** appears to be the first case where exciton-split peaks appear in solution as two distinct bands separated by 70 nm.



Acknowledgment. We are grateful to P. Zhou for assistance in CD measurements. The studies were supported by NIH Grant GM 34509 (to K.N.) and grants from the Ministry of Education, Science, and Culture, General (B) No. 01470026, Priority Area Nos. 01648501, 02230201, and 02250103, and International Joint Research No. 02044014 (to N.H.).

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1,2,3,4,5-Tetrathiametallolanes of Group 14 Metals, RR′MS_4 (M = Si, Ge, and Sn): Synthesis and Crystal Structures

Norihiro Tokitoh, Hiroyuki Suzuki, Tsuyoshi Matsumoto, Yasusuke Matsuhashi, and Renji Okazaki*

Department of Chemistry, Faculty of Science
The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku
Tokyo 113, Japan

Midori Goto

National Chemical Laboratory for Industry
1-1 Higashi, Tsukuba, Ibaraki 305, Japan

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The chemistry of polychalcogenides, particularly that of metal-containing cyclic polychalcogenides, is currently enjoying great popularity.[1] Polychalcogenido complexes of metals are interesting not only because of their unique structures and reactivities but also because of their possible applications. They can, for example, be used as versatile chalcogen sources to prepare chalcogen rings of predetermined size,[2] and they are also suspected to play a role in catalysis (particularly in hydrodesulfurization).[3] For transition-metal compounds there have been several reports on the synthesis of cyclic polychalcogenides such as Cp_2TiS_5,[2a,4]

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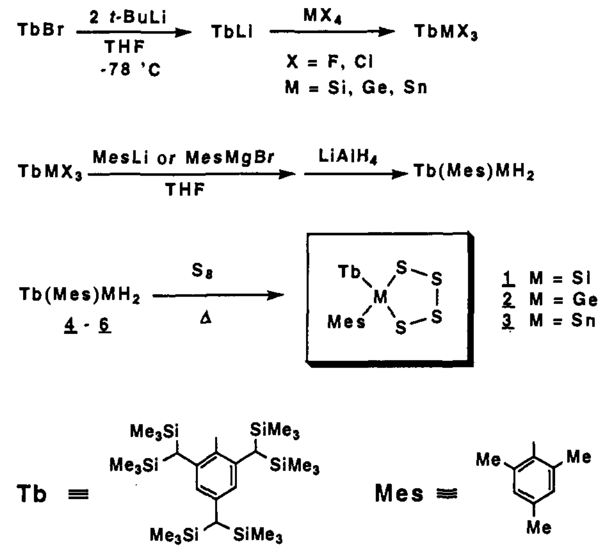
Scheme I



Cp_2VS_5,[5] Cp_2VSe_5,[5b] Cp_2MoS_4,[2b,6a] and Cp_2WS_4[6b] (Cp = η^5-C_5H_5). Recently, a new type of zinc polychalcogenides, $(N\text{-MeIm})_2ZnS_6$ and $(N\text{-MeIm})_2ZnSe_4$, has also been successfully synthesized by direct chalcogenation of zinc dust in *N*-methylimidazole (*N*-MeIm).[7] However, as for the main-group element analogues, group 14 metal-containing cyclic polychalcogenides such as $RR'MY_x$ (M = Si, Ge, Sn, and Pb; Y = S, Se, and Te) have been hitherto unknown. In the course of our study on sterically congested molecules we have developed an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tb hereafter).[8] We report herein the first synthesis of 1,2,3,4,5-tetrathiametallolanes of group 14 metals, $Tb(Mes)MS_4$ (Mes = mesityl; **1**, M = Si; **2**, M = Ge; **3**, M = Sn) by taking advantage of this new bulky group.[9]

The synthesis of metallolanes **1**, **2**, and **3** was accomplished by the thermal sulfurization of the corresponding metal dihydrides $Tb(Mes)MH_2$ (**4**, M = Si; **5**, M = Ge; **6**, M = Sn),[10] derived from the Tb-substituted metal trihalides, with elemental sulfur (5 equiv mol as S_8 in each reaction) as shown in Scheme I. Dihydrosilane **4** was quite inert to molten sulfur even at 200 °C but gave rise to the tetrathiasilolane **1** (7%) at 230 °C. On the other hand, dihydrogermane **5** was readily sulfurized by heating in molten sulfur at 180 °C for 10 min leading to the selective formation of tetrathiagermolane **2** (57%). Tetrathiastannolane **3** was more readily obtained in 92% yield by exposure of dihydrostannane **6** to sulfur in refluxing THF for 18 h. It is noteworthy that the sulfurization of **6** proceeded in THF even at room temperature to give **3** (21%; reaction time, 37 h).

