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Chemistry of $[CpCr(CO)_3]_2$. An Insertion Mechanism for the Formation of $Cp_2Cr_2(CO)_5Se_2$ and $Cp_2Cr_2(CO)_4Se_2$ from $Cp_2Cr_2(CO)_4Se$. Carbonylation and Crystal Structure of $Cp_2Cr_2(CO)_4Se_2$[1]

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The complexes $Cp_2Cr_2(CO)_4Se_2$ (2) and $Cp_2Cr_2(CO)_5Se_2$ (3) are obtained as dark brown crystals, from the reaction of elemental selenium with $Cp_2Cr_2(CO)_6$ or $Cp_2Cr_2(CO)_4Se$ (1). Synthetic and spectral evidence indicates that the reaction proceeds via the insertion of a Se atom into the Cr≡Se bond of **1**. Complexes **2** and **3** have been characterized by elemental and spectral analyses. The X-ray structure of **2** shows a symmetrical μ-η^2-Se_2 ligand bridging the two chromium centers. Crystal data: monoclinic $P2_1/c$; $a = 10.566$ (2) Å, $b = 12.983$ (3) Å, $c = 11.964$ (2) Å; $\beta = 101.05$ (3)°; $Z = 4$; $R = 0.055$. The slow conversion of **2** under a CO atmosphere to a mixture of **1**, **3**, and $Cp_4Cr_4Se_4$ (4) as well as the transformation of the very labile complex **3** to **1**, **2**, and **4** has been demonstrated by NMR spectral studies.

Introduction

For more than 2 decades, metal–metal bonded complexes have sustained continuing interest. In recent years, there has been a shift in emphasis from the well-studied preparative and structural context to one of reactivity.[2,3] Our interest in the metal–metal bonded dimer $[CpCr(CO)_3]_2$ has led us to investigate its reactivity toward elemental sulfur[4,5] followed by elemental selenium.[1] The primary aim is a comparative study of the reactivity of complexes from analogous sulfur and selenium systems. The secondary objective lies in the interest in transition-metal selenium chemistry, in accord with the recent resurgent activity after a lull of 20 years since the discovery of the first selenium complexes $Fe_2(CO)_6Se_2$ and $Fe_3(CO)_9Se_2$ by Hieber and Grüber in 1958.[6] From literature examples of the last decade, it is becoming increasingly apparent that Se as a ligand rivals S in the variety of its bonding modes,[7,8] e.g. as a η^2-Se_2 ligand,[9–11] as a bridging ligand of types μ-Se,[10,12–18] μ-η^1-Se_2,[14,17,19] and μ-η^2-Se_2,[13,17,20,21] as tricapping μ_3-Se,[22–31] μ_4-Se,[27,30] and μ_5-Se[27] types, and even as five- and six-membered $IrSe_4$[32] and $TiSe_5$[33] rings, respectively. Lately, the linear multiple M≡E≡M bond, established for S,[34,35] was first structurally demonstrated for Se by Weiss in 1983 for a V≡Se≡V complex[36] and then simultaneously reported for $[CpCr(CO)_2]_2Se$ (1) obtained by different synthetic pathways by ourselves,[1] Herrmann[37] and Weiss,[38] and for a [Mo≡Se≡

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[1] Presented in part by L.Y.G. at the 188th National Meeting of the American Chemical Society, Philadelphia, Aug. 1984; paper INOR 52. See also: Goh, L. Y.; Chen, W.; Sinn, E. *J. Chem. Soc., Chem. Commun.* **1985**, 462.

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Mo]$^{2+}$ complex by Enemark.[39]

Our preliminary communication[1] has described the synthesis of both $[CpCr(CO)_2]_2Se$ (**1**) and $Cp_2Cr_2(CO)_4Se_2$ (**2**) from the reaction of $[CpCr(CO)_3]_2$ with elemental Se_8 together with their structures. This paper describes the isolation of a third product, $Cp_2Cr_2(CO)_5Se_2$ (**3**), from the same reaction with excess Se_8 and also presents the spectral evidence for the carbonylation of $Cp_2Cr_2(CO)_4Se_2$ (**2**) to the pentacarbonyl complex **3**. The mechanistic pathway for the transformation of **1** to **2** and **3** is discussed. Full structural details are presented for **2**.

Experimental Section

General Comments. All reactions were carried out either by using conventional Schlenk techniques or in an argon or nitrogen atmosphere in a Vacuum Atmospheres Dribox equipped with a Model HE493 Dri-Train.

Reagents and Solvents. $Cr(CO)_6$ was obtained from Strem Chemicals, Inc. Black selenium powder was Hopkin and Williams ANALAR grade. $[CpCr(CO)_3]_2$ was synthesized as described before.[40] 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.

Physical Measurements and Elemental Analyses. NMR spectra were measured on a JEOL FX100 spectrometer. Chemical shifts were referenced to residual C_6H_6 in benzene-d_6 or to $(CH_3)_4Si$. IR spectra were measured in the range 4000–200 cm^{-1} by means of a Perkin-Elmer 1330 or Beckman IR 4240 instrument. Electron-impact mass spectra were measured on Kratos AEI MS3074. Elemental analyses were performed by the Analytical Unit of the Australian National University and Pascher Laboratories of Bonn, Germany.

Preparation of $Cp_2Cr_2(CO)_5Se_2$ (3). A suspension of $Cp_2Cr_2(CO)_6$ (200 mg, 0.5 mmol) and gray-black Se_8 powder (200 mg, 2.53 mmol) in toluene (10 mL) was stirred in a Schlenk flask at 5–10 °C and the reaction monitored via NMR measurements at intervals. An orange-brown solution of $Cp_2Cr_2(CO)_4Se$ (**1**) [δ 4.36 in C_6D_6] was initially obtained. At ca. 30 min, the NMR spectrum showed in addition to the main component **1**, a shoulder at δ 4.31 before the resonances pertaining to **3** and **2** at δ 4.48 and 4.07 began to be noticeable at ca. 1 h. It took 6 h to maximize the yield of **3**. The red-brown solution then consisted of a mixture of **3**, **2**, **1**, and $Cp_4Cr_4Se_4$ (**4**) (δ 5.13) in an approximate molar proportion of 4:1:1:0.1 together with a small amount of the unidentified intermediate possessing δ 4.30. Under an atmosphere of CO, a slightly higher proportion of **3** was obtained, viz., 5:1:1:0.1. A similar reaction for 3 h at ambient temperature under argon gave a mixture of **3**, **2**, **1**, and **4** with a molar ratio of 4:3:3:0.2.

