

Tetranuclear Complexes from the Reaction of Tetraphosphorus Triselenide with Cyclopentadienylchromium Tricarbonyl Dimer. Synthesis, Thermal Degradation, and X-ray Crystal Structures of $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{Se}_3) \cdot \frac{1}{2}\text{C}_6\text{H}_6$ and $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)^1$

Lai Yoong Goh*

Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260

Wei Chen* and Richard C. S. Wong

Department of Chemistry, University of Malaya, 59100 Kuala Lumpur, Malaysia

Received July 27, 1998

The reaction of $[\text{CpCr}(\text{CO})_3]_2$ with P_4Se_3 has been investigated. Under mild conditions, $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{Se}_3)$ (**4**) was the main product (48% yield), alongside low yields of $\text{CpCr}(\text{CO})_3\text{H}$ (**5**), $\text{CpCr}(\text{CO})_2\text{P}_3$ (**6**), $[\text{CpCr}(\text{CO})_2]_2\text{P}_2$ (**7**), and $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)$ (**8**). Product isolation under various reaction conditions, together with ^1H NMR spectral monitoring of the reaction and thermolytic studies of the complexes **4** and **8**, indicates that **4** and **5** were the primary products of the reaction. Thermolysis of **4** led to **8**, which in turn degraded to give **6**, **7**, and $\text{Cp}_4\text{Cr}_4\text{Se}_4$ (**9**). The complexes **4** and **8** were also obtained from the reaction of $[\text{CpCr}(\text{CO})_2]_2\text{Se}$ (**3**) with P_4Se_3 or P_4S_3 ; the reaction with the latter also gave $[\text{CpCr}(\text{CO})_2]_2\text{S}$ (**10**), the sulfur analogue of **3**, as an additional product. Mechanistic pathways via the monomeric $\text{CpCr}(\text{CO})_3$ species and the Cr_2Se complex **3** are proposed. The cothermolysis of $[\text{CpCr}(\text{CO})_2]_2$ ($\text{Cr}=\text{Cr}$) (**2**) with P_4Se_3 led to the isolation of **5**, **6**, **7**, and **9**. All the complexes have been characterized spectroscopically, while **4** and **8** have also been studied by X-ray diffraction analysis. The complex **8** possesses an unusual open-book framework with a P–P bond as its backbone and a 2-fold symmetry axis passing through its midpoint.

Introduction

The role of main group polyatomic and heteroatomic aggregates in transition metal complexes and clusters is receiving much current interest.² Our efforts in this area have involved the $[\text{CpCr}(\text{CO})_3]$ radical-induced reactions of the chalcogens,^{3,4} pnictogens P_4 ,^{5,6} and As_4 ,⁷

followed by tetraphosphorus trisulfide P_4S_3 .⁸ We have extended this investigation to tetraphosphorus triselenide P_4Se_3 . Reported work in this area, mainly by Stoppioni and co-workers, describe basically three types of reactions, viz., (i) the reactions of $[\text{MCl}(\text{COD})]_2$ ($\text{M} = \text{Rh}, \text{Ir}$; COD = cycloocta-1,5-diene) in the presence of triphos [triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane], yielding the P_3Se_3 complexes $[(\text{triphos})\text{M}(\text{P}_3\text{Se}_3)]$, wherein the metal fragment has replaced a basal P atom in the P_4Se_3 cage molecule;⁹ (ii) the reactions of $[(\text{np}_3)\text{M}]$ ($\text{M} = \text{Ni}$ or Pd , np_3 = tris(2-diphenylphosphinoethyl)amine), leading to complexes $[(\text{np}_3)\text{M}(\text{P}_4\text{Se}_3)]$, which contain an intact P_4Se_3 cage coordinated via its apical P atom;¹⁰ and (iii) the reaction of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ in the presence of tppme [tppme = 1,1,1-tris(diphenylphosphinomethyl)ethane] to yield $[\text{Co}(\text{tppme})(\text{P}_2\text{Se})] \cdot \text{BF}_4$, containing a heterocyclic P_2Se unit η^3 -bonded to the Co atom.¹¹ The crystal structures of all these

(1) Presented in part by L.Y.G. at the 7th International Symposium on Inorganic Ring Systems, 7–12 Aug, 1994, Banff, Canada. See also the proceedings in: Goh, L. Y.; Chen, W.; Wong, R. C. S. *Phosphorus, Sulfur Silicon* **1994**, 93–94, 209.

(2) (a) Roof, L. C.; Kolis, J. W. *Chem. Rev.* **1993**, 93, 1037. (b) Di Vaira, M.; Stoppioni, P. *Coord. Chem. Rev.* **1992**, 120, 259. (c) Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 1104. (d) Di Maio, A.-J.; Rheingold, A. L. *Chem. Rev.* **1990**, 90, 169. (e) Scheer, M.; Herrmann, E. Z. *Chem.* **1990**, 30, 41. (f) Norman, N. C. *Chem. Soc. Rev.* **1988**, 17, 269. (g) Whitmire, K. H. *J. Coord. Chem.* **1988**, 17, 95. (h) Di Vaira, M.; Stoppioni, P.; Peruzzini, M. *Polyhedron* **1987**, 6, 351. (i) Huttner, G. *Pure Appl. Chem.* **1986**, 58, 585. (j) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, 25, 56. (k) Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* **1985**, 24, 924. (l) Brunner, H.; Nuber, B.; Poll, L.; Wachter, J. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 1627. (m) Haiduc, I.; Sowerby, D. B. In *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic: London, 1987; Vol. 2, p 701.

(3) Goh, L. Y.; Hambley, T. W.; Robertson, G. B. (a) *J. Chem. Soc., Chem. Commun.* **1983**, 1458; (b) *Organometallics* **1987**, 6, 1051.

(4) Goh, L. Y.; Chen, W.; Sinn, E. (a) *J. Chem. Soc., Chem. Commun.* **1985**, 462; (b) *Organometallics* **1988**, 7, 2020.

(5) Goh, L. Y.; Wong, R. C. S.; Chu, C. K.; Hambley, T. W. (a) *J. Chem. Soc., Dalton Trans.* **1989**, 1951; (b) *J. Chem. Soc., Dalton Trans.* **1990**, 977.

(6) Goh, L. Y.; Wong, R. C. S.; Sinn, E. (a) *J. Chem. Soc., Chem. Commun.* **1990**, 1484; (b) *Organometallics* **1993**, 12, 888.

(7) Goh, L. Y.; Wong, R. C. S.; Mak, T. C. W. *Organometallics* **1991**, 10, 875.

(8) (a) Goh, L. Y.; Chen, W.; Wong, R. C. S. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 1728. (b) Goh, L. Y.; Chen, W.; Wong, R. C. S.; Karaghiosoff, K. *Organometallics* **1995**, 14, 3886.