Compounds **1**, **2**, and **3** showed satisfactory spectral and analytical data.[11] When their Raman spectra were taken for powdered samples with a 514.5 nm line of an argon laser in the region of 300–1700 cm^{-1}, characteristic Raman lines nearby 500 cm^{-1} assignable to the S_4 stretching were observed in each case (**1**, 505 cm^{-1}; **2**, 507 cm^{-1}; **3**, 494 cm^{-1}). Their final molecular structures were definitely determined by crystallographic analyses, and an ORTEP drawing of **1** is shown as a representative in Figure 1 along with the selected interatomic distances and bond angles. Pale yellow crystals of **1**, **2**, and **3** solvated with chloroform were all monoclinic systems, space group $P2_1/n$, with very similar cell dimension regardless of the center metals.[12] Of particular note is the preferred distorted half-chair conformation of nearly envelope type in all the three MS_4 rings, where the two central sulfur atoms in the S_4 unit lie at irregular distances from and on opposite sides of the plane that contains the central metal and two coordinated sulfur atoms (**1**, 0.21 (2*S*), 1.02 (3*S*); **2**, 0.26 (2*S*), 0.99 (3*S*); **3**, 0.93 (2*S*), 0.31 Å (3*S*)).[13] In each of these metallolanes the S_4 unit is asymmetrically bound with two unequal metal–sulfur bond lengths, and there is almost no alternation in the S–S bonds of sulfur chains in contrast to the previously reported Cp_2MS_4 systems (M = Mo, W), which show distinct alternation in S–S bonds with no asymmetry in the binding of the S_4 unit.[14]

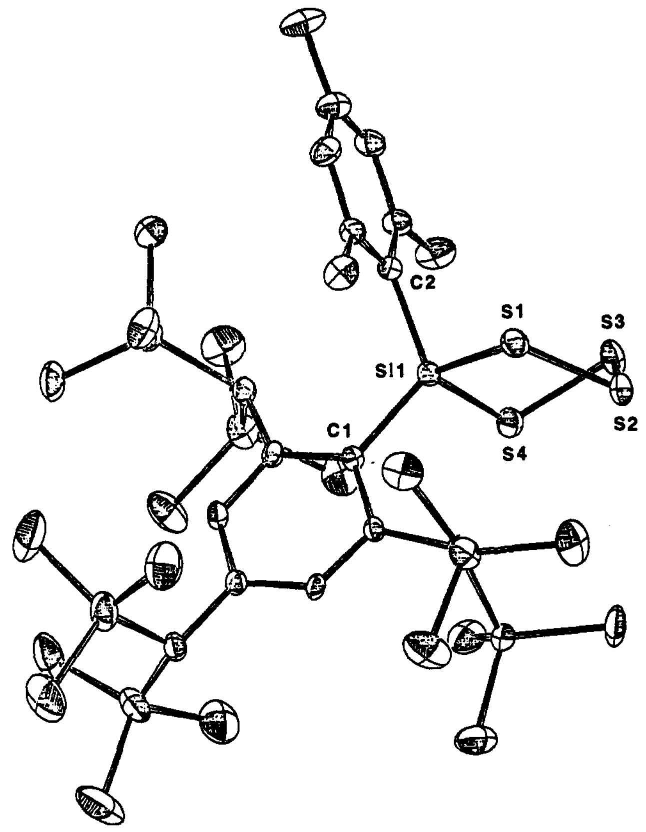


Figure 1. ORTEP drawing of **1**. Selected bond lengths (Å) and angles (deg): Si(1)–S(1), 2.224 (3); S(1)–S(2), 2.051 (4); S(2)–S(3), 2.046 (5); S(3)–S(4), 2.057 (3); S(4)–Si(1), 2.155 (3); Si(1)–C(1), 1.898 (6); Si(1)–C(2), 1.897 (7); S(1)–Si(1)–S(4), 100.4 (1); Si(1)–S(1)–S(2), 102.9 (2); S(1)–S(2)–S(3), 99.6 (2); S(2)–S(3)–S(4), 97.4 (2); S(3)–S(4)–Si(1), 100.3 (1); C(1)–Si(1)–S(1), 119.2 (3); C(1)–Si(1)–S(4), 103.4 (3); C(2)–Si(1)–S(1), 96.5 (3); C(2)–Si(1)–S(4), 118.5 (2); C(1)–Si(1)–C(2), 118.3 (3).