After filtration from excess Se_8 through Celite, the solution was concentrated to 3–4 mL and saturated with CO and a little *n*-hexane added. Standing 2 h at −5 °C gave **3** as a dark reddish brown crystalline solid in the form of spiky "blobs" (120 mg, 0.23 mmol, 46% yield). IR: ν(CO) at 2010 s, 1955 vsbr, 1912 vsbr, 1875 msh, and 1832 s cm^{-1} (KBr) or at 2035 s, 1965 vs unresolved from 1945 vs, 1925 sh, 1895 m, and 1855 m cm^{-1} (C_6H_6). ^{1}H NMR (benzene-d_6 at 30 °C): δ 4.48 (s, Cp) and 4.04 (s, Cp). ^{1}H NMR (toluene-d_8 at −90 °C): δ 4.31 (s, Cp) and 3.61 (s, Cp). ^{13}C NMR (toluene-d_8 at 30 °C): δ(Cp) at 92.99 and 90.07. ^{13}C NMR (toluene-d_8 at −90 °C): δ(Cp) 92.01 and 89.83; δ(CO) at 265.66, 255.76, 245.62, 239.23, and 235.80. After 5 h at ambient temperature a C_6D_6 solution was partially converted to **1**, **2**, and $Cp_4Cr_4Se_4$. MS: *m/z* (for isotope ^{80}Se) 788 ($Cp_4Cr_4Se_4$), 723 ($Cp_3Cr_4Se_4$), 658 ($Cp_2Cr_4Se_4$), 593 ($CpCr_4Se_4$), 528 (Cr_4Se_4), 394 ($Cp_2Cr_2Se_2$), 314 (Cp_2Cr_2Se), 277 ($CpCrSe_2$), 249 ($CpCr_2Se$), 225 ($CpSe_2$). Anal. Calcd for $(C_5H_5)_2Cr_2(CO)_5Se_2$: C, 33.81; H, 2.02; Cr, 19.52; Se, 29.64. Found: C, 33.02; H, 1.90; Cr, 18.99; Se, 28.75.

Preparation of $Cp_2Cr_2(CO)_4Se_2$ (2). (i) In the absence of CO, a concentrated solution of the above product in toluene (ca. 3 mL) gave dark brown needles of **2** (97 mg, 0.19 mmol, 38% yield) after 1 h at −30 °C. The mother liquor in toluene–*n*-hexane yielded a further crop of **2** (94 mg, 0.19 mol, 38% yield) after 3 days at −30 °C). IR: ν(CO) at 1948 vs, 1890 vs, and 1832 s cm^{-1} (KBr) or at 1975 vs, 1935 m, 1902 s, and 1860 w cm^{-1} (toluene). ^{1}H NMR (benzene-d_6 at 30 °C): δ 4.08 (s, Cp). ^{1}H NMR (toluene-d_8): δ 4.13 (30 °C) and 3.83 (−90 °C). ^{13}C NMR (benzene-d_6 at 30 °C): δ 90.92 (Cp) and 258.67 (CO). ^{13}C NMR (toluene-d_8 at −90 °C): δ 90.69 (Cp) and 259.27 (CO). MS: *m/z* (for isotope ^{80}Se) 788 ($Cp_4Cr_4Se_4$), 723 ($Cp_3Cr_4Se_4$), 658 ($Cp_2Cr_4Se_4$), 593 ($CpCr_4Se_4$), 528 (Cr_4Se_4), 425.85 $\{Cp_2Cr_2(CO)_4Se\}$, 393.79 ($Cp_2Cr_2Se_2$), 369.87 $\{Cp_2Cr_2(CO)_2Se\}$, 341.87 $\{Cp_2Cr_2(CO)Se\}$, 328.77 ($CpCr_2Se_2$), 313.87 (Cp_2Cr_2Se), 304.81 $\{CpCr_2(CO)_2Se\}$, 276.81 ($CpCrSe_2$), 252.88 $\{CpCr(CO)_2Se\}$, 248.84 ($CpCr_2Se$), 224.89 $\{CpCr(CO)Se\}$, 196.89 (CpCrSe), 182.02 (Cp_2Cr), 131.86 (CrSe), 116.98 (CpCr). Anal. Calcd for $(C_5H_5)_2Cr_2(CO)_4Se_2$: C, 33.35; H, 2.00; Cr, 20.63; Se, 31.32. Found: C, 33.41; H, 2.16; Cr, 21.3; Se, 31.5. After several months at ambient temperature, an analytically pure crystalline sample of **2** was found to have transformed into a mixture **3**, **2**, and **1** with **3** as the main component. A solution in C_6D_6 after standing several hours at 0 °C or ambient temperature was partially converted to **3**, **1**, and **4**; after 4 days at 24 °C, the molar proportion of **2**, **3**, **1**, and **4** was 6:2:3:0.2.

(ii) The concentrated product solution in toluene (ca. 5 mL) from a similar reaction of $Cp_2Cr_2(CO)_6$ (400 mg, 1 mmol) with Se_8 (303 mg, 3.84 mmol) was loaded on to a column (15 × 22 cm) of alumina (Merck standardized, Activity II–III) that had been deactivated with ether and washed with *n*-hexane. Elution with toluene (10 mL) and 5% ether in toluene (20 mL) gave an orange band from which was obtained **1** (86 mg, 0.202 mmol, 20% yield); 10% ether in toluene (20 mL) gave a brown eluate, which yielded dark brown crystalline needles (162 mg) consisting of **2** (0.29 mmol, 29% yield) contaminated by ca. 10% of **1**. Next a brown eluate with 20–50% ether in toluene (35 mL) gave a mixture (178 mg) of **3**, **2**, and **1** of the same molar composition as the original crude product. Recrystallization in THF–*n*-hexane at −30 °C for 4 h gave **2** (110 mg, 0.218 mmol, 22%) as the first crop, followed by **3** (50 mg, 0.086 mmol, 8.6%).

Conversion of $Cp_2Cr_2(CO)_4Se$ (1) to $Cp_2Cr_2(CO)_4Se_2$ (2). $Cp_2Cr_2(CO)_4Se$ (35 mg, 0.08 mmol) in THF (3 mL) was stirred with Se_8 powder (75 mg, 0.94 mmol of Se) for 7 h at ambient temperature. Excess Se_8 was removed by filtration. Concentration of the filtrate to dryness gave a brown residue (30 mg, 0.058 mmol, 72%), shown by its ^{1}H NMR and IR spectra to consist of mainly **2** with trace amounts of **1** and **4**.

NMR Studies. (a) Conversion of $Cp_2Cr_2(CO)_4Se$ (1) to 2 and 3. To a 0.05 M solution of **1** in 0.5 mL of C_6D_6 in a 5-mm NMR tube was added Se_8 (10 mg, 0.127 mmol) under argon, and the mixture was agitated in between spectral scans in an ultrasonic bath maintained at 5–10 °C. The time-dependent spectral changes are illustrated in Figure 1.

