$MeOCH_2CH_2$), 103670-50-4; II (R = R′ = $-CH_2(CH_2)_2CH_2-$), 103670-51-5; II (R = R′ = $-CH_2(CH_2)_3CH_2-$), 103670-52-6; $Me_2C{=}CBr_2$, 13353-06-5; $MeC(Et){=}CBr_2$, 103670-53-7; $MeC(EtOCH_2){=}CBr_2$, 103670-54-8; $MeC(MeO(Me)CH){=}CBr_2$, 103670-57-1; $MeC(MeOCH_2CH_2){=}CBr_2$, 103670-56-0; $MeC(Ph){=}CCl_2$, 5264-26-6; $PhC(CF_3){=}CBr_2$, 103670-60-6; $Ph_2C{=}CBr_2$, 2592-73-6; $(MeOCH_2)_2C{=}CBr_2$, 103670-58-2; $MeOCH_2C(MeOCH_2CH_2){=}CBr_2$, 103670-59-3; $\overline{CH_2(CH_2)_2CH_2C}{=}CBr_2$, 103670-61-7; $\overline{CH_2(CH_2)_3CH_2C}{=}CBr_2$, 60014-85-9; $Me_2CHC(SnMe_3)_3$, 103670-62-8; $Et(Me)CHC(SnMe_3)_3$, 103670-63-9; $EtOCH_2(Me)CHC(SnMe)_3$, 103670-64-0; $MeO(Me)CH(Me)CHC(SnMe)_3$, 103670-65-1; $MeOCH_2CH_2(Me)CHC(SnMe)_3$, 103670-66-2; $Ph(Me)CHC(SnMe_3)_3$, 103670-67-3; $(MeOCH_2)_2CHC(SnMe_3)_3$, 103670-68-4; $\overline{CH_2(CH_2)_2CH_2C}HC(SnMe_3)_3$, 103670-69-5; $\overline{CH_2(CH_2)_3CH_2C}HC(SnMe_3)_3$, 103670-70-8; (*Z*)-*t*-$BuCH{=}C(Br)SnMe_3$, 103670-71-9; (*Z*)-$PhCH{=}C(Br)SnMe_3$, 103670-72-0; $Me_2C{=}C(Br)SnMe_3$, 103670-73-1; (*Z*)-$Ph(Me)C{=}C(Br)SnMe_3$, 103670-74-2; $Ph_2C{=}C(Br)SnMe_3$, 103670-75-3; *n*-$BuCH{=}C(SnMe_2Br)_2$, 103670-76-4; c-$HexCH{=}C(SnMe_2Br)_2$, 103670-77-5; *t*-$BuCH{=}C(SnMe_2Br)_2$, 103670-78-6; $MeOCH_2CH_2CH{=}C(SnMe_2Br)_2$, 103670-79-7; $MeO(C_6H_{10})CH{=}C(SnMe_2Br)_2$, 103670-80-0; $PhCH{=}C(SnMe_2Br)_2$, 103670-81-1; $PhCH{=}C(SnMe_2Cl)_2$, 103670-82-2; $Ph_2C{=}C(SnMe_2Br)_2$, 103670-83-3; $MeO(C_6H_{10})CH{=}C(SnMe_3)SnMe_2Br$, 103670-84-4; $Me_3SnSnMe_3$, 661-69-8; $PhC{\equiv}CMe$, 673-32-5; (*E*)-$Ph(Me)C{=}C(Br)SnMe_3$, 103670-85-5; (*E*)-$PhCH{=}C(SnMe_2Cl)SnCl_3$, 103670-87-7; (*E*)-$PhCH{=}C(SnMe_3)CH_2CH{=}CH_2$, 87673-51-6; CBr_4, 558-13-4; $Me_2C{=}O$, 67-64-1; $Me(Et)C{=}O$, 78-93-3; $Me(EtOCH_2)C{=}O$, 14869-34-2; $Me(Et_2NCH_2)C{=}O$, 1620-14-0; $Me(MeOCH_2CH_2)C{=}O$, 6975-85-5; $Me(MeO(Me)CH)C{=}O$, 17742-05-1; $(MeOCH_2)_2C{=}O$, 18664-32-9; $MeOCH_2(MeOCH_2CH_2)C{=}O$, 25680-86-8; $Ph(CF_3)C{=}O$, 434-45-7; $\overline{CH_2(CH_2)_2CH_2C}{=}O$, 120-92-3; $\overline{CH_2(CH_2)_3CH_2C}{=}O$, 108-94-1; Me_3SnLi, 17946-71-3; $PhCH{=}CCl_2$, 698-88-4; (*E*)-$PhCBr{=}CBrPh$, 20432-10-4; (*E*)-$PhCI{=}CIPh$, 20432-11-5; (*E*)-$PhCI{=}CHI$, 71022-74-7; Me_3SnNa, 16643-09-7; Me_3SnK, 38423-82-4; (*E*)-$PhCBr{=}CBrMe$, 67824-63-9; Me_3SnH, 1631-73-8; *t*-$BuCH{=}C(SnMe_3)_2$, 78338-46-2; $PhCH{=}C(SnMe_3)_2$, 78338-47-3; *n*-$BuCH{=}C(SnMe_3)_2$, 78338-45-1; c-$HexCH{=}C(SnMe_3)_2$, 89029-46-9; $MeOCH_2CH_2CH{=}C(SnMe_3)_2$, 103670-88-8; $MeO(C_6H_{10})CH{=}C(SnMe_3)_2$, 103670-89-9; (*Z*)-*n*-$BuCH{=}C(Br)SnMe_3$, 103670-90-2; (*Z*)-$MeO(C_6H_{10})CH{=}C(Br)SnMe_3$, 103670-91-3; (*Z*)-$MeO(C_6H_{10})CH{=}C(SnMe_2Br)SnMe_3$, 103670-92-4; (*E*)-*n*-$BuCH{=}C(Br)SnMe_3$, 103670-93-5; (*E*)-*t*-$BuCH{=}C(Br)SnMe_3$, 103670-94-6; (*E*)-$MeO(C_6H_{10})CH{=}C(Br)SnMe_3$, 103670-95-7; (*E*)-$PhCH{=}C(Br)SnMe_3$, 103670-96-8; (*E*)-$PhCH{=}C(Cl)SnMe_3$, 103670-97-9; $Me(Et_2NCH_2)C{=}CBr_2$, 103670-55-9; (*E*)-$Ph(Me_3Sn)C{=}C(Ph)SnMe_3$, 27435-08-1; (*E*)-$MeOCH_2(Me_3Sn)C{=}C(CH_2OMe)SnMe_3$, 103670-86-6; phenylacetylene, 536-74-3; 4-benzylidenehepta-1,6-diene, 54624-35-0; tolan, 501-65-5; allyl bromide, 106-95-6.