Pure pentathiolane (S_5) has not yet been synthesized probably due to its unfavorable bond geometry, and the strain in penta-

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[9] Only inseparable complex mixture was obtained by the sulfurization of less hindered group 14 metal dihydrides such as dihydrodimesitylgermane, indicative of the crucial role of the bulky Tb group in the successful isolation of **1**–**3**.

[10] The physical properties of the new metal dihydrides **4**, **5**, and **6** are detailed in the supplementary material.

[11] The physical properties of **1**, **2**, and **3** are detailed in the supplementary material.

[12] Crystal and experimental data for **1**: $C_{36}H_{70}S_4Si_7\cdot CHCl_3$, fw = 947.30, crystal size (mm) 0.6×0.6×0.1, monoclinic, space group $P2_1/n$, a = 12.292 (3) Å, b = 13.034 (2) Å, c = 33.532 (9) Å, β = 91.60 (1); V = 5370 (2) $Å^3$, Z = 4, D_c = 1.172 g/cm^3, R = 0.078 (R_w = 0.078), $w = 1/(A|F_o|^2 + B|F_o| + C)$, A = 0.0048, B = –0.359, C = 15.06. Data were collected through a capillary glass tube with Mo $K\alpha$ radiation (λ = 0.71069 Å) on an Enraf-Nonius CAD-4, μ = 4.96 cm^{-1}; 4906 unique reflections ($I > 3\sigma(I)$) were observed ($2° < 2\theta < 55°$). Full details of the crystallographic structure analyses of **1**, **2**, and **3** are described in supplementary material.

[13] For Cp_2MoS_4 these distances are approximately equal (0.53 and 0.65 Å), and the conformation of this MS_4 ring is almost half-chair; see ref 2c.

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thiolane becomes evident from the separation of 3.59 Å between the terminal atoms in the curled chain.[15] The successful isolation of **1**, **2**, and **3** suggests that the introduction of group 14 metals with tetrahedral environment and the longer M–S bonds compared to the S–S bond in orthorhombic sulfur (2.037 (5) Å)[16] eases the ring strain of these unprecedented tetrathiametallolane ring systems.[17]

Further investigation of the formation mechanism and reactivity of the novel 1,2,3,4,5-tetrathiametallolanes is currently in progress.

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Supplementary Material Available: Spectral data of **1–6**, ORTEP drawings of **2** and **3** along with the selected bond lengths and angles, and crystallographic data with tables of thermal and positional parameters for **1**, **2**, and **3** (25 pages). Ordering information is given on any current masthead page.

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(17) No 1,2,3,4-tetrathiolane derivative (R_2CS_4) has been isolated so far as we know.

An Unusual 17-Electron Organometallic Radical, $CpCr(NO)(PPh_3)(CH_2SiMe_3)$[1]

F. Geoffrey Herring, Peter Legzdins,* W. Stephen McNeil, and Michael J. Shaw

Department of Chemistry
The University of British Columbia
Vancouver, British Columbia, Canada V6T 1Z1

Raymond J. Batchelor and Frederick W. B. Einstein*

Department of Chemistry, Simon Fraser University
Burnaby, British Columbia, Canada V5A 1S6

Received April 16, 1991

Paramagnetic organometallic complexes of the transition metals have recently been the focus of considerable attention primarily because of their demonstrated involvement as reaction intermediates and their importance in various catalytic processes.[2-4] Despite the relatively large number of organotransition-metal radicals that have been identified to date, few have also been structurally characterized in the solid state.[2,5] We wish to report the synthesis, characterization, and some unusual chemical properties of the thermally stable 17-electron radical $CpCr(NO)(PPh_3)(CH_2SiMe_3)$ [Cp = η^5-C_5H_5].[6,7] This radical is a convenient precursor to previously unknown chromium nitrosyl complexes such as neutral hydrides and cationic dinitrosyl phosphine species.