(b) Carbonylation of $Cp_2Cr_2(CO)_4Se_2$ (2). The proton NMR spectra of 0.05 M solutions of **2** in C_6D_6 in two serum-capped 5-mm tubes under 1 atm of CO and argon, respectively, were monitored at intervals and the tubes vigorously agitated at 8 °C between spectral scans, on a mechanical shaker. The spectral changes are illustrated in Figure 2. Similar studies were also carried out at ambient temperature (24 °C).

(c) Decomposition of $Cp_2Cr_2(CO)_5Se_2$ (3). A freshly prepared solution (ca. 0.08 M) of **3** (27 mg, 0.05 mmol) in C_6D_6 (0.6 mL) was capped under argon in a 5-mm tube and its decomposition followed at ambient temperature. NMR spectra were recorded at progressively longer intervals, and those representing significant changes are shown in Figure 3.

Crystal Structure Analyses. Fine needles of **2** were obtained overnight from toluene–*n*-hexane at −28 °C. Details of the data collection are summarized in Table I. Cell dimensions and space group data were obtained by standard methods on an Enraf-

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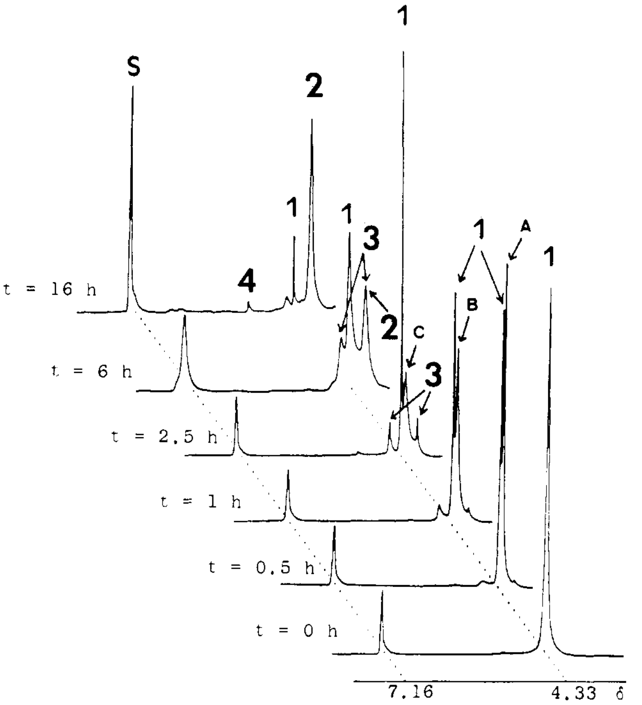

Figure 1. Time-dependent ^{1}H NMR spectra showing the formation of $Cp_2Cr_2(CO)_5Se_2$ (**3**) (δ 4.05 and 4.48) and $Cp_2Cr_2(CO)_4Se_2$ (**2**) (δ 4.05) from the reaction of a 0.05 M solution of $Cp_2Cr_2(CO)_4Se$ (**1**) in benzene-d_6 with Se_8 in 5 molar excess at 8–10 °C under intermittent ultrasound agitation. Other labeled peaks are assigned as follows: S, solvent (δ 7.16); A, B, and C, unidentified intermediates (δ 4.28, 4.26, and 4.30, respectively); **4**, $Cp_4Cr_4Se_4$ (δ 5.13) [all spectral scans at 8 °C, except for t = 16 h (28 °C; **1**, δ 4.36; **2**, δ 4.08)].

Table I. Crystal Data for 2

mol formula	$C_{14}H_{10}Cr_2O_4Se_2$
cryst system	monoclinic
space group	$P2_1/c$
cell constants	
a, Å	10.566 (2)
b, Å	12.983 (3)
c, Å	11.964 (2)
β, deg	101.05 (3)
V, Å^3	1611 (1)
Z	4
cryst dimens, mm	0.20 × 0.25 × 0.525
temp, K	293
radiatn, wavelength	graphite-monochromatized Mo Kα, 0.7107 Å
diffractometer	Enraf-Nonius CAD-4
transmissn coeff	max 0.63, min 0.44
2θ range, deg	1.5–54
collectn range	h, 0–12; k, 0–14; l, −12 to +12
no. of obsd reflctns	1119 ($F_o^2) > 3\sigma(F_o^2$)
R	0.055
$R_w = [\sum_w(F_o - F_o)^2/\sum_w F_o^2]^{1/2}$	0.060
weighting scheme	$w = [2F_o/\sigma(F_o^2)]^2$

Nonius four-circle CAD-4 diffractometer. The θ -2θ scan technique was used, as previously described,[41] to record the intensities for all nonequivalent reflections for which 1.5° < 2θ < 54°. Scan widths were calculated as $(A + B \tan \theta)°$, where A is estimated from the mosaicity of the crystal and B allows for the increase in peak width due to $K\alpha_1 - K\alpha_2$ splitting. The values of A and B were 0.6 and 0.35, respectively.

The intensities of three standard reflections showed no greater fluctuations (4%) during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization and absorption. Of the 1858 independent intensities, there were 1119 with $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[42] These data were used in the final refinement of the structural parameters.

Table II. Positional Parameters for 2

atom	x	y	z
Se(1)	0.8102 (2)	0.2687 (2)	0.7558 (2)
Se(2)	0.8678 (2)	0.2577 (2)	0.5822 (2)
Cr(1)	0.9811 (3)	0.1354 (2)	0.7364 (3)
Cr(2)	0.6339 (3)	0.2180 (3)	0.5878 (3)
O(11)	0.843 (2)	−0.001 (1)	0.871 (1)
O(12)	0.906 (2)	−0.038 (1)	0.574 (1)
O(21)	0.580 (2)	0.039 (1)	0.723 (1)
O(22)	0.661 (2)	0.045 (1)	0.433 (2)
C(11)	0.892 (2)	0.053 (2)	0.819 (2)
C(12)	0.937 (2)	0.032 (1)	0.635 (2)
C(21)	0.606 (2)	0.109 (2)	0.672 (2)
C(22)	0.657 (2)	0.113 (2)	0.494 (2)
C(1)	1.143 (3)	0.133 (2)	0.877 (2)
C(2)	1.164 (2)	0.072 (2)	0.793 (3)
C(3)	1.180 (3)	0.143 (3)	0.709 (2)
C(4)	1.148 (3)	0.233 (2)	0.746 (2)
C(5)	1.134 (2)	0.226 (2)	0.845 (2)
C(6)	0.512 (2)	0.285 (2)	0.440 (2)
C(7)	0.439 (2)	0.241 (3)	0.508 (2)
C(8)	0.459 (2)	0.306 (3)	0.613 (2)
C(9)	0.543 (1)	0.365 (1)	0.594 (2)
C(10)	0.579 (2)	0.364 (2)	0.506 (2)