Supplementary Material Available: Thirteen tables of ^1H, ^{13}C, and ^{119}Sn NMR and coupling constant data (14 pages). Ordering information is given on any current masthead page.

Chemistry of Chromium Chalcogen Complexes. Self-Condensation of $Cp_2Cr_2(CO)_4S$ and $Cp_2Cr_2(CO)_5S_2$ under Thermolytic Conditions. Crystal Structure of $Cp_4Cr_4(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2$

Wei Chen and Lai Yoong Goh*

Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia

Thomas C. W. Mak*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, NT., Hong Kong

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Thermolysis of $Cp_2Cr_2(CO)_5S_2$ (**2**) (Cp = η^5-C_5H_5) in toluene at ca. 100 °C afforded initially $Cp_2Cr_2(CO)_4S$ (**1**) and finally $Cp_4Cr_4S_4$ (**4**) in 86% isolated yield. Similar decomposition of **1** for 1.5 h yielded a mixture of $Cp_4Cr_4(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2$ (**3**) and **4**, which were separated by chromatography on silica gel. Compound **3** was isolated in 61% yield as brown-black air-stable cuboid crystals: monoclinic, space group $C2/c$, a = 17.557 (6) Å, b = 8.136 (3) Å, c = 18.009 (6) Å, β = 126.19 (2)°, Z = 4. The molecule adopts a cubane-like configuration with triply bridging S and CO ligands which are indistinguishable due to disorder. Thermolysis of **3** in benzene-d_6 over 6 h at 60 °C gave an equimixture of **4** and an unknown complex with δ(Cp) 5.13 in the ^1H NMR spectrum. Plausible mechanistic pathways are discussed in terms of self-condensation reactions wherein the linearly bridging multiply bonding S of **1**, the doubly bridging μ-S_2 ligand of **2**, and the triply bridging μ_3-S ligand of **3** each plays an integral role in the initial dimerizations leading to the formation of the cubanes **3** and **4**.

Introduction

Systematic approaches toward a strategy for the synthesis of high nuclearity complexes are a recurring theme in recent research in cluster chemistry.[1-4] Many of the methods employed make use of main-group elements including sulfur, selenium, phosphorus, arsenic, carbon, nitrogen, and germanium. Of these elements, sulfur has featured most prominently[3-6] by virtue of its ability to act

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(1) (a) Vahrenkamp, H. In *Transition Metal Chemistry—Current Problems of General, Biological and Catalytic Relevance*; Müller, A., Diemann, E., Eds.; Verlag Chemie, 1981; p 35 and references therein. (b) *Philos. Trans. R. Soc. London, A* **1981**, *No. 308*, 17 and references therein.

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(4) Adams, R. D.; Horvath, I. T.; Mathur, P. *Organometallics* **1984**, *3*, 623 and references therein.

(5) (a) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 322. (b) Richter, F.; Vahrenkamp, H.; *Ibid.* **1980**, *19*, 65; **1979**, *18*, 531. (c) Vahrenkamp, H.; Wucherer, E. J. *Ibid.* **1981**, *20*, 680. (d) Markó, L. *Gazz. Chim. Ital.* **1979**, *109*, 247.

(6) Adams, R. D.; Mannig, D.; Segmuller, B. E. *Organometallics* **1983**, *2*, 149.

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in a bridging capacity. It is now known that bridging ligands are particularly valuable in the synthesis and stabilization of cluster compounds.[7,8] The uncoordinated electron pairs on a ligand like sulfur are believed to serve as coupling agents for the initial processes involved in the formation of cluster molecules (eq 1). Vahrenkamp has

$$\mathrm{M}_m\mathrm{E}{:} + \mathrm{M'}_n \rightarrow \mathrm{M}_m(\mu\text{-E})\mathrm{M'}_n \tag{1}$$

applied this principle on numerous occasions;[1,5a] Adams has utilized the sulfido ligand extensively to couple small clusters.[4] However, while most of the emphasis has been centered on the synthesis of mixed-metal clusters,[9] examples of self-condensation reactions as a route to cluster formation are rarely reported.[6] In this paper, we describe the formation of the cubane clusters $Cp_4Cr_4(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2$ (**3**) and $Cp_4Cr_4S_4$ (**4**) from the dimerization of $Cp_2Cr_2(CO)_4S$ (**1**) and $Cp_2Cr_2(CO)_5S_2$ (**2**), respectively, and propose plausible mechanisms for their formation.