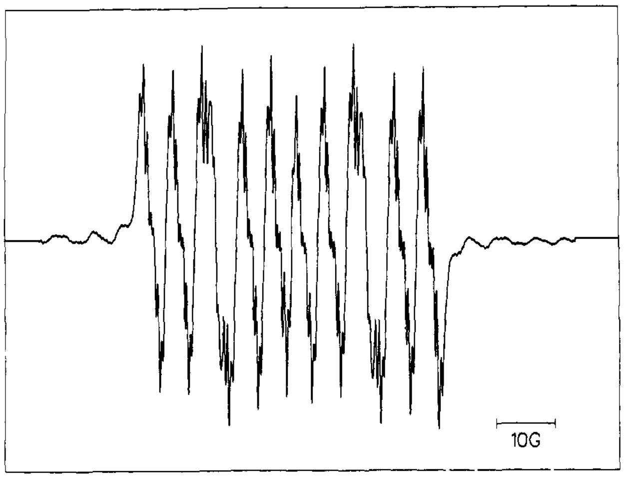
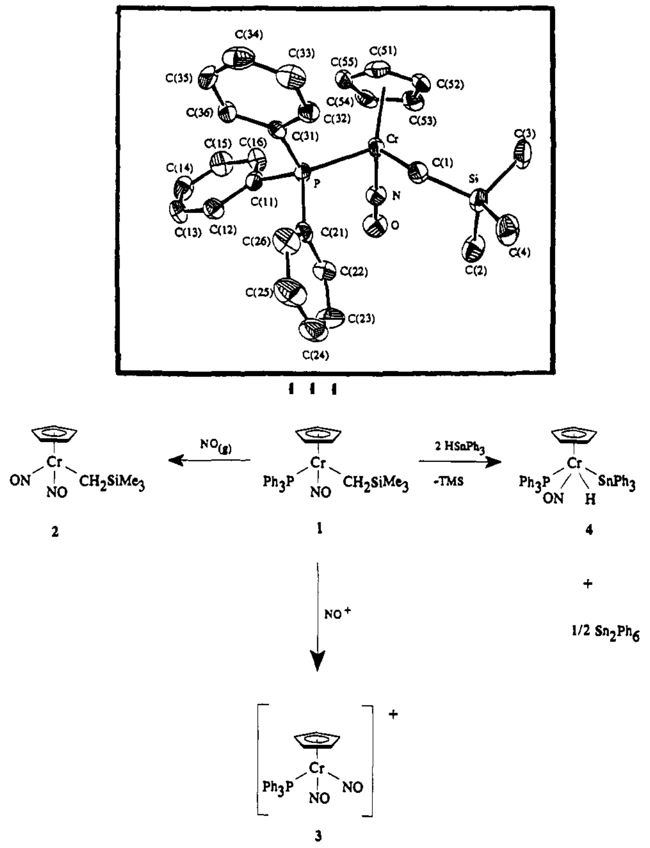


Figure 1. X-band ESR spectrum of $CpCr(NO)(PPh_3)(CH_2SiMe_3)$ in hexanes at 25 °C; $a_{CH_aCH_b}$ = 12.0 G, $a_{CH_aCH_b}$ = 1.0 G, a_P = 26.0 G, a_N = 5.0 G, and a_{Cp} = 0.6 G; g_{iso} = 1.9979.

Scheme I



In a typical experiment, treatment of a green suspension of $CpCr(NO)(PPh_3)I$[8] (1.00 g, 1.86 mmol) in THF (20 mL) with Me_3SiCH_2MgCl (2 mL of 1.0 M solution in Et_2O, 2.0 mmol) resulted in the formation of a red-brown solution which became dark green and deposited a white precipitate over 24 h. The solvent was removed in vacuo. The residues were extracted with Et_2O, and the extracts were filtered through alumina. Addition of hexanes and cooling to −20 °C afforded analytically pure $CpCr(NO)(PPh_3)(CH_2SiMe_3)$ (**1**) as clusters of needles (0.61 g, 66% yield).[9] Dark green **1** is a paramagnetic solid (μ = 1.47 μ_B)[10]

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(6) The congeneric molybdenum and tungsten mononitrosyl complexes remain unknown at present.

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(9) Anal. Calcd for $C_{23}H_{20}NOSiPCr$: C, 51.51; H, 3.76; N, 2.61. Found: C, 51.22; H, 3.77; N, 2.65. IR (KBr) ν_{NO} 1611 cm^{-1}. IR (hexanes) ν_{NO} 1631 cm^{-1}. FAB-MS *m/z* 498 [P^+], 409 [$P^+ - CH_2SiMe_3$].

0002-7863/91/1513-7049$02.50/0