(9) (a) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *J. Chem. Soc., Chem. Commun.* **1983**, 903. (b) Di Vaira, M.; Mann, B. E.; Peruzzini, M.; Stoppioni, P. *Inorg. Chem.* **1988**, 27, 3725.

(10) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. (a) *J. Organomet. Chem.* **1983**, 258, 373; (b) *Inorg. Chem.* **1983**, 22, 2196.

complexes show that the metal atom is positioned in a protected environment, provided by the *enveloping* tripod ligand and the P_xSe_y unit. Unlike these, the complexes derived from this present investigation possess Cr atoms in *nonprotected* environments, being incorporated as peripheral [CpCr(CO)₂]_n (*n* = 2 or 3) fragments on P_xSe_y frameworks. This paper describes the full details of these findings, a preliminary account of which has been published.¹²

Experimental Section

General Procedures. All reactions were carried out using conventional Schlenk techniques under an inert atmosphere of nitrogen or under argon in a Vacuum Atmospheres Dribox equipped with a model HE 493 Dri-Train.

Physical Measurements and Elemental Analysis. ¹H and ¹³C NMR spectra were measured on a JEOL FX100 100 MHz, JEOL JNM-GSX 270 270 MHz, or Varian VXR-300S 300 MHz FT NMR spectrometer, with chemical shifts referenced to residual C₆H₆ in benzene-*d*₆ or to (CH₃)₄Si in toluene-*d*₈. ³¹P NMR spectra were measured on a JEOL JNM-G5X 270 96.15 MHz or a Varian VXR-300S 121.42 MHz spectrometer, with chemical shifts referenced to external H₃PO₄. IR spectra in Nujol mulls or solution were measured in the range 4000–200 cm^{−1} by means of a Perkin-Elmer 1600 FTIR instrument. Mass spectra were run on a VG ProSpec spectrometer. The visible spectrum of CrO₄^{2−} (for Cr analysis) was measured on a Beckmann DU-7 spectrometer.

Elemental S and P analyses were performed by the Analytical Unit of the Research School of Chemistry, Australian National University. C, H analyses were performed by the Industrial Research & Consultancy Unit of Universiti Sains Malaysia. Chromium was analyzed as CrO₄^{2−} in an alkaline medium.¹³

Solvents and Reagents. [CpCr(CO)₃]₂ (**1**) was synthesized as described by Manning¹⁴ from chromium hexacarbonyl (99% purity from Aldrich Chemical Co.). [CpCr(CO)₂]₂ (**2**) was obtained from thermolysis of **1**.¹⁵ CpCr(CO)₂Se (**3**) was prepared as previously reported.^{4a} P₄Se₃ was synthesized from its elements.¹⁶ All solvents were dried over sodium/benzophenone and distilled before use. Celite (Fluka AG), silica gel (Merck Kieselgel 60, 35–70 and 230–400 Mesh), and TLC plates (Merck Kieselgel 60F₂₅₄) were dried at 150 °C overnight before chromatographic use.

Reaction of [CpCr(CO)₃]₂ with Tetraphosphorus Triselenide, P₄Se₃. (a) At Ambient Temperature for 6 days: Isolation of Cp₄Cr₄(CO)₉(P₄Se₃) (4**).** A deep green suspension of [CpCr(CO)₃]₂ (**1**) (200 mg, 0.50 mmol) and P₄Se₃ (180 mg, 0.50 mmol) in toluene (25 mL) was stirred at ambient temperature for 6 days until all the dimer had reacted. The resultant dark brown reaction mixture was concentrated to dryness and the residue extracted with THF (3 × 15 mL), leaving behind on the walls of the flask an orange-yellow film of P₄Se₃ (ca. 75 mg, 0.21 mmol, 42% recovery), identified by its EI mass spectrum [*m/z* (main fragments): 362 (P₄Se₃), 173 (P₃Se), 111 (PSe), and (low-intensity fragments): 299 (P₂Se₃), 281 (P₄Se₂), 253 (P₃Se₂), 191 (PSe₂), 142 (P₂Se), 124 (P₄), 93 (P₃) and 62 (P₂)]. The combined extracts were concentrated, adsorbed onto Celite (ca. 1.5 g) which was evacuated to

dryness, and then loaded onto a silica gel column (1.5 cm × 15 cm) prepared in 1:1 *n*-hexane/toluene. Elution gave six fractions: (i) a yellow solution in *n*-hexane/toluene (2:1, 15 mL) which yielded yellow crystalline solids (20 mg), the ¹H and ³¹P NMR spectra of which indicated the presence of a 5:2 molar mixture of CpCr(CO)₃H (**5**) (ca. 7% yield, δ(Cp) 4.02 and δ(Cr–H) −5.62 in benzene-*d*₆)¹⁷ and CpCr(CO)₂P₃ (**6**) (ca. 2% yield, δ(Cp) 3.92⁵ and TLC: *R*_f = 0.65 versus an authentic sample, with 3:2 *n*-hexane/toluene as eluent); (ii) an orange solution in *n*-hexane/toluene (2:1, 10 mL) which gave fine light brownish orange solids of unreacted P₄Se₃ (10 mg, 0.03 mmol, 6.0% recovery); (iii) a magenta solution in *n*-hexane/toluene (2:3, 25 mL) which gave fine dark magenta crystalline solids of [CpCr(CO)₂]₂P₂ (**7**) (33 mg, 0.08 mmol, 16.0% yield), identified by its ¹H NMR in benzene-*d*₆ (δ(Cp) 4.15)⁵ and TLC versus an authentic sample (*R*_f = 0.41 with 3:2 *n*-hexane/toluene as eluent); (iv) a reddish brown solution in *n*-hexane/toluene (2:3, 30 mL) which when evaporated to dryness yielded fine dark brown solids of Cp₄Cr₄(CO)₈(P₂Se₂) (**8**) (30 mg, 0.033 mmol, 13.2% yield); anal. calcd for C₂₈H₂₀Cr₄O₈P₂Se₂ C, 36.86; H, 2.21; Cr, 22.80; P, 6.79; Se, 17.31; found C, 37.61; H, 2.30; Cr, 22.96; P, 6.84; Se, 16.99; (v) a yellowish brown solution in *n*-hexane/toluene (1:3, 45 mL) from which was obtained dark brown solids of Cp₄Cr₄(CO)₉(P₄Se₃) (**4**) (130 mg, 0.12 mmol, 48.0% yield); anal. calcd for C₂₈H₂₀Cr₄O₉P₄Se₃ C, 32.22; H, 1.86; Cr, 19.24; P, 11.46; Se, 21.91; found C, 32.61; H, 2.30; Cr, 19.13; P, 12.97; Se, 21.91; (vi) a greenish brown solution in ether (20 mL) which gave an uncharacterizable dirty brown oily residue (ca. 25 mg).