Experimental Section

General Comments. All reactions were carried out either with use of conventional Schlenk techniques or in an argon or nitrogen atmosphere in a Vacuum Atmospheres Dribox equipped with a Model HE493 Dri-Train. Diethyl ether and tetrahydrofuran (THF) were dried over sodium/benzophenone and distilled before use. Other solvents were refluxed over calcium hydride and distilled prior to use. Silica gel, Merck Kieselgel 60, was activated at 140 °C overnight before chromatographic use. Complexes 1 and 2 were prepared as indicated in a previous communication[10] and described in detail in a forthcoming paper.

Physical Measurements and Elemental Analyses. NMR spectra were measured on a JEOL FX100 spectrometer, and chemical shifts were referenced to $(CH_3)_4Si$ in C_6D_6. IR spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 1330 instrument. Mass spectra were performed on Kratos AEI MS 3074. Elemental analyses were performed by the Analytical Unit of the Australian National University and by courtesy of Dr. K. Crouse of the University of Agriculture Malaysia.

Thermolysis of $Cp_2Cr_2(CO)_4S$ (1). Preparation of $Cp_4Cr_4(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2$ (3). A dark greenish brown solution (ca. 0.03 M) of complex 1 (118 mg, 0.312 mmol) in toluene (10 mL) was stirred at a temperature just below reflux. The reaction was monitored at half-hourly intervals in the CO region of the IR spectrum, until 1 has completely reacted (1.5 h). (A more dilute solution (ca. 25 mL) in a stoppered flask required an approximate 9-h reflux time to reach complete reaction.) The solution was now brown. Cooling to room temperature and then to −28 °C followed by filtration gave the product as fine dark solids (56 mg). This corresponded to a 57% yield based on the NMR spectral indication of a 8:1 mixture of $Cp_4Cr_4(CO)_2S_2$ (**3**) and $Cp_4Cr_4S_4$ (**4**). Concentration of the filtrate gave a further 18 mg (ca. 20% yield) of similar composition. The final mother liquor (4 mg of residue) was found to consist of a mixture of 1, 3, 4, and traces of one or two other C_5H_5-containing compounds (δ 5.13 and 6.77).

Trituration of the product mixture of **3** and **4** above with 35 mL of toluene was found to dissolve ca. 40 mg. This solution was loaded onto a silica gel column (1 cm × 20 cm) prepared in *n*-hexane–ether. A green band slowly eluted with 1:1 *n*-hexane–toluene (10 mL) followed by toluene (5 mL), giving **4** (10 mg). Next a dark brown band eluted with 20% toluene in ether (10 mL) followed by 20% THF in ether (10 mL). This gave complex **3** as a fine brown-black solid (30 mg, 0.051 mmol, 33%, which is equivalent to a total yield of 61% based on the starting complex **1**). Spectral characteristics are given in Table V. Anal. Calcd for $C_{22}H_{20}Cr_4S_2O_2$: C, 44.90; H, 3.42; Cr, 35.34; S, 10.90. Found: C, 44.57; H, 3.50; Cr, 34.64; S, 10.86. Recrystallization from THF/cyclohexane over 10 days at ambient temperature gave cuboid diamond-shaped crystals suitable for X-ray diffraction analysis.

Table I. Data Collection and Processing Parameters for 3

molecular formula	$C_{22}H_{20}Cr_4O_2S_2$
M_r	588.515
space group	$C2/c$[a]
a, Å	17.557 (6)
b, Å	8.136 (3)
c, Å	18.009 (6)
β, deg	126.19 (2)
U, Å^3	2076 (1)
Z	4
D_{measd}, g cm^{-3}	1.85 (in $CCl_4/BrCH_2CH_2Br$)
D_{calcd}, g cm^{-3}	1.88
radiatn	graphite monochromatized Mo Kα, λ = 0.71069 Å
μ, cm^{-1}	22.04
cryst size, mm	0.22 × 0.11 × 0.08
transmissn factors	0.785–0.943
$F(000)$	1183.82
temp, K	298
diffractometer	Nicolet R3m
scan type and speed	ω–2θ; 2.02–8.37 deg min^{-1}
scan range	1° below Kα_1 to 1° above Kα_2
bkgd counting	stationary counts for one-half of scan time at each end of scan
collectn range	$h,k,\pm l$; $2\theta_{\max} = 50°$
unique data measd	1837
obsd data	1477 [$\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$]
no. of variables	146
final R, R_w	0.058, 0.071
weighting scheme	$w = [\sigma^2(F_o) + 0.0008\lvert F_o\rvert^2]^{-1}$
residual extremes in final difference map	1.00, −0.71 e Å^{-3}

[a] Favored by intensity statistics.

Thermolysis of $Cp_2Cr_2(CO)_5S_2$ (2). A solution (ca. 0.04 M) of 2 prepared from $[CpCr(CO)_3]_2$ (100 mg, 0.25 mmol) and S_8 (18.8 mg, 0.59 mmol of S) in toluene (6 mL) was filtered from excess S_8 and stirred for 3 h at a temperature just below reflux. Black crystalline particles of $Cp_4Cr_4S_4$ (4) (40 mg, 0.067 mmol, 54% yield) was removed by filtration. From the yellowish brown green mother liquor was isolated the monosulfur complex 1 (27 mg, 0.071 mmol, 29%).