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for 2

	Bond Distances		
Se(1)–Se(2)	2.277 (1)	Cr(2)–Se(1)	2.551 (3)
Cr(1)–Se(1)	2.544 (3)	Cr(2)–Se(2)	2.538 (2)
Cr(1)–Se(2)	2.551 (2)	Cr(2)–C(21)	1.80 (2)
Cr(1)–C(11)	1.83 (2)	Cr(2)–C(22)	1.81 (2)
Cr(1)–C(12)	1.81 (2)	Cr(2)–C(6)	2.16 (2)
Cr(1)–C(1)	2.16 (2)	Cr(2)–C(7)	2.12 (2)
Cr(1)–C(2)	2.10 (2)	Cr(2)–C(8)	2.24 (2)
Cr(1)–C(3)	2.19 (2)	Cr(2)–C(9)	2.14 (2)
Cr(1)–C(4)	2.15 (2)	Cr(2)–C(10)	2.16 (2)
Cr(1)–C(5)	2.21 (2)		
	Bond Angles		
Cr(1)–Se(1)–Cr(2)	100.2 (1)	C(11)–Cr(1)–C(12)	80.7 (7)
Cr(1)–Se(1)–Se(2)	63.6 (1)	Se(1)–Cr(2)–Se(2)	53.1 (2)
Cr(2)–Se(1)–Se(2)	63.1 (2)	Se(1)–Cr(2)–C(21)	86.2 (5)
Cr(1)–Se(2)–Cr(2)	100.3 (1)	Se(1)–Cr(2)–C(22)	121.2 (6)
Cr(1)–Se(2)–Se(1)	63.3 (1)	Se(2)–Cr(2)–C(21)	115.9 (6)
Cr(2)–Se(2)–Se(1)	63.7 (1)	Se(2)–Cr(2)–C(22)	83.6 (5)
Se(1)–Cr(1)–Se(2)	53.1 (1)	C(21)–Cr(2)–C(22)	79.0 (8)
Se(1)–Cr(1)–C(11)	84.1 (5)	Cr(1)–C(11)–O(11)	175 (2)
Se(1)–Cr(1)–C(12)	118.0 (5)	Cr(1)–C(12)–O(12)	176 (2)
Se(2)–Cr(1)–C(11)	122.1 (5)	Cr(2)–C(21)–O(21)	175 (2)
Se(2)–Cr(1)–C(12)	87.2 (4)	Cr(2)–C(22)–O(22)	174 (2)

A three-dimensional Patterson synthesis was used to determine the heavy-atom positions, which phased the data sufficiently well to permit location of the remaining non-hydrogen atoms from Fourier syntheses. Full-matrix least-squares refinement was carried out as previously described.[41] Anisotropic temperature factors were introduced for the non-hydrogen atoms. The hydrogen atoms were inserted in their calculated positions and refined.

The model converged with R = 5.5% and R_w = 6.0%. A final Fourier difference map was featureless. A listing of the observed and calculated structure factors is available together with calculated thermal parameters and selected least-squares planes through groups of atoms. The principal programs used are as previously described.[41,43]

Final positional parameters for the atoms are given in Table II. Table III contains the most important interatomic distances and bond angles. The digits in parentheses in the tables are the

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(41) Freyberg, D. P.; Mockler, G. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1976**, 447.

(42) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

(43) Chen, W.; Goh, L. Y.; Bryan, R. F.; Sinn, E. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 796.

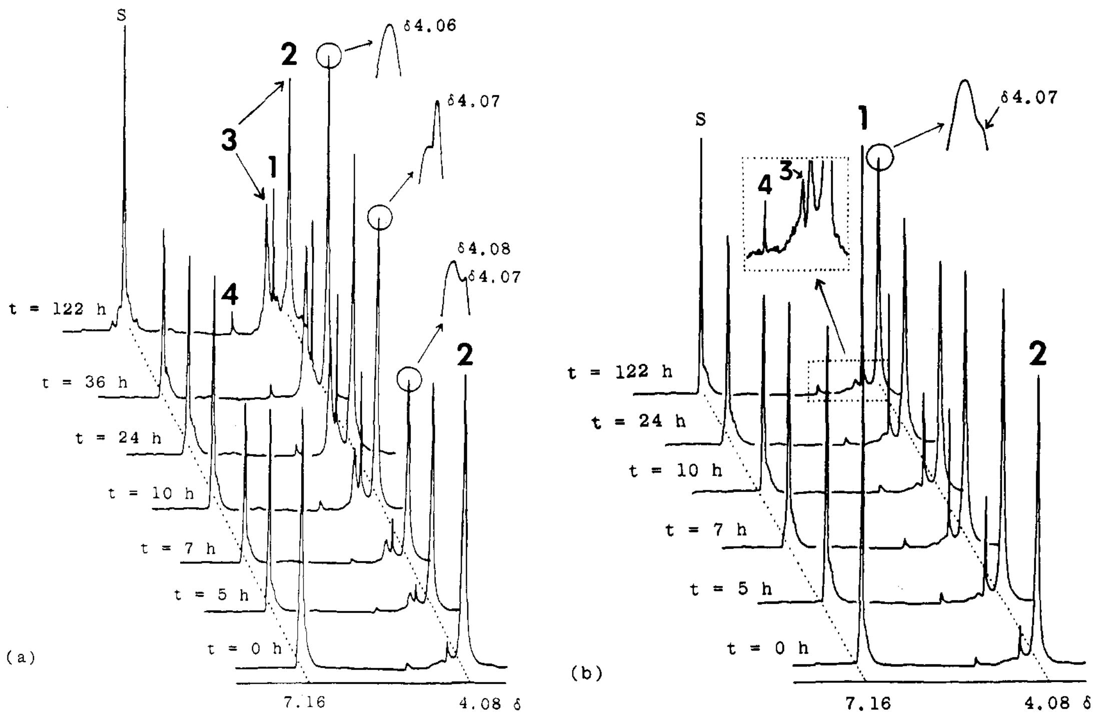

Figure 2. Time-dependent ^{1}H NMR spectra of a 0.05 M solution of $Cp_2Cr_2(CO)_4Se_2$ (2) at 8 °C under 1 atm of (a) CO and (b) argon. Labeled peaks are assigned as follows: S, solvent (δ 7.16); 1, $Cp_2Cr_2(CO)_4Se$ (δ 4.36); 2, $Cp_2Cr_2(CO)_4Se_2$ (δ 4.08); 3, $Cp_2Cr_2(CO)_5Se_2$ (δ ca. 4.06, 4.48); 4, $Cp_4Cr_4Se_4$ (δ 5.13) (spectral scans at 28 °C).

estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Figure 4 shows a stereoview of the molecule, while Figure 5 shows the molecular packing in the unit cell. As is evident from the packing diagram (Figure 5), the structure consists of relatively isolated molecules.