(b) At Ambient Temperature for 12 days: Isolation of Cp₄Cr₄(CO)₈(P₂Se₂) (8**).** A deep green suspension of **1** (500 mg, 1.24 mmol) and P₄Se₃ (449 mg, 1.24 mmol) in toluene (30 mL) was stirred at ambient temperature for 12 days. The resultant yellowish brown mixture was concentrated to dryness, and the residue was extracted with THF (2 × 25 mL), leaving behind an orange-yellow film of P₄Se₃ (ca. 120 mg, 0.33 mmol, 27% recovery) on the walls of the flask. The extracts were concentrated, adsorbed onto Celite (ca. 1.5 g) which was evacuated to dryness, and loaded onto a silica gel column (2 cm × 15 cm) prepared in 1:1 *n*-hexane/toluene. Elution gave five fractions: (i) a yellow solution in *n*-hexane/toluene (2:1, 45 mL) which when evaporated to dryness yielded yellow crystalline solids (90 mg), the ¹H and ³¹P NMR spectra of which showed a 3:2 molar mixture of CpCr(CO)₃H (**5**) (ca. 7% yield) and CpCr(CO)₂P₃ (**6**) (ca. 8% yield); (ii) an orange solution in *n*-hexane/toluene (1:1, 40 mL) which gave brownish orange crystalline solids of P₄Se₃ (25 mg, 0.07 mmol, 5.6% recovery); (iii) a reddish brown solution in *n*-hexane/toluene (2:3, 60 mL) which gave dark brown solids of Cp₄Cr₄(CO)₈(P₂Se₂) (**8**) (190 mg, 0.21 mmol, 33.9% yield); (iv) a yellowish brown solution in *n*-hexane/toluene (1:3, 60 mL) which gave dark brown solids of Cp₄Cr₄(CO)₉(P₄Se₃) (**4**) (130 mg, 0.12 mmol, 19.4% yield); (v) a greenish brown solution in ether (30 mL) followed by THF (30 mL) which yielded a greenish brown oily residue (100 mg). Rechromatography of this residue on a silica gel column (2 × 10 cm) prepared in 1:1 *n*-hexane/toluene, gave a yellowish brown fraction in *n*-hexane/toluene (1:3, 45 mL), which when concentrated yielded an additional dark brown crop of **4** (51 mg, 0.047 mmol, 7.6% yield).

(c) Cothermolysis at 60 °C. A deep green solution of **1** (250 mg, 0.62 mmol) in toluene (20 mL), containing partially dissolved P₄Se₃ (225 mg, 0.62 mmol) was stirred at 60 °C for 2 h. The resultant dark brown reaction mixture was concentrated to dryness. The residue was extracted using THF (3 × 15 mL), leaving behind a film of orange-yellow precipitate of unreacted P₄Se₃ (ca. 55 mg, 24% recovery) on the walls of the flask. The combined extracts were concentrated, adsorbed onto Celite (ca. 2 g) which was evacuated to dryness, and then

(11) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *J. Chem. Soc., Dalton Trans.* **1984**, 359.

(12) Goh, L. Y.; Chen, W.; Wong, R. C. S.; Zhou, Z.-Y.; Fun, H. K. *Mendeleev Commun.* **1995**, 60.

(13) Haupt, G. W. *J. Res. Nat. Bur. Stand.* **1952**, 48, 414.

(14) Birdwhistle, R.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* **1978**, 157, 239.

(15) Hackett, P.; O'Neil, P. S.; Manning, A. R. *J. Chem. Soc., Dalton Trans.* **1974**, 1625.

(16) Irgolic, K.; Zingaro, R. A.; Kudchadker, M. *Inorg. Chem.* **1965**, 4, 1421.

(17) Cooley, N. A.; MacConnachie, P. T. F.; Baird, M. C. *Polyhedron* **1988**, 7, 1965.

loaded onto a silica gel column (1.5 cm \times 17 cm) prepared in 1:1 *n*-hexane/toluene. Seven fractions were eluted: (i) a yellow solution in *n*-hexane/toluene (2:1, 20 mL) which upon concentration to dryness yielded brownish yellow solids (32 mg), the ^1H NMR spectrum of which showed an approximately 1:6 molar mixture of $\text{CpCr}(\text{CO})_3\text{H}$ (**5**) (ca. 2% yield) and $\text{CpCr}(\text{CO})_2\text{P}_3$ (**6**) (ca. 8% yield); (ii) an orange solution in *n*-hexane/toluene (1:1, 15 mL) which gave fine light brown solids of unreacted P_4Se_3 (15 mg, 0.04 mmol, 6.7% recovery); (iii) an orange-brown solution in *n*-hexane/toluene (7:3, 35 mL) which gave deep brown crystals of $[\text{CpCr}(\text{CO})_2]_2\text{Se}$ (**3**) (51 mg, 0.12 mmol, 19.4% yield), identified by its NMR and IR spectral characteristics;^{4a} (iv) a magenta solution in *n*-hexane/toluene (2:3, 20 mL) which gave fine dark magenta crystals of $[\text{CpCr}(\text{CO})_2]_2\text{P}_2$ (**7**) (22 mg, 0.05 mmol, 8.7% yield); (v) a reddish brown solution in *n*-hexane/toluene (2:3, 45 mL) which gave fine dark brown crystalline solids of $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)$ (**8**) (45 mg, 0.05 mmol, 16.1% yield); (vi) a yellowish brown solution in *n*-hexane/toluene (1:3, 60 mL) which gave dark brown solids of $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{Se}_3)$ (**4**) (123 mg, 0.11 mmol, 35.5% yield); (vii) a dirty brown eluate in toluene (10 mL) followed by toluene/ether (1:1, 20 mL) which gave dark brown solids of $\text{Cp}_4\text{Cr}_4\text{Se}_4$ (**9**) (8.5 mg, 0.01 mmol, 3.5% yield), identified by its ^1H NMR in benzene- d_6 [$\delta(\text{Cp})$ 5.13],^{4b} mass spectrum,¹⁸ and TLC against an authentic sample (R_f = 0.49 with 3:2:2 *n*-hexane/toluene/ether as eluent).