The product composition was found to vary with the duration of the reaction time as follows: (i) after 3 h of reflux in 20 mL of toluene under H_2, the above reaction gave two batches of isolated solids, i.e., (a) 64 mg (ca. 0.109 mmol, 44%) consisting of a 2:3 mixture of $Cp_4Cr_4(CO)_2S_2$ (**3**) and $Cp_4Cr_4S_4$ (**4**) and (b) $Cp_4Cr_4S_4$ (5 mg, 0.008 mmol, 3%) [this is equivalent to overall yields of 18% (**3**) and 29% (**4**)]; (ii) after ca. 8 h of reflux in 50 mL of toluene under H_2 or Ar, 54 mg of $Cp_4Cr_4S_4$ (0.09 mmol, 86%) was obtained. The spectral features of 4 are given in Table V. Anal. Calcd for $C_{20}H_{20}Cr_4S_4$: C, 40.26; H, 3.38; Cr, 34.86; S, 21.50. Found: C, 40.14; H, 3.31; Cr, 34.31; S, 21.55.

Thermolysis of $Cp_4Cr_4(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2$ (3). A brown saturated solution of 3 in C_6D_6 in a 5-mm NMR tube under argon was maintained at 60 °C and its ^1H NMR spectrum recorded at intervals. After ca. 6 h, the solution was green with green solids precipitated on the walls and at the bottom of the tube. Total decomposition was indicated by the complete disappearance of the resonances at δ 9.95 and 5.65 in the NMR spectrum which now showed the presence of an approximately 1:1 mixture of $Cp_4Cr_4S_4$ (**4**) (δ 4.905 with a slight shoulder at δ 4.85) and one or more unidentified compounds with δ 5.13 (most probably due to C_5H_5) and intense broad resonances at δ 0.53 and δ −3.5. The precipitated solids when redissolved in C_6D_6 showed a mixture of 4 and the unknown (δ 5.13) in the relative proportion of 1:2.

Crystal Structure Analysis of 3. Data collection and processing followed established procedures in our laboratory,[11] and details are summarized in Table I. No significant crystal decay was observed from monitoring of two standard reflections.

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Scheme I

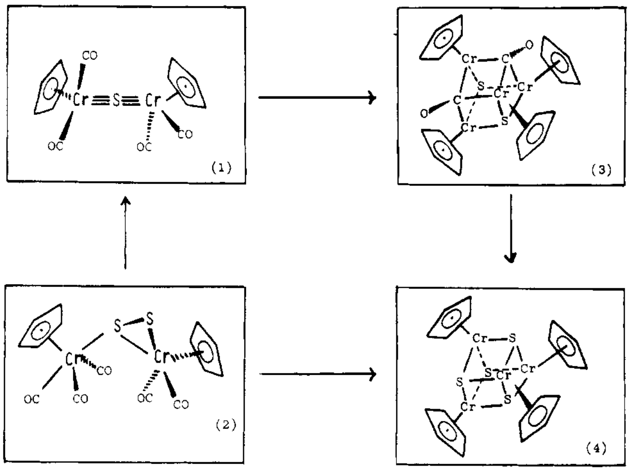

Table II. Atomic Coordinates[a] for 3 (×10^5 for Chromium Atoms and ×10^4 for the Other Atoms)

atom	x	y	z
Cr(1)	8971 (7)	4497 (12)	27125 (7)
Cr(2)	3061 (7)	−18621 (12)	34036 (7)
S(1)	472 (2)	835 (3)	3664 (2)
S(2)	1162 (2)	−2237 (4)	2847 (2)
O(1)	830 (7)	1660 (13)	4210 (7)
O(2)	1668 (7)	−3106 (13)	3131 (7)
C(1)	1141 (6)	−2082 (11)	4921 (5)
C(2)	1328 (6)	−3439 (11)	4596 (6)
C(3)	517 (7)	−4341 (10)	4029 (6)
C(4)	−195 (6)	−3548 (13)	4018 (6)
C(5)	180 (7)	−2143 (12)	4557 (5)
C(6)	2426 (6)	578 (11)	3330 (5)
C(7)	2209 (6)	1899 (11)	3642 (6)
C(8)	1554 (6)	2913 (10)	2905 (6)
C(9)	1394 (6)	2201 (11)	2129 (6)
C(10)	1923 (6)	765 (12)	2372 (6)

[a] Site occupancy factors are 0.5 for O(1) and O(2), 0.687 for S(1) and S(2), and unity for the other atoms.

Table III. Interatomic Distances (Å) and Selected Bond Angles (deg) for 3[a]