Results and Discussion

Preparative Results. Deep green solutions of $[CpCr(CO)_3]_2$ in toluene or THF reacted with 1 equiv[1,37] or more[1] of gray-black Se_8 powder to produce within minutes a brownish orange solution of $Cp_2Cr_2(CO)_4Se$ (1) in quantitative yield. This on further reaction with a 5-fold excess of Se_8 after 6 h at ca. 5 °C resulted in a mixture of $Cp_2Cr_2(CO)_5Se_2$ (3), $Cp_2Cr_2(CO)_4Se_2$ (2), 1, and $Cp_4Cr_4Se_4$ (4) in the molar proportion 4:1:1:0.1, under an argon atmosphere. A CO atmosphere yielded a slightly higher proportion of 3, viz. 5:1:1:0.1. Concentration followed by crystallization in a CO-saturated *n*-hexane–toluene mixture at −5 °C for 2 h gave 3 as dark reddish brown crystals in 46% yield. In the absence of a CO atmosphere, crystallization at −30 °C gave only 2 as dark brown needles in 76% isolated yield. Attempted separation of the product mixture by chromatography on alumina (Activity II–III) was only partially successful, giving initial fractions of 1 and 2 in 20 and 29% yields, respectively, followed by a third fraction consisting of a mixture of 3, 2, and 1, possessing the same composition as the initial product mixture. Crystallization of this fraction in *n*-hexane–THF at −30 °C gave 2 (22% yield) and 3 (8.6% yield) as two consecutive crops of crystals. This indicates that a conversion of 3 to 2 together with minor amounts of 1 had occurred on the column. This lability was later demonstrated by an NMR study which will be discussed below. It is not surprising therefore that it was previously reported[37b] that only 2 in 98% yield was obtained after chromatography of a product solution on Kieselgel with 1 as a minor byproduct.

Owing to the labile nature of 3, all attempts to obtain single crystals from various solvents proved fruitless even at −78 °C under an atmosphere of CO. Single crystals of 1 or 2 were invariably obtained in admixture with microcrystalline 3 and 4. In the absence of a direct structural analysis, the nature of the Se_2 bonding mode was deduced from a comparison of its NMR and IR spectra with that of the S_2 analogue.[4,5] The matching similarity of both the NMR resonances and the CO stretching frequencies of the IR spectra in both the solid and solution phases are illustrated in Table IV and Figure 6, respectively. This inferential evidence supports the presence of an unsymmetrical μ-η^1,η^2-briding Se_2 group that has been structurally demonstrated in the structure of the S_2 analogue[4,5] shown in Figure 7. Precedent for such a Se_2 bonding mode has been reported by Herrmann for the structure of a $CrFeSe_2$ complex[19] and more recently proposed for the permethylcyclopentadienyl analogue $(\eta^5\text{-}C_5Me_5)_2Cr(CO)_5Se_2$, obtained from the reaction of K $[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]$ with Se_2Cl_2.[44] Indeed, diselenium complexes appear to match disulfur complexes in their varied structural types.[7b]

Table IV. NMR Spectral Data (ppm) of $Cp_2Cr_2(CO)_5E_2$

^{1}H (benzene-d_6)[a]			^{13}C (toluene-d_8)		
E = S	E = Se	assignmt	E = S[b]	E = Se[c]	assignmt
4.17	4.04	C_5H_5	90.72	89.83	C_5H_5
4.51	4.48		92.82	92.01	
			266.50	265.66	CO
			256.07	255.76	
			246.60	245.62	
			239.46	239.23	
			234.03	235.80	

[a] At 30 °C. [b] At −68 °C. [c] At −90 °C.

Structure of $Cp_2Cr_2(CO)_4Se_2$ (2). The stereoview of a single molecule of 2 (Figure 4) illustrates the symmetrical bonding mode of the Se_2 bridge. The Se–Se distance (2.277 Å) lies within the range of values 2.255/2.295 Å[13,17,20,21] reported for μ-η^2-Se_2 ligands in other complexes. The value

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(44) Herrmann, W. A.; Rohrmann, J. *Chem. Ber.* **1986**, *119*, 1437.

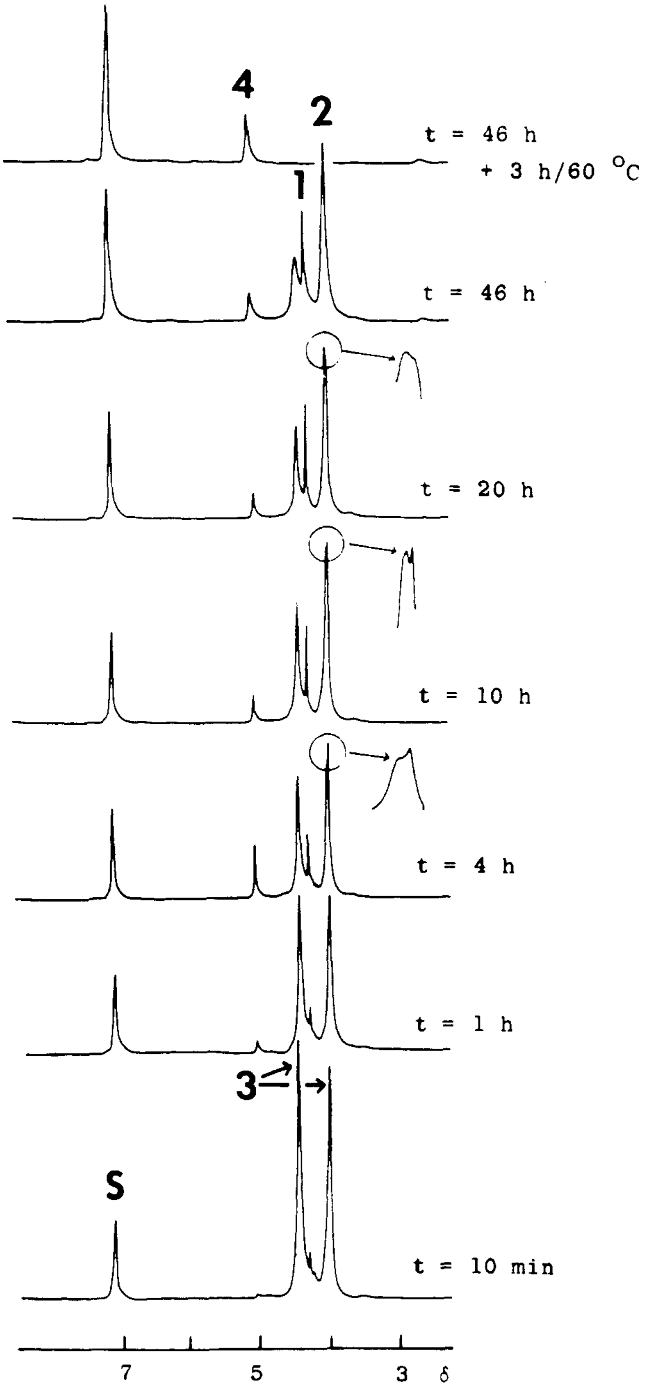

Figure 3. The time-dependent ^1H NMR spectral changes of a 0.08 M solution of **3** in benzene-d_8 at 30 °C: S, solvent (δ 7.16); **1**, $Cp_2Cr_2(CO)_4Se$ (δ 4.36); **2**, $Cp_2Cr_2(CO)_4Se_2$ (δ 4.08); **3**, $Cp_2Cr_2(CO)_5Se_2$ (δ 4.04 and 4.48); **4**, $Cp_4Cr_4Se_4$ (δ 5.13).