Reaction of $[\text{CpCr}(\text{CO})_2]_2$ (2**) with P_4Se_3 .** A deep green suspension of **2** (100 mg, 0.29 mmol) and P_4Se_3 (104 mg, 0.29 mmol) in toluene (15 mL) was stirred at ambient temperature. No reaction was observed after 24 h. The temperature was therefore raised to 60 $^\circ\text{C}$ and the reaction continued until **2** had completely reacted (ca. 18 h). The resultant dirty brown suspension containing some dark insoluble solids was filtered through a 1.5 cm \times 2 cm disk of Celite. The filtrate was concentrated, adsorbed onto silica gel (ca. 5 g) which was evacuated to dryness, and loaded onto a silica gel column (5 cm \times 15 cm) prepared in *n*-hexane. Elution gave three fractions: (i) a yellow eluate in *n*-hexane/toluene (9:1, 15 mL) which when dried yielded brownish orange solids (53 mg), which were extracted with *n*-hexane (3 \times 10 mL), leaving behind unreacted P_4Se_3 (15 mg, 0.042 mmol, 14.4% recovery); concentration of the extracts yielded a brownish yellow residue (38 mg), the ^1H NMR spectrum of which showed the presence of a 3:1 molar mixture of $\text{CpCr}(\text{CO})_3\text{H}$ (**5**) and $\text{CpCr}(\text{CO})_2\text{P}_3$ (**6**) with isolated yields of 29 mg (0.14 mmol, 24.1% yield) and 9 mg (0.03 mmol, 5.2% yield), respectively; (ii) a magenta eluate in *n*-hexane/toluene (1:1, 20 mL) which gave dark magenta solids of $[\text{CpCr}(\text{CO})]_2\text{P}_2$ (**7**) (13 mg, 0.03 mmol, 10.3% yield); (iii) a dirty brown eluate in toluene (10 mL) followed by toluene/ether (1:1, 15 mL) which gave dark brown solids of $\text{Cp}_4\text{Cr}_4\text{Se}_4$ (**9**) (37 mg, 0.05 mmol, 34.5% yield).

Reaction of $[\text{CpCr}(\text{CO})_2]_2\text{Se}$ (3**) with P_4Se_3 .** An orange-brown mixture of **3** (100 mg, 0.24 mmol) and P_4Se_3 (62 mg, 0.17 mmol) in toluene was stirred at ambient temperature for 6 days. The resultant reddish brown mixture was filtered through a 2 cm \times 1 cm disk of Celite (ca. 1.5 g). The filtrate was then adsorbed onto silica gel (ca. 3 g), evacuated to dryness and loaded onto a silica gel column (1.5 cm \times 10 cm) prepared in *n*-hexane. Four fractions were eluted: (i) a pale yellow solution with *n*-hexane (35 mL) which when concentrated to dryness yielded fine greenish yellow crystalline solids of $\text{CpCr}(\text{CO})_3\text{H}$ (**5**) (ca. 6 mg, 0.03 mmol, 6% yield) and $\text{CpCr}(\text{CO})_2\text{P}_3$ (**6**) (ca. 2 mg, 0.01 mmol, 2% yield); (ii) an orange-brown solution with *n*-hexane/toluene (2:1, 30 mL) which when concentrated to dryness yielded fine orange-brown crystalline solids of unreacted **3** (8 mg, 0.02 mmol, 8% recovery); (iii) a reddish brown solution with *n*-hexane/toluene (2:3, 50 mL) which when concentrated to dryness yielded fine dark brown crystalline solids of $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)$ (**8**) (82 mg, 0.09 mmol,

81.8% yield based on reacted **3**); (iv) a dark brown eluate in *n*-hexane/toluene (1:2, 30 mL) which when concentrated to dryness yielded dark brown solids of $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{Se}_3)$ (**4**) (5 mg, 0.005 mmol, 4.2% yield).

Reaction of $[\text{CpCr}(\text{CO})_2]_2\text{Se}$ (3**) with P_4S_3 .** An orange-brown mixture of **3** (400 mg, 0.94 mmol) and P_4S_3 (150 mg, 0.68 mmol) in toluene was stirred at ambient temperature for 6 days. The resultant greenish brown mixture was filtered through a frit. The recovered yellow precipitate was evacuated dry after washing with toluene. Its EI mass spectrum showed the fragmentation pattern of P_4S_3 [m/z 220 (P_4S_3), 157 (P_3S_2), 125 (P_3S), 94 (P_2S), 63 (PS), and 31(P)]. The filtrate was then adsorbed onto silica gel (ca. 5 g), evacuated to dryness, and loaded onto a silica gel column (2 cm \times 15 cm) prepared in 2:1 *n*-hexane/toluene. Five fractions were eluted: (i) a pale yellow solution in *n*-hexane (45 mL) which when concentrated to dryness yielded fine greenish yellow crystalline solids of $\text{CpCr}(\text{CO})_3\text{H}$ (**5**) (ca. 17 mg, 0.08 mmol, 5% yield) and $\text{CpCr}(\text{CO})_2\text{P}_3$ (**6**) (ca. 5 mg, 0.02 mmol, 1% yield); (ii) a greenish brown fraction eluted with *n*-hexane/toluene (2:1, 45 mL) which when concentrated to dryness yielded fine deep green crystalline solids of $[\text{CpCr}(\text{CO})_2]_2\text{S}$ (**10**) (55 mg, 0.15 mmol, 15.5% yield), identified via its ^1H NMR ($\delta(\text{Cp})$ 4.36)^{3b} and its TLC characteristics versus an authentic sample (R_f = 0.60 with 2:3 *n*-hexane/toluene as eluent);¹⁹ (iii) a reddish brown solution in *n*-hexane/toluene (3:2, 70 mL) which when concentrated to dryness yielded fine dark brown crystalline solids of $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)$ (**8**) (215 mg, 0.24 mmol, 51.1% yield); (iv) a dark brown solution in *n*-hexane/toluene (2:3, 50 mL) which when concentrated to dryness yielded fine dark brown solids of $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{Se}_3)$ (**4**) (35 mg, 0.03 mmol, 6.4% yield); (v) a dark brown solution in toluene/ether (2:1, 20 mL plus 1:1, 30 mL) which when concentrated to dryness yielded an unidentified dark brown oily Cp-containing ($\delta(\text{Cp})$ 7.76, 7.69) residue (35 mg).