Bond Distances			
Cr(1)–Cr(2)	2.773 (2)	Cr(1)–S(1)	2.259 (5)
Cr(1)–S(2)	2.218 (3)	Cr(1)–C(6)	2.220 (9)
Cr(1)–C(7)	2.223 (8)	Cr(1)–C(8)	2.235 (9)
Cr(1)–C(9)	2.231 (11)	Cr(1)–C(10)	2.234 (14)
Cr(1)–Cr(1)′	2.768 (3)	Cr(1)–Cr(2)′	2.651 (1)
Cr(1)–S(1)′	2.232 (2)	Cr(2)–S(1)	2.227 (3)
Cr(2)–S(2)	2.267 (5)	Cr(2)–C(1)	2.217 (8)
Cr(2)–C(2)	2.219 (8)	Cr(2)–C(3)	2.232 (9)
Cr(2)–C(4)	2.243 (13)	Cr(2)–C(5)	2.226 (13)
Cr(2)–Cr(1)′	2.651 (1)	Cr(2)–Cr(2)′	2.760 (2)
Cr(2)–S(2)′	2.226 (2)	S(1)–O(1)	1.041 (10)[b]
S(1)–Cr(1)′	2.232 (2)	S(2)–O(2)	1.006 (11)[b]
S(2)–Cr(2)′	2.226 (2)	C(1)–C(2)	1.377 (14)
C(1)–C(5)	1.403 (15)	C(2)–C(3)	1.375 (11)
C(3)–C(4)	1.396 (17)	C(4)–C(5)	1.388 (13)
C(6)–C(7)	1.367 (15)	C(6)–C(10)	1.408 (13)
C(7)–C(8)	1.401 (11)	C(8)–C(9)	1.379 (16)
C(9)–C(10)	1.393 (13)		
Bond Angles			
Cr(2)–Cr(1)–Cr(1)′	57.2	Cr(2)–Cr(1)–Cr(2)′	61.1 (1)
Cr(1)′–Cr(1)–Cr(2)′	61.5	Cr(1)–Cr(2)–Cr(1)′	61.3 (1)
Cr(1)–Cr(2)–Cr(2)′	57.3	Cr(1)′–Cr(2)–Cr(2)′	61.6
S(1)–Cr(1)–S(2)	101.3 (1)	S(1)–Cr(1)–S(1)′	101.6 (1)
S(2)–Cr(1)–S(1)′	106.2 (1)	S(2)–Cr(2)–S(2)′	102.0 (1)
S(1)–Cr(2)–S(2)	100.8 (1)	S(1)–Cr(2)–S(2)′	106.1 (1)
Cr(1)–S(1)–Cr(2)	76.4 (1)	Cr(2)–S(1)–Cr(1)′	73.0 (1)
Cr(1)–S(2)–Cr(2)	76.4 (1)	Cr(1)–S(1)–Cr(1)′	76.1 (1)
Cr(2)–S(2)–Cr(2)′	75.8 (1)	Cr(1)–S(2)–Cr(2)′	73.2 (1)
Cr(1)–S(1)–O(1)	121.3 (9)[b]	Cr(2)–S(1)–O(1)	140.0 (6)[b]
Cr(1)–S(2)–O(2)	144.4 (6)[b]	Cr(2)–S(2)–O(2)	119.1 (9)[b]
⟨C–Cr–C⟩	36.3 (4)[c]	⟨C–C–C⟩	108.0 (9)[c]

[a] Primed atoms are generated by the symmetry transformation ($-x$, y, $^1/_2 - z$). [b] Note that the carbonyl C atoms overlap the S atoms in the disordered molecule. [c] Average values in the cyclopentadienyl rings.

Lorentz–polarization effects and absorption corrections[12,13] were applied. The structure was solved by the heavy-atom and Fourier methods. Space group symmetry requires that molecule 3 be located on a crystallographic C_2 axis. The triply bridging carbonyl and sulfur ligands are indistinguishable due to disorder; they were accordingly treated as two O atoms of half-site occupancy and two S atoms of the same variable site occupancy. [The carbonyl C atoms could not be located since they virtually coincide with the S positions; their scattering was reflected by the common site occupancy of the S atoms, which refined to a value of 0.687 (4).] All non-hydrogen atoms were assigned anisotropic thermal parameters. Hydrogen atoms were generated geometrically (C–H = 0.96 Å), assigned fixed istropic temperature factors, and allowed to ride on their respective parent C atoms. All computations were performed on a Data General Corp. Nova 3/12 minicomputer with the SHELXTL program package.[14] Analytic expression of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[15] Blocked-cascade least-squares refinement[16] yielded the R indices and other parameters listed in Table I.

Results and Discussion

Thermolysis Reactions. The thermolysis of 1 in toluene at ca. 100 °C for 1.5 h or longer in a closed system gave 3 in 61% yield together with 4 and trace amounts of one or two C_5H_5-containing compounds, showing δ 5.13 and 6.77. As will be reported in a forthcoming paper, preparative studies showed that the μ-S_2 complex 2 is readily converted to the monosulfur complex 1 at ambient temperature. In fact, NMR measurements demonstrated 2 is labile even at −60 °C. As expected this decomposition is very much accelerated at elevated temperatures and in view of the thermal transformability of 1 as discussed above, the product composition varies with the duration of the reaction time. Thus, after 3 h at ca. 100 °C in toluene, a 0.04 M solution of 2 gave a mixture of 1 and 4 in 29 and 54% isolated yields, respectively, while on another occasion complexes 3 and 4 were isolated in 18 and 29% yields, respectively. A longer reaction time of 8 h gave only 4 in 86% isolated yield. This attainment of greater than 50% yield of 4 together with the observation that complex 3 in benzene-d_6 converted to an equimixture of 4 and an unknown compound with δ 5.13 suggests that 2 decomposes to 4 via two pathways, one of which proceeds via 1 as illustrated in Scheme I.

Structure of $Cp_4Cr_4(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2$ (3). A stereoview of the molecular structure of 3 is illustrated in Figure 1. Atomic coordinates are listed in Table II. Bond lengths and selected bond angles are listed in Table III. The structure shows a close resemblance to that of $Cp_4Cr_4(\mu_3\text{-}S)_4$ (4), which consists of a cubane arrangement of alternating Cr and μ_3-S atoms at the corners of a distorted cube,[17] with two of the S atoms replaced by μ_3-CO groups.