also lies between that of a normal Se—Se single bond (2.336 Å) and that of a Se═Se double bond (2.19 Å).[45] All the four Cr–Se distances are very close (Δ_{max} = 0.013 Å). Likewise, other bond lengths and angles (Table III) indicate a fairly symmetrical structure.

Spectra. NMR. The complex $Cp_2Cr_2(CO)_4Se_2$ (**2**) exhibits singlet peaks for the Cp rings in the ^1H spectrum in toluene-d_8 at both 30 °C (δ 4.13) and −90 °C (δ 3.83). Likewise the ^{13}C spectrum shows a singlet for the Cp rings (δ 90.92 at 30 °C and δ 90.69 at −90 °C) and for the CO ligands (δ 258.67 at 30 °C and δ 259.27 at −90 °C). For complex **3**, the resonances of the nonequivalent Cp rings and CO ligands are listed in Table IV.

IR. Like the analogous $Cp_2Cr_2(CO)_4S_2$[5], the CO region of the IR spectrum of **2** in solution shows a four-band pattern. The close resemblance of the CO stretching frequencies of $Cp_2Cr_2(CO)_5Se_2$ (**3**) to those of the S analogue is apparent in Figure 6.

MS. The parent ions of both complexes are not observed. Both complexes undergo decomposition in the mass beam and form high mass fragments, the highest observed being $Cp_4Cr_4Se_4$. Indeed, the spectrum of **3** shows only the fragmentation pattern of $Cp_4Cr_4Se_4$. That of **2** also exhibits the fragmentation pattern of $Cp_2Cr_2(CO)_4Se$ (**1**).

Conversion of $Cp_2Cr_2(CO)_4Se$ (1) to $Cp_2Cr_2(CO)_5Se_2$ (3) and $Cp_2Cr_2(CO)_4Se_2$ (2). The inference from the preparative results discussed above that **1** was the intermediate in the formation of **2** and **3** from the reaction of excess Se_8 with $[CpCr(CO)_3]_2$ was indeed confirmed by their formation from the reaction of isolated crystals of **1** with Se_8. Thus at low temperatures (0–5 °C), the product solution consisted of a mixture of **3**, **2**, **1**, and **4** in the relative proportion of 4:1:1:0.1 after 6 h, whereas at ambient temperature, the main product was **2** in ca. 70% yield.

Further evidence for this conclusion comes from an NMR study at 8–10 °C which is illustrated in Figure 1. Ultrasonic agitation of a 0.05 M solution of **1** in C_6D_6 with elemental Se for 30 min first produced an unidentified species possessing a Cp resonance at δ 4.28, before the Cp resonances of **3** (δ 4.48 and 4.05) became discernible. This uncharacterized resonance varying between δ 4.26 and δ 4.30 slowly diminished, accompanied by an increase in intensity of the resonances of **3**, followed by that of **2** (δ 4.05) which was visible only after 3 h. At 6 h, there existed a mixture of **1**, **2**, and **3** in an approximate molar proportion of 2:1:1. After reacting for a further 10 h, the mixture consisted mainly of **2**, with a minor quantity of **1**. These results indicate that the pentacarbonyl complex **3** with the unsymmetrical Se_2 bridge is first formed via the addition of a Se atom to **1** with intermolecular rearrangement of coordinated CO ligands. In such a case, the theoretical yield can only be 4/5 (i.e. 80%), as is obvious from eq i. Indeed, the maximum observed yield on various

$$\underset{\mathbf{1}}{5Cp_2Cr_2(CO)_4Se} \xrightarrow{Se_8} \underset{\mathbf{3}}{4Cp_2Cr_2(CO)_5Se_2} + \underset{\mathbf{4}}{{}^1/_2Cp_4Cr_4Se_4} \qquad \text{(i)}$$

occasions have always been approximately 70%. This is then followed by a slow extrusion of CO to form the more stable symmetrically bridged tetracarbonyl complex **2**.

In agreement with the observed 20% increase in the relative yield of **3** in the presence of a CO atmosphere, an NMR spectral study did show that the slow conversion of **2** in solution to **3** is greatly enhanced under 1 atm of CO, both at 8 (Figure 2) and 24 °C. It will be noted in Figure 2 that the yield of **3** relative to **2**, **1**, and **4** reached a maximum (5:1:1:0.1) after 48 h. This reaction rate is approximately 8 times slower than the observed rate for the formation of **3** from **1**, which gave an optimum yield at ca. 6 h. Hence the transformation of **1** to **3** via **2**, as shown in eq ii, is at most only a very minor contributory pathway,

$$\underset{\mathbf{1}}{Cp_2Cr_2(CO)_4Se} \xrightarrow{Se_8} \underset{\mathbf{2}}{Cp_2Cr_2(CO)_4Se_2} \xrightarrow{CO} \underset{\mathbf{3}}{Cp_2Cr_2(CO)_5Se_2} \qquad \text{(ii)}$$

if it occurs at all. The increase in yield of **3** under CO must

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[45] Wells, A. F. In *Structural Inorganic Chemistry*, 4th ed.; Clarendon: Oxford, 1975; pp 571–573.