Thermolysis of $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{Se}_3)$ (4**).** A brown solution of **4** (80 mg, 0.074 mmol) in toluene (15 mL) was maintained with stirring at 60 $^\circ\text{C}$ for 4 h. The resultant reddish brown solution was concentrated to ca. 2 mL. Addition of *n*-hexane (0.5 mL) followed by overnight cooling at -28°C yielded dark magenta crystalline solids of $[\text{CpCr}(\text{CO})_2]_2\text{P}_2$ (**7**) (10 mg, 0.025 mmol, 16.9% yield). The mother liquor was concentrated to ca. 2 mL and loaded onto a silica gel column (1.5 cm \times 20 cm) prepared in *n*-hexane. Four fractions were eluted: (i) an orange-yellow solution in *n*-hexane/toluene (3:1, 25 mL), which when concentrated to dryness yielded brownish yellow crystals of $\text{CpCr}(\text{CO})_2\text{P}_3$ (**6**) (5 mg, 0.02 mmol, 6.8% yield); (ii) a magenta solution in *n*-hexane/toluene (1:1, 40 mL) which gave dark magenta crystals of $[\text{CpCr}(\text{CO})_2]_2\text{P}_2$ (**7**) (5 mg, 0.01 mmol, 6.8% yield); (iii) a brown solution in *n*-hexane/toluene (1:2, 35 mL) which gave dark brown solids of $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)$ (**8**) (35 mg, 0.04 mmol, 54.1% yield); (iv) a dirty brown solution in ether (20 mL) which gave fine dark brown solids of $\text{Cp}_4\text{Cr}_4\text{Se}_4$ (**9**) (9 mg, 0.01 mmol, 13.5% yield).

Thermolysis of $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)$ (8**).** A reddish brown solution of **8** (60 mg, 0.066 mmol) in toluene (15 mL) was maintained at 80 $^\circ\text{C}$ with stirring for 3 h. The resultant magenta-brown solution was concentrated to ca. 2 mL and chromatographed as described above. Four fractions were eluted: (i) an orange-yellow solution in *n*-hexane/toluene (3:1, 20 mL) which when evaporated to dryness yielded brownish yellow crystals of $\text{CpCr}(\text{CO})_2\text{P}_3$ (**6**) (3 mg, 0.01 mmol, 3.8% yield); (ii) a magenta solution in *n*-hexane/toluene (1:1, 35 mL) which gave fine dark magenta crystals of $[\text{CpCr}(\text{CO})_2]_2\text{P}_2$ (**7**) (30 mg, 0.07 mmol, 53.0% yield); (iii) a greenish brown solution in toluene (10 mL) followed by ether (20 mL) which gave fine dark brown solids of $\text{Cp}_4\text{Cr}_4\text{Se}_4$ (**9**) (19 mg, 0.02 mmol, 30.3% yield); (iv) a brown solution in ether/THF (1:1, 15 mL), which gave a dark brown oily uncharacterizable residue (5 mg).

(18) Goh, L. Y.; Mak, T. C. W. *J. Organomet. Chem.* **1989**, 363, 77.(19) Goh, L. Y. *J. Chem. Soc., Dalton Trans.* **1989**, 431.

Table 1. Data Collection and Processing Parameters

	4	8
molecular formula	Cp ₄ Cr ₄ (CO) ₉ P ₄ Se ₃ ·0.5C ₆ H ₆	Cp ₄ Cr ₄ (CO) ₈ P ₂ Se ₂
<i>M</i> _r	1120.26	912.34
cryst color and habit	black triangular prism	black tetrahedron
cryst size (mm)	0.3 × 0.3 × 0.1	0.2 × 0.2 × 0.2
unit cell params		
<i>a</i> (Å), α (deg)	29.06(1), 90.0	14.893(1), 90.0
<i>b</i> (Å), β (deg)	12.895(1), 104.23(2)	14.894(4), 90.0
<i>c</i> (Å), γ (deg)	21.377(7), 90.0	13.670(2), 90.0
<i>V</i> (Å ³), <i>Z</i>	7764(4), 8	3032.2(9), 4
<i>D</i> _x (Mg m ⁻³)	1.917	1.999
cryst system	monoclinic	orthorhombic
space group	<i>C</i> 2/ <i>c</i>	<i>C</i> 222 ₁
radiation	Mo Kα	Mo Kα
abs coeff (mm ⁻¹)	4.12	3.95
temp (K)	300	300
collection method	ω	ω/2θ
no. of reflns measd	5283	2872
no. of ind reflns	4955	2666
no. of obsd reflns	1774 (<i>I</i> > 2σ(<i>I</i>))	2321 (<i>I</i> > 2σ(<i>I</i>))
<i>R</i> = Σ <i>F</i> _o - <i>F</i> _c /Σ <i>F</i> _o ^a	0.137	0.0386
<i>wR</i> = [Σ(<i>wF</i> _o ² - <i>F</i> _c ²)/Σ(<i>wF</i> _o ²)] ^{0.5} ^a	0.195	0.083
no. of params refined	264	199
<i>S</i>	0.978	1.015
weighting scheme, <i>w</i> = <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3	[σ ² (<i>F</i> _o ²) + (0.0665 <i>P</i>) ²] ⁻¹	[σ ² (<i>F</i> _o ²) + (0.04 <i>P</i>) ² + 12 <i>P</i>] ⁻¹
(Δ/σ) _{max}	0.004	0.009
(Δρ) _{max} (e Å ⁻³)	0.906	0.483

^a Refined on *F*².

Table 2. Isolated Product Yields (%)

product	reaction conditions				
	1 [CpCr(CO) ₃] ₂ + 1 P ₄ Se ₃			thermolysis	
	6 days/RT	12 days/RT	2 h/60 °C	4 (4 h/60 °C)	8 (3 h/80 °C)
[CpCr(CO) ₂] ₂ Se (3)	0	0	19	0	0
Cp ₄ Cr ₄ (CO) ₉ (P ₄ Se ₃) (4)	48	27	36	0	0
CpCr(CO) ₃ H (5)	7	7	2	0	0
CpCr(CO) ₂ P ₃ (6)	2	8	8	7	4
[CpCr(CO) ₂] ₂ P ₂ (7)	16	0	9	24	53
Cp ₄ Cr ₄ (CO) ₈ (P ₂ Se ₂) (8)	13	33.5	16	54	0
Cp ₄ Cr ₄ Se ₄ (9)	0	0	3.5	13.5	30

Table 3. Time-Dependent Variation of Product Composition^a from the Reaction of [CpCr(CO)₃]₂ with an Equimolar Equivalent of P₄Se₃ under Ultrasonication at Ambient Temperature

complex ^b	time (h)			
	3	5	7	9
[CpCr(CO) ₃] ₂ (1)	63	0	0	0
[CpCr(CO) ₂] ₂ (2)	3	7	10	9
[CpCr(CO) ₂] ₂ Se (3)	13	31	16	8
Cp ₄ Cr ₄ (CO) ₉ (P ₄ Se ₃) (4)	4	27	39	41
CpCr(CO) ₂ P ₃ (6)	0	1	2	3
[CpCr(CO) ₂] ₂ P ₂ (7)	0	4	6	8
Cp ₄ Cr ₄ (CO) ₈ (P ₂ Se ₂) (8)	0	6	8	8

^a Product yields obtained by integration of Cp resonances in ¹H NMR spectrum of product mixture. ^b Do not include the complex/complexes possessing a cluster of unassignable Cp resonances at δ 5.22, 4.99, 4.86, 4.76, and 4.72 (total intensity of peaks ca. 10%).