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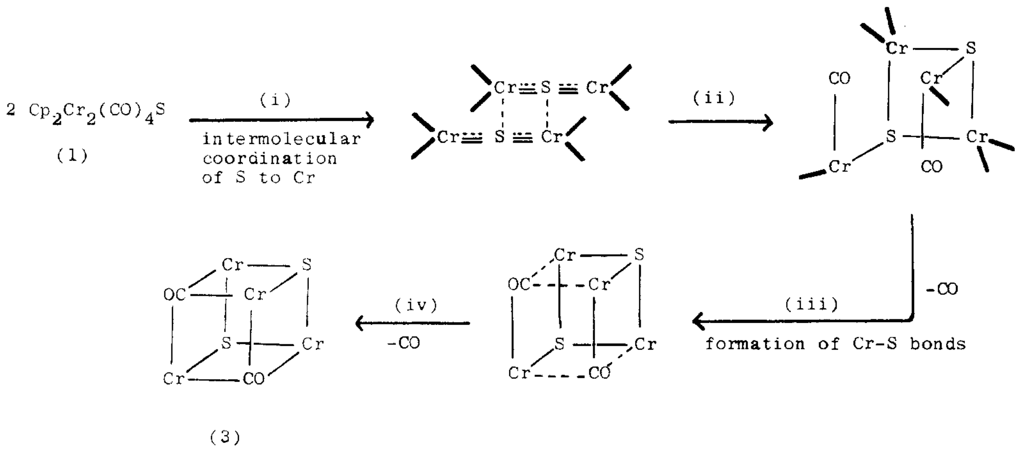
Scheme II



η^5-Cp ligands are omitted for clarity. —— original bonds, ---- new bonds, ▬ CO ligands.

Table IV. Comparison of Selected Bond Lengths and Angles of 3 and 4

	3	4
Cr–Cr, Å	2.651–2.773 (3)	2.818–2.891 (14)
Cr–Cr–Cr, deg	57.2–61.6 (1)	58.7–61.3 (1)
S–Cr, Å	2.218–2.267 (5)	2.255–2.263 (10)
S–Cr–S, deg	100.8–106.2 (1)	98.6–102.3 (4)
Cr–S–Cr, deg	73.0–76.4 (1)	77.1–79.7 (4)

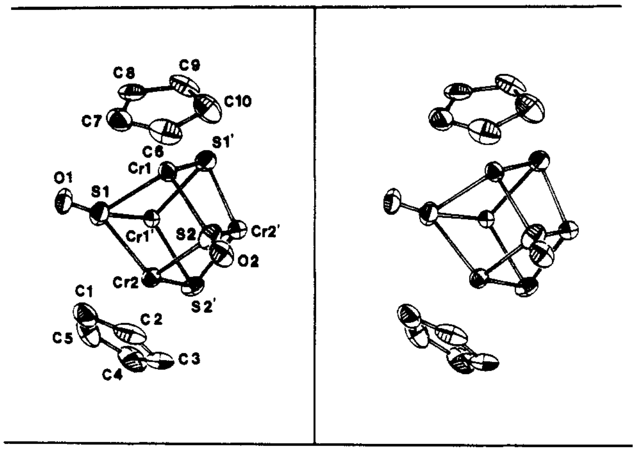


Figure 1. Stereoview of the molecular structure of $Cp_4Cr_4(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2$ (**3**). The primed atoms are related to the unprimed ones by twofold rotational symmetry, and some have been omitted for clarity. The thermal ellipsoids are drawn at the 30% probability level.

Since the thermal ellipsoids of S(1) and S(2) have normal shapes (Figure 1) and the measured S(1)–O(1) and S(2)–O(2) bond lengths differ insignificantly from the interatomic distance in the carbonyl ligand, the superposition of the S and C(carbonyl) atoms in the disordered model is validated. As expected on the bases of the size difference between the S and C atoms, **3** shows a higher degree of distortion from a regular cube than **4**. The significant variations in bond lengths and angles from **4** are given in Table IV. It is noteworthy that the Cr–Cr interatomic distances are all shorter than those in **4**,[17] indicating a higher degree of metal–metal bonding between the four Cr atoms in the molecule (Cr–Cr bond order = $1^1/_3$) in accordance with the requirements of the 18-electron rule.

As far as we are aware, the only other reported case of a $M_4(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2$ cluster moiety is found in $Cp_2Cr_2Fe_2(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2(CO)_6$, where each Fe atom is linked to three terminal CO's and each Cr is η^5-bonded to a Cp ring.[18] However, this cluster molecule adopts a noncubane geometry, in which the S atoms or CO groups are noncoplanar with any two of the metal atoms. Presumably this structural variation from the cubane arrangement found in **3** could be caused by the greater steric demands of the three terminal CO's on the Fe atoms as compared to a Cp ring.

Spectra. The spectroscopic data for **3** are in accord with the structure established by X-ray diffraction. Its IR spectrum shows a very strong abroad band at 1645 cm^{-1} which is characteristic of μ_3-CO groups. The parent ion of both **3** and **4** are seen in their respective mass spectra, but as judged from Table V, their breakdown patterns are very different. While **4** undergoes stepwise cleavage of C_5H_5 to give finally the Cr_4S_4 moiety, **3** after cleavage of its two CO groups undergoes sequential loss of Cp followed by Cr, and no such Cr_mS_m species is observed. This observed difference attests to the unusually high stability of the Cr_4S_4 cubane skeleton. The NMR measurement of **4** shows a singlet for the Cp rings in both the ^1H and ^{13}C spectra. The Cp rings of **3** are magnetically nonequivalent and are observed as two singlets of equal intensity in both the ^1H and ^{13}C spectra (Table V). The ^1H resonances demonstrate variable-temperature behavior; thus the singlets appear at δ 5.03 and 5.16 at −88 °C, δ 5.65 and 9.95 ($\nu_{1/2}$ = 33 Hz) at room temperature and δ 6.26 and 14.23 ($\nu_{1/2}$ = 60 Hz) at 90 °C. The origin of this behavior is not yet understood and currently still under investigation.