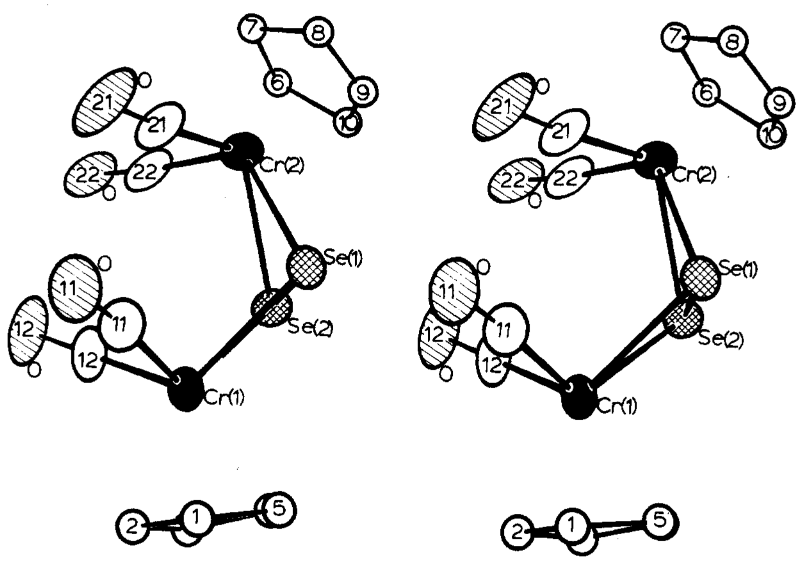

Figure 4. Stereoview of $Cp_2Cr_2(CO)_4Se_2$ (**2**).

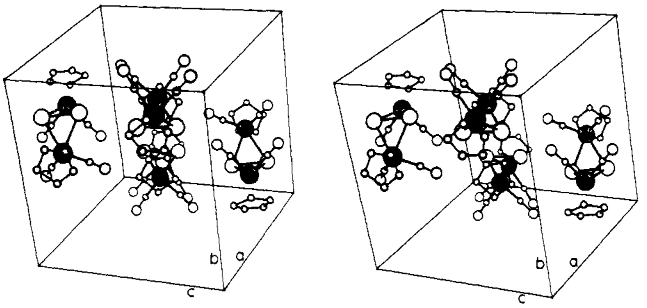

Figure 5. Molecular packing of **2** in the unit cell.

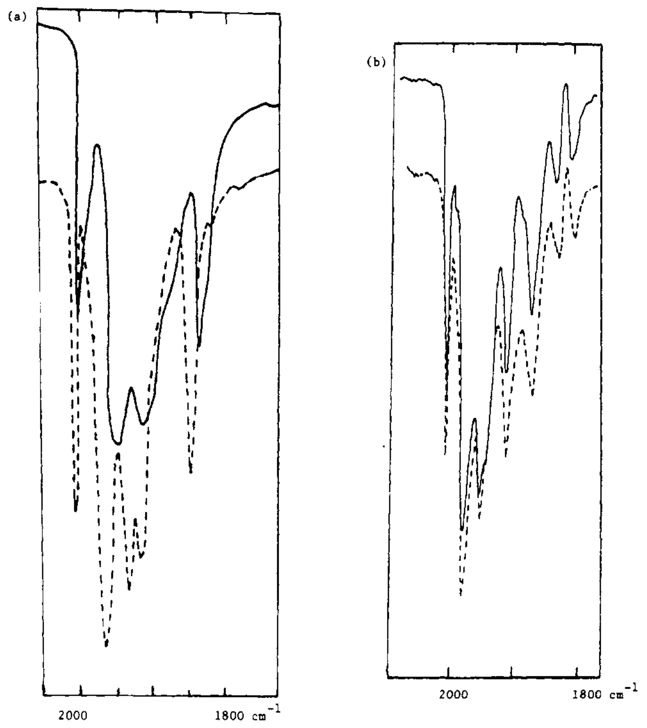

Figure 6. CO stretching frequencies of $Cp_2Cr_2(CO)_5E_2$ (---, E = S; —, E = Se) in (a) KBr disk and (b) C_6H_6 solution.

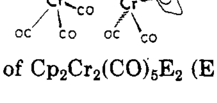

Figure 7. Structure of $Cp_2Cr_2(CO)_5E_2$ (E = S, Se).

be the result of the inhibitory effect of gaseous CO on CO ligand loss from **3**, as indicated by the persistence of the relative proportion of **3** in the product mixture over the observed period of 122 h, as well as the extremely slow decomposition to $Cp_4Cr_4Se_4$ (**4**) which is deposited. At 24 °C under CO, the formation of **3** optimizes at 24 h with a **3**:**2**:**1** proportion of 4.5:1:1.7. As expected, **3** decays much faster than as observed at 8 °C. Thus, at 97 h, the product mixture consisted of **3**, **2**, **1**, and **4** with the relative ratio of 3:1:1.5:0.1.

Mechanism of Formation. In view of the demonstrated spontaneous dissociation of $[CpCr(CO)_3]_2$ into the monomeric species $CpCr(CO)_3^\bullet$ in solution[46] and the substitution lability of such 17e species,[47–49] it is conceivable that the initial step involves a radical attack of $CpCr(CO)_3^\bullet$ and/or $CpCr(CO)_2^\bullet$ on the Se_8 ring, resulting in its cleavage and a simultaneous or subsequent abstraction of a Se atom to form the substituted radical $CpCr(CO)_2Se^\bullet$. Such atom abstraction reactions have been found to be a characteristic process of transition-metal-centered radicals.[48] A subsequent process, as depicted in eq iii, involving the coupling

$$(CO)_3CpCr^\bullet + SeCrCp(CO)_2^\bullet \rightarrow \underset{\mathbf{1}}{(CO)_2CpCr{\equiv}Se{\equiv}CrCp(CO)_2} + CO$$

$$(CO)_2CpCr^\bullet + SeCrCp(CO)_2^\bullet \rightarrow \underset{\mathbf{1}}{(CO)_2CpCr{\equiv}Se{\equiv}CrCp(CO)_2} \quad \text{(iii)}$$

of $CpCr(CO)_3^\bullet$ or $CpCr(CO)_2^\bullet$ with the substituted $CpCr(CO)_2Se^\bullet$ radical will then generate the linear multiply bonded $[CpCr(CO)_2]_2Se$ species. Indeed this mechanism has been proposed for the formation of the triply bonded dimers $[CpM(CO)_2]_2$ from the photogenerated $CpM(CO)_3^\bullet$ radicals[49b] (eq iv). In general, ample precedence for the

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(46) Adams, R. D.; Collins, D. E.; Cotton, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 749.

(47) (a) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 947. (b) Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095.

(48) (a) Cooley, N. A.; Watson, K. A.; Fortier, S.; Baird, M. C. *Organometallics* **1986**, *5*, 2563 and references therein. (b) Hanckel, J. M.; Lee, K.-W.; Rushman, P.; Brown, T. L. *Inorg. Chem.* **1986**, *25*, 1852 and references therein. (c) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187 and references therein.

(49) (a) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065. (b) Ginley, D. S.; Bock, C. R.; Wrighton, M. S. *Inorg. Chim. Acta* **1977**, *23*, 85 and references therein.