NMR Tube Reactions. The following reactions were studied in septum-capped 5 mm tubes under argon via ¹H NMR spectral analysis.

(a) Reaction of [CpCr(CO)₃]₂ (1) with P₄Se₃. A deep green mixture of **1** (5 mg, 0.012 mmol) and P₄Se₃ (5 mg, 0.014 mmol) in benzene-*d*₆ (0.5 mL) was ultrasonicated at ambient temperature. Its ¹H NMR spectrum was recorded at intervals, and the estimated product compositions are presented in Table 3. After 9 h, the reaction mixture was reddish brown.

(b) Reaction of [CpCr(CO)₂]₂Se (3) with P₄X₃ (X = S, Se). An orange-brown 2 mM mixture of **3** with an equimolar equivalent of P₄Se₃ in benzene-*d*₆ was vigorously agitated with

the aid of a mechanical shaker. The reaction at ambient temperature was monitored at 24 h intervals for 4 days. A similar reaction was performed using P₄S₃.

(c) Thermolytic Degradation of Cp₄Cr₄(CO)₈(P₂Se₂) (8). An approximately 2 mM solution of **8** in benzene-*d*₆ was maintained at 50 °C, and its ¹H NMR spectrum recorded at hourly intervals up to 6 h. A final spectrum was scanned after 36 h.

Crystal Structure Analyses. Diffraction-quality single crystals of **4** and **8** were obtained as black triangular prisms and tetrahedra, respectively, from *n*-hexane/toluene after 7 and 10 days, respectively, at -28 °C.

The crystals used for unit cell determination and data collection were coated with epoxy glue to prevent decomposition in air. Details of the crystal parameters, data collection, and structure refinement are given in Table 1. The raw data were processed and corrected for Lorentz-polarization effects as well as for absorption.²⁰

The structure of **4** was solved by the direct method MULTAN 80²¹ and refined by full-matrix least-squares refinement using the SHELXL93²² package on an IBM486PC. Only the Cr, P, and Se atoms were refined anisotropically, while the C

(20) North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *24A*, 351.

(21) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; DeClerq, J. P.; Woolfson, M. M. MULTAN80; University of York, England, 1980.

(22) Sheldrick, G. M. *SHELXL93*; Institut für Anorganische Chemie, Universität Göttingen, Tammannstr. 4, 3400 Göttingen, Bundesrepublik Deutschland.

and O atoms were refined isotropically. A benzene ring was located on a 2-fold axis. The H atoms on the Cp rings were generated geometrically, while those on the solvent were left out. The H atoms were allowed to ride on their parent carbon atoms with temperature factors equal to 1.2 times its respective carbon atoms. The poor crystal quality resulted in a high *R*-factor of 13.7% for $I > 2\sigma(I)$ reflections.

The absolute structure²³ of **8** was solved by direct methods using the program SHELXS86²⁴ and were refined by using SHELXL93²² on an IBM486 PC. The non-hydrogen atoms were refined anisotropically, while the H atoms were generated geometrically and were allowed to ride with temperature factors equal to 1.2 times that of its parent carbon atoms. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.^{25a,b}

Results and Discussion

Reaction of [CpCr(CO)₃]₂ with P₄Se₃. (a) Product Isolation. The reaction of a deep green suspension of [CpCr(CO)₃]₂ (**1**) with 1 molar equiv of P₄Se₃ in toluene for 6 days at ambient temperature produced a dark brown mixture, from which were isolated Cp₄Cr₄(CO)₉(P₄Se₃) (**4**), CpCr(CO)₃H (**5**), CpCr(CO)₂P₃ (**6**), [CpCr(CO)₂]₂P₂ (**7**), and Cp₄Cr₄(CO)₈(P₂Se₂) (**8**) in 48, 7, 2, 16, and 13% yields, respectively. A prolonged reaction for 12 days yielded the complexes **4** (27%), **5** (7%), **6** (8%), and **8** (33.5%). The same reaction at 60 °C for 2 h produced the complexes [CpCr(CO)₂]₂Se (**3**) (19%), **4** (36%), **5** (2%), **6** (8%), **7** (9%), **8** (16%), and Cp₄Cr₄Se₄ (**9**) (3.5%). These product compositions and yields are summarized in Table 2 for comparison.

It may be noted that whereas the above reaction required 6 days at ambient temperature and 2 h at 60 °C for completion, the analogous reactions with P₄S₃ had taken 13 days and 3 h, respectively. This rate difference may be partially attributed to the relative P–X bond strengths (X = S, 444 ± 8 kJ mol^{−1}; X = Se, 363.6 ± 10 kJ mol^{−1}).²⁶

The main products isolated were **4**, the Se analogue of Cp₄Cr₄(CO)₉(P₄S₃), and **8**, a new tetrachromium complex for which there is no S analogue. It is significant that the yields of **4** (48%) and **8** (13%) after 6 days have changed to 27 and 33.5%, respectively, after 12 days of reaction. This suggests that the complex **8** had been derived from **4**, rather than directly from **1**, since all of **1** had completely reacted after 6 days. By then, **7** had also completely decomposed with a concomitant increase in **6**, a thermal degradation process that had been observed before in studies of **1** with P₄.^{5b} As in the reaction with P₄S₃,⁸ CpCr(CO)₃H (**5**) was an unexpected side product from this reaction, although in substantially lower yields (ca. 7%), which persisted unchanged throughout the reaction. The source of the “H” still remains uncertain, since all solvents had been meticulously dried. The hydride species was present in the crude product mixture prior to chromatographic workup and had also been observed as very weak signals in the

proton NMR spectra of crude product mixtures from the reactions of **1** with Ph₂E₂ (E = S, Se),²⁷ although its identity was not recognized at the time, owing to the variability of the chemical shift of the Cp resonance.^{27,28} In our earlier study of **1** with P₄S₃, we had demonstrated that the formation of **5** was suppressed by the presence of isoprene, the reagent used for the synthesis of the dimer **1** from the hydride **5**,¹⁷ and had deduced that the formation of an appreciable yield of the hydride was a consequence of the cage effect of P₄S₃ on the CpCr(CO)₃• radical, rendering its reverse dimerization unfavorable versus hydrogen atom abstraction from a hydrogen source. We had also detected the formation of the hydride in an NMR-scale reaction in deuteriobenzene, thus ruling out the stringently dried solvent as the source of “H”, thereby implying that the Cp ligands are the only other probable alternative source. However, hydrogen atom abstraction from Cp ligands by metal-centered radicals has not been reported, although halogen atom abstraction from organic halides by CpCr(CO)₃• has been well established from the work of Baird,²⁹ and atom-transfer reactions have been noted to constitute a common feature of metal-centered radicals.³⁰