Reaction Pathways. The mechanisms for the transformation of **1** to **3** and **2** to **4**, as indicated in Scheme I, are not firmly established. However, we believe that the most probable mechanism must involve an initial dimerization of **1** or **2**, respectively, via an intermolecular coordination of S to Cr, as shown in step i of Scheme II and III. A subsequent intramolecular rearrangement (step ii), with S–S bond cleavage if necessary, would result in an "unbonded" cubane skeleton. This is followed by bond formation to the cubane precursor (step iii), accompanied most probably by prior rather than concomitant cleavage of CO groups to produce unsaturated sites. The involvement of cleavage of some of the CO's in the rate-deter-

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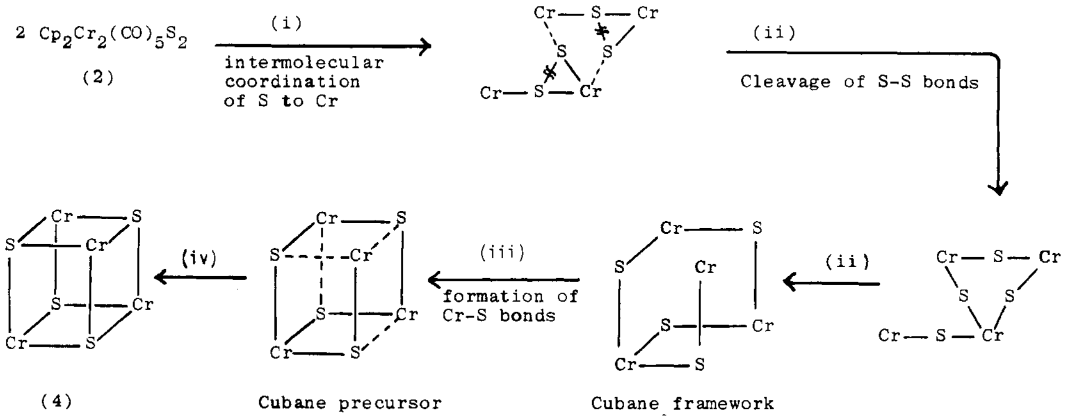
Table V. Spectral Data

complex	NMR[a]		IR,[b] cm^{-1}	mass spectra, m/e (calcd) [assignts]
	^{1}H, δ	^{13}C, δ		
3	5.65 (s, Cp), 9.95 (s, $\nu_{1/2}$ = 33 Hz, Cp)[c]	99.29 (s, Cp), 91.88 (s, Cp) (s, Cp)	1645 vs, b (μ_3-CO); other bands, 3100 w, 1420 m, 1350 vw, 1260 vw, 1100 vw, 1060 w, 1015 m, sh, 1003 m, 905 vw, 835 m, sh, 795 s, 600 vw, 530 vw, 500 m, 410 vw	588 (587.8) [$Cp_4Cr_4(CO)_2S_2$], 560 (559.9) [$Cp_4Cr_4(CO)S_2$], 532 (531.9) [$Cp_4C_4S_2$], 466.8 (466.8) [$Cp_3Cr_4S_2$], 414.9 (414.9) [$Cp_3Cr_3S_2$], 349.9 (349.8) [$Cp_2Cr_3S_2$], 297.9 (297.9) [$Cp_2Cr_2S_2$], 232.9 (232.9) [$CpCr_2S_2$], 201.0 (200.9) [$CpCr_2S$], 182.0 (182.0) [Cp_2Cr]
4	4.90 (s, Cp)	89.99 (s, Cp)	3100 w, sh, 3090 w, 1800 vw, b, 1625 w, vb, 1435 s, 1440 s, sh, 1360 vw, 1270 vw, 1120 vw, 1070 vw, sh, 1062 w, 1025 m, 1006 s, 910 w, b, 840 m, sh, 836 s, 798 vs, 725 vw, 595 vw, 465 vw, 400 vw, b, 332 s	595.8075 (595.8068) [$Cp_4Cr_4S_4$], 530.7672 (530.7677) [$Cp_3Cr_4S_4$], 465.72 (465.73) [$Cp_2Cr_4S_4$], 400.69 (400.69) [$CpCr_4S_4$], 335.66 (335.65) [Cr_4S_4], 297.91 (297.90) [$Cp_2Cr_2S_2$], 232.87 (232.87) [$CpCr_2S_2$], 182.03 (182.02) [Cp_2Cr], 116.98 (116.98) [CpCr]

[a] Measured at ambient temperature unless otherwise specified. Chemical shifts referred to Me_4Si in C_6D_6 or toluene-d_8. Multiplicity designation: s, singlet. [b] Measured in KBr disk. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; b, broad. [c] Exhibits variable-temperature behavior. At −88 °C, δ(Cp) appears as sharp singlets at 5.03 and 5.16, which shift to 6.26 (sharp singlet) and 14.24 (broad singlet, $\nu_{1/2}$ = 60 Hz), respectively, at 90 °C.

Scheme III



η^5-Cp and CO ligands are omitted. —— original bonds, ---- new bonds, —⫽— bond breaking

mined step is supported by the observed rate retardation in the conversion of 1 to 3 in a closed system, presumably caused by an inhibition to decarbonylation by an increase of CO pressure.