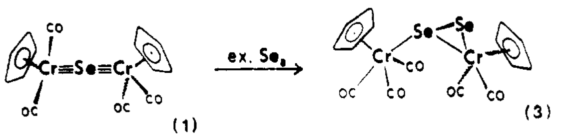
$$(CO)_3(C_5R_5)M{-}M(C_5R_5)(CO)_3 \xrightarrow[CO]{h\nu/N_2} (CO)_2(C_5R_5)M{\equiv}M(C_5R_5)(CO)_2 \quad \text{(iv)}$$

$$M = Mo, W; R = H, CH_3$$

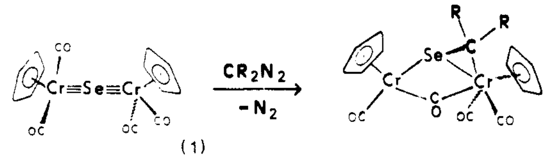
coupling of metal-centered substituted radicals comes from the work of Brown[47,48b] and Wrighton.[49]

The finding that $Cp_2Cr_2(CO)_5Se_2$ (3) or $Cp_2Cr_2(CO)_4Se_2$ (2) are not formed directly from the reaction of $[CpCr(CO)_3]_2$ with Se_8 indicates that the coupling of two $CpCr(CO)_2Se^•$ radicals does not occur. This contrasts with the analogous S complexes which are formed instantaneously from the reaction of $[CpCr(CO)_3]_2$ with S_8. This difference most probably arises from the greater persistence of the $CpCr(CO)_2Se^•$ radical compared with $CpCr(CO)_2S^•$ on account of the greater size of Se. It has previously been observed that the extent of dissociation of $[CpCr(CO_2)L]_2$ increases with the bulkiness of L,[40] and indeed with a sufficiently bulky L (e.g. PPh_3) the chromium-centered radical $CpCr(CO)_2PPh_3^•$ has recently been isolated as yellow crystals in quantitative yield.[48a]

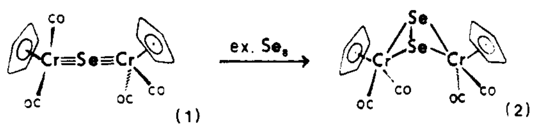
It is therefore suggested that the complexes 3 and 2 are formed by virtue of the reactivity of the Cr≡Se bond in 1, which seems to undergo addition reactions with much ease. The insertion of a Se atom across the Cr≡Se to form 3 (eq v) causes a similar change to the bonding mode of Se as does the addition of the CR_2 group in R_2CN_2 reported previously[37b] (eq vi). Likewise, the insertion of a Se atom to produce 2 (eq vii) seems to find an analogy in the structural transformation observed in the addition of $Fe_2(CO)_9$[37c] (eq viii).



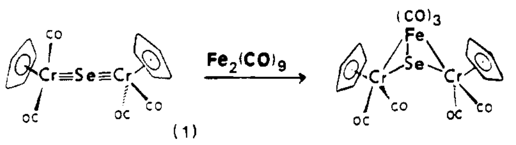
(v)



(vi)



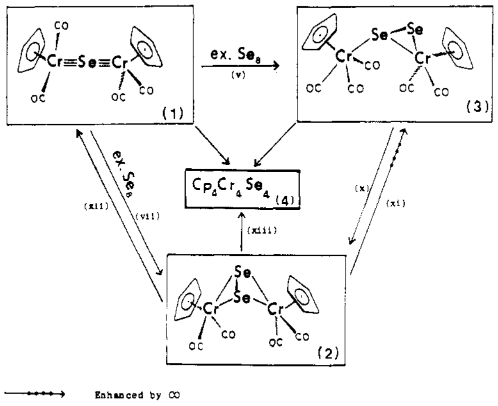
(vii)

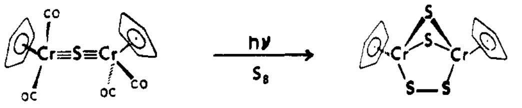


(viii)

Insertion of a Se atom into M–Se single bonds has been reported for the Fe–Se–Fe single bond in $[CpFe(CO)_2]_2Se$ to give a FeSeSeFe chain-type complex[19] but has not been observed before for M≡Se cumulated bonds. Further evidence for this insertion mechanism comes from the isolation of $Cp_2Cr_2(CO)_4S$ from the reaction of 1 with elemental sulfur.[50] By comparison, the Cr≡S bond of the analogous $[CpCr(CO)_2]_2S$ complex is rather inert and does not undergo a S atom insertion,[51] neither does it undergo the normally facile diazoalkane addition.[37] Only under photoexcitation, have we been able to insert S atoms, with the concomitant loss of all the CO ligands to form $Cp_2Cr_2S_4$[52] (eq ix).

Scheme I





(ix)

Lability of $Cp_2Cr_2(CO)_5Se_2$ (3). The time-dependent ^1H NMR spectral changes of a 0.08 M solution of 3 in C_6D_6 in a closed 5-mm tube at ca. 30 °C showed a slow conversion to 2, 1, and 4, possessing resonances δ 4.08, 4.36, and 5.13, respectively. These three peaks are equally prominent after 4 h (Figure 3). The end product, after accelerated decomposition for 3 h at 60 °C at the final stage, following a degradation process of 46 h at ambient temperature, was solely 4. These transformations are best represented by Scheme I, which also includes the formation 3 and 2 from 1 (represented by routes v, vii, and x). Though as discussed in the earlier section, the experimental evidence is in favor of pathway x for the formation of 2, route vii cannot be completely ruled out. A slow simultaneous transformation of 2 to 3, 1, and $Cp_4Cr_4Se_4$ via pathways xi–xiii, respectively, has been independently demonstrated for a solution of 2 at 8 °C (Figure 2b) or 24 °C, as well as for an analytically pure sample of the crystalline solid after several months at ambient temperature. A detailed study has established that the conversion of 1 to $Cp_4Cr_4Se_4$ occurs via several intermediate species.[53]

It is also observed that the rate of degradation of 3 in this study is much slower than under preparative conditions. This is consistent with the inhibitory effect of released CO in the capped NMR tube, as discussed earlier.

Acknowledgment. Financial support from the University of Malaya and NSF Grant CHE8300516 is gratefully acknowledged.

Registry No. 1, 91043-03-7; 2, 98606-16-7; 3, 115305-71-0; 4, 98584-40-8; $Cp_2Cr_2(CO)_6$, 12194-12-6.

Supplementary Material Available: Listings of anisotropic thermal parameters for 2, hydrogen atom coordinates, and some bond lengths and angles (4 pages); a listing of observed and calculated structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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(50) Goh, L. Y. *J. Chem. Soc., Dalton Trans.*, in press.

(51) Goh, L. Y., unpublished results.

(52) Goh, L. Y.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1986**, 1474.

(53) Goh, L. Y.; Mak, T. C. W., submitted for publication.