(b) NMR Spectral Studies. The reaction of [CpCr(CO)₃]₂ (**1**) with 1 molar equiv of P₄Se₃ under ultrasonication at ambient temperature has been monitored via its ¹H NMR spectral changes, and the result is presented in Table 3. After 3 h, the spectrum showed the presence of the monoselenium complex [CpCr(CO)₂]₂Se (**3**) (13%), Cp₄Cr₄(CO)₉(P₄Se₃) (**4**) (4%), [CpCr(CO)₂]₂ (**2**) (3%), and unassignable Cp proton resonances at δ 5.22, 4.99, 4.87, 4.76, and 4.72 (total intensity 9%), together with unreacted **1** (63% recovery). **1** had completely reacted within ca. 5 h, giving **3** (31%) and **4** (27%) as main products, together with CpCr(CO)₂P₃ (**6**) (1%), [CpCr(CO)₂]₂P₂ (**7**) (4%), and Cp₄Cr₄(CO)₈(P₂Se₂) (**8**) (6%), as well as the above-mentioned unassignable Cp resonances (14%). Subsequently, after 9 h, the relative yield of **3** had decreased to 8%, while there are increased amounts of **4** (41%), **6** (3%), **7** (8%), and Cp₄Cr₄(CO)₈(P₂Se₂) (**8**) (8%). Indeed, this observation of a buildup in the amount of **3**, followed by decrease, is significant and had prompted a study on the reaction of the chromium–selenium complex **3** with P₄X₃ (X = S, Se), which is discussed in the following section.

Reaction of [CpCr(CO)₂]₂Se (3**) with P₄X₃ (X = Se, S). (a) Product Isolation.** The reaction of an orange-brown mixture of **3** and P₄Se₃ in toluene was more than 90% complete after 6 days at ambient temperature, producing Cp₄Cr₄(CO)₉(P₄Se₃) (**4**), CpCr(CO)₃H (**5**), CpCr(CO)₂P₃ (**6**), and Cp₄Cr₄(CO)₈(P₂Se₂) (**8**) in 4, 6, 2, and 82% yields, respectively.

A similar reaction of the Cr≡Se complex (**3**) with P₄S₃ in toluene gave the same products in similar yields [**4** (6%), **5** (5%), **6** (1%), **8** (51%)] and, in addition, [CpCr(CO)₂]₂S (**10**) (16%).

(b) NMR Spectral Studies. A time-dependent varia-

(23) Flack, H. D. *Acta Crystallogr.* **1983**, A39, 876.

(24) Sheldrick, G. M. *Acta Crystallogr.* **1990**, A46, 467.

(25) (a) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1. (b) *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C, Tables 4.2.6.8 and 6.1(26). Drowart, J.; Myers, C. E.; Szwarc, R.; Auwera-Mahieu, A.; Uy, O. M. *High Temp. Sci.* **1973**, 5, 482.

(27) Goh, L. Y.; Tay, M. S. Unpublished observations.

(28) MacConnachie, C. A.; Nelson, J. M.; Baird, M. C. *Organometallics* **1992**, 11, 2521.

(29) Huber, T. A.; Macartney, D. H.; Baird, M. C. (a) *Organometallics* **1993**, 12, 4715; (b) *Organometallics* **1995**, 14, 592.

(30) Brown, T. L. Atom Transfer Reactions and Radical Chain Processes Involving Atom Transfer. In *Organometallic Radical Processes*; Troglor, W., Ed.; Elsevier: Lucerne, Switzerland, 1990; p 67.

tion of the product composition from the reaction of **3** with 1 molar equiv of P₄Se₃ at ambient temperature has been monitored via ¹H NMR spectral scans for several days. After 1 day, the main product formed was Cp₄Cr₄(CO)₉(P₄Se₃) (**4**) together with small amounts of CpCr(CO)₃H (**5**), Cp₄Cr₄(CO)₈(P₂Se₂) (**8**), and Cp₄Cr₄Se₄ (**9**). Over 2–3 days, a gradual increase of the products **4**, **5**, **8**, and **9** was observed. Finally, after 4 days, most of **4** had degraded to **8**, accompanied by formation of **9**. A similar spectral study of the reaction of **3** with P₄S₃ also showed that **4** was the predominant product after 1 day, with a more substantial amount of the hydride **5**. The reaction of **3** was found to be complete after 3 days, giving **4** and **5** as the main products in estimated yields of 44 and 31%, respectively. After an additional day, **4** was found to have degraded to **8** and **9**, while the quantity of hydride had remained unchanged.

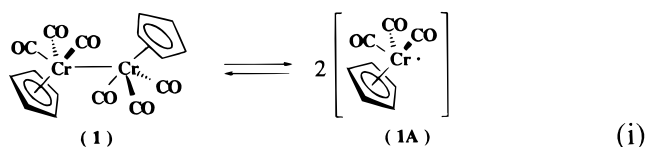
Reaction of [CpCr(CO)₂]₂ (2**) with P₄Se₃.** No reaction was observed in a mixture of **2** with 1 molar equiv of P₄Se₃ after 24 h at ambient temperature. At 60 °C, the reaction took ca. 18 h to reach completion, giving CpCr(CO)₃H (**5**), CpCr(CO)₂P₃ (**6**), [CpCr(CO)₂]₂P₂ (**7**), and Cp₄Cr₄Se₄ (**9**) in 24, 5, 10, and 34.5% yields, respectively. This product mixture resembles closely that from a similar reaction with P₄S₃, including the substantial yield of the hydride **5**, the formation of which must have involved intramolecular carbonyl scrambling in the complex **2**. It is significant that neither Cp₄Cr₄(CO)₉(P₄Se₃) (**4**) nor Cp₄Cr₄(CO)₈(P₂Se₂) (**8**) was obtained or detected in the reaction.

There are two possible pathways in this reaction. The products may be formed directly from the fragmentation of the P₄Se₃ cage by the Cr≡Cr bonded complex **2**, or they may be derived from the thermal degradation of an intermediate product. The latter route would lead to the formation of [CpCr(CO)₂]₂Se (**3**), as demonstrated in the thermolytic studies above. However, neither **3**, **4**, nor **8** was detected, suggesting that **4** or **8** is an unlikely primary product in this reaction.