The condensation process illustrated in Scheme II involves the change of a terminal CO ligand and a linearly bridging multiply bonded S ligand to one of the μ_3-η^3 6e-donor face-bridging type. The bonding change observed for the S ligand is unprecedented. As far as we are aware, coupling reagents with S playing a vital role have always involved complexes of the tetrahedrane M_3S: type with a triply briding sulfur[1,4,5b,19,23] or of the M_2S_2 type with doubly bridging sulfur.[5c,18,20-22] Scheme III shows that the disulfido ligand in 2 also plays an integral role in the condensation process.

Finally the conversion of 3 to 4 must involve intermolecular exchange processes between two cubane molecules. One may envisage an initial coupling of a tetrahedrane Cr_3S: site of one molecule to a Cr atom of another molecule to produce an expanded cluster I or an initial face-to-face coupling to produce IIA and/or IIB. The formation of $Cp_4Cr_4S_4$ (4) from these expanded clusters must involve interchange of S and CO ligands coupling with relevant Cr–S and Cr–CO bond dissociations at elevated temperatures. However, although the mobility of CO ligands in polynuclear metal complexes is well-documented,[24] mobility of sulfido ligands has yet to be established.

Finally, in conclusion, this study demonstrates that S atoms playing three different structural roles, viz., the linearly bridging multiply metal-bonded S in 1, the bridging disulfur in 2, and the triply bridging μ_3-S in 3, are

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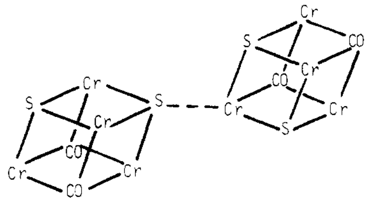
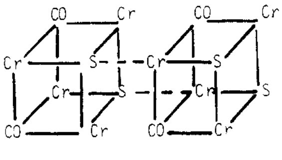
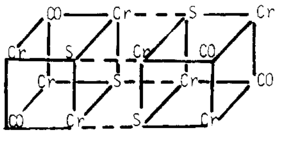


(I)



(IIA)



(IIB)

capable of initiating condensation via the formation of donor–acceptor S→M bonds. It is also observed that like other reported reactions involving CpCr entities and S ligands,[25,26] the thermolysis reactions studied also gave the cubane $Cp_4Cr_4S_4$ as the end product, indicating a great driving force toward its formation.

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Registry No. **1**, 71549-26-3; **2**, 89401-43-4; **3**, 103835-71-8; **4**, 79469-27-5; $[CpCr(CO)_3]_2$, 12194-12-6.

Supplementary Material Available: Tables of hydrogen atom coordinates and anisotropic thermal parameters (2 pages); a table of observed and calculated structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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Reactions of η^1-Allyl Complexes of Palladium(II) with Electrophiles. Molecular Structure of a [2 + 3] Cycloadduct of (η^1-Allyl)palladium with Maleic Anhydride

Hideo Kurosawa,* Akira Urabe, Kunio Miki, and Nobutami Kasai*

Department of Applied Chemistry, Osaka University, Suita, Osaka 565, Japan

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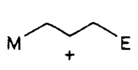
(η^1-Allyl)arylpalladium complexes react with some electrophiles (HCl, Br_2, NBS; NBS = *N*-bromosuccinimide) to give selective Pd–allyl bond cleavage (allylic substitution) with 1,3-transposition, while the corresponding (η^3-allyl)arylpalladium analogues react with these electrophiles via selective Pd–Ar bond cleavage. The η^1-allyl complexes also react with CCl_4 and $CHCl_3$ under very mild conditions to give good yields of $CH_2{=}CHCHR(CR'Cl_2)$ (R = H, Me; R′ = Cl, H). Reactions of maleic anhydride with some of the above (η^1-allyl)palladium complexes afford 1:1 adducts arising from formal [2 + 3] cycloaddition. The molecular structure of an adduct, $\mathrm{Pd\underline{CHCH_2\overline{CHC(O)OC(O)C}HC}H_2](C_6F_5)((\mathit{Z})\text{-}Ph_2PCH{=}CHPPh_2)}$, has been determined by X-ray crystallography. Crystal data: triclinic, space group $P\bar{1}$, $a = 9.526$ (3) Å, $b = 14.218$ (5) Å, $c = 14.122$ (5) Å, $\alpha = 70.47$ (3)°, $\beta = 96.48$ (3)°, $\gamma = 92.64$ (3)°, and $Z = 2$. The palladium and the carbonyl substituents are located trans to each other with respect to the five-membered ring. Possible pathways to the cycloadduct are discussed in terms of this stereoselectivity.

The chemistry of (η^1-allyl)metal compounds is receiving increasing attention from both synthetic and physicochemical points of view. The main-group metal derivatives are especially versatile reagents for the introduction of an allylic unit at electrophilic centers. Even though synthetic application of the transition-metal analogues is somewhat less developed, the η^1-allyl complexes of certain elements, e.g., Fe, are known to exhibit unique reactivities toward unsaturated electrophiles which appear to be difficult to realize in the main-group metal counterparts (e.g., [2 + 3] cycloaddition).[1,2]

The high reactivity of the η^1-allyl complexes toward electrophiles has been discussed in terms of electronic factors which contribute toward activation of the ground-state electronic structure, e.g., σ–π conjugation,[4] or to stabilization of the transition-state (or intermediate) structure, e.g., β-metallocarbonium ion **1**[5] or cationic olefin–metal complex **2**.[1] In this regard it seems of particular



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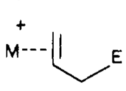

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