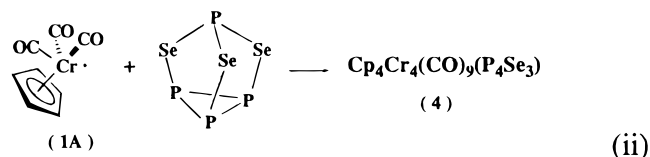
Thermolysis Studies. (a) Isolation of Products from Cp₄Cr₄(CO)₉(P₄Se₃) (4**) and Cp₄Cr₄(CO)₈(P₂Se₂) (**8**).** The thermolysis of a brown solution of Cp₄Cr₄(CO)₉(P₄Se₃) (**4**) in toluene at 60 °C for 4 h led to the isolation of **8** (54% yield) as the major product, together with CpCr(CO)₂P₃ (**6**), [CpCr(CO)₂]₂P₂ (**7**), and Cp₄Cr₄Se₄ (**9**) in 7, 24, and 13.5% yields, respectively. A similar thermolysis of a reddish brown solution of **8** at 80 °C for 3 h gave **6** (4%), **7** (53%), and **9** (30%) as isolated complexes. The degradation of **4** to **8** indicates that the former is the primary product in the reaction of **1** with P₄Se₃. Further degradation of **8** subsequently gave **6**, **7**, and **9** as secondary products. These product compositions and yields are included in Table 2.

(b) NMR Spectral Study of Cp₄Cr₄(CO)₈(P₂Se₂) (8**).** The thermolytic degradation of Cp₄Cr₄(CO)₈(P₂Se₂) (**8**) in benzene-*d*₆ at 50 °C was monitored via its ¹H NMR spectral changes. After 2 h, the formation of [CpCr(CO)₂]₂Se (**3**) (ca. 5%) and Cp₄Cr₄Se₄ (**9**) (ca. 5%) was observed. After a further 2 h, approximately 50% of **8** had decomposed (i.e., *t*_{1/2} ca. 4 h) and **3** and **9** were found to be present to the extent of ca. 4 and 15%, respectively. After ca. 36 h, **8** had completely degraded to mainly **9** and a small amount of [CpCr(CO)₂]₂P₂ (**7**).

Reaction Pathways. In accord with the established facile dissociation of **1** into the monomeric 17-electron species CpCr(CO)₃ (**1A**) (eq i), it is anticipated that its

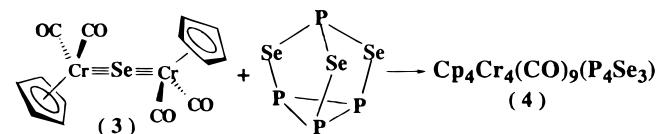


reaction with P₄Se₃, described in the preceding sections, proceeds through this radical species.³¹ The product isolation and NMR spectral studies seem to indicate that in this reaction **1A** is capable of two modes of action, viz., (a) a direct interaction with the P₄Se₃ cage, resulting in multiple P–P and P–Se bond cleavages, followed by structural rearrangement and concomitant coordination of CpCr(CO)_{*n*} (*n* = 2,3) fragments, as postulated for the reaction of P₄S₃,⁸ leading to the formation of the complex Cp₄Cr₄(CO)₉(P₄Se₃) (**4**) (eq ii),



and (b) a route involving an initial abstraction of Se from the P₄Se₃ molecule, forming [CpCr(CO)₂]₂Se (**3**), which subsequently reacts with a P₄Se₃ molecule to give the tetranuclear complex **4** (Scheme 1). That **3** is indeed an

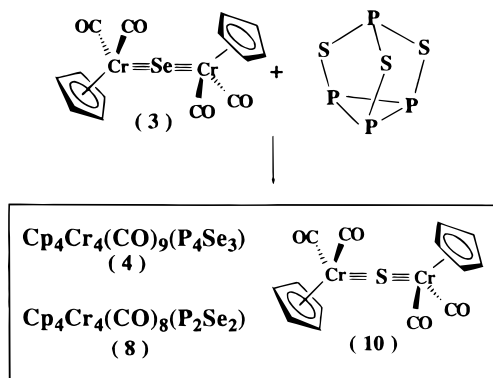
Scheme 1



intermediate is substantiated by various previously described observations, which include (i) its relatively high concentration in the early stages of the reaction at ambient temperature, followed by a buildup to a maximum level before declining with an accompanied increase in the yield of **4** (Table 3); (ii) the conspicuous absence of **3** among the final products from the ambient temperature reaction, as contrasted with a significant yield (13%) of [CpCr(CO)₂]₂S (**10**), the S analogue of **3**, from a similar reaction with P₄S₃,⁸ and (iii) the reaction of an authentic sample of **3** with P₄Se₃ to yield **4** and the hydride **5**. Indeed, the formation of **3** as a necessary initial step in the reaction is consistent with the observed faster rate of the reaction of **3** with P₄Se₃ (complete in ca. 6 days). This unexpected ability of **3** to react with the P₄Se₃ cage was also observed for the analogous P₄S₃ molecule, producing likewise the tetranuclear complexes **4** and **8** (Scheme 2), to the exclusion of any mixed S/Se analogues, Cp₄Cr₄(CO)₉(P₄Se_{*x*}S_(3-*x*)). The isolation of the additional product,

(31) (a) Goh, L. Y.; D'Aniello, M. J., Jr.; Slater, S.; Muetterties, E. L.; Tavanaiepour, I.; Chang, M. I.; Fredrich, M. F.; Day, V. W. *Inorg. Chem.* **1979**, *18*, 192. (b) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217, and ref 40 therein. (c) Adams, R. D.; Collins, D. E.; Cotton, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 749. (d) Madach, T.; Vahrenkamp, H. *Z. Naturforsch. B* **1978**, *33b*, 1301. (e) McLain, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 643. (f) Goh, L. Y.; Lim, Y. Y. *J. Organomet. Chem.* **1991**, *402*, 209.

Scheme 2



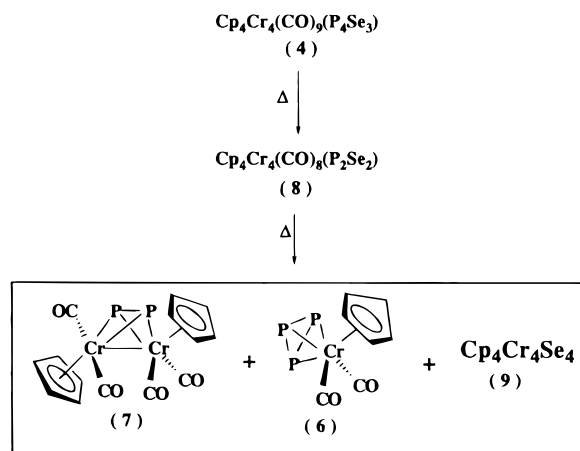
$[\text{CpCr}(\text{CO})_2]_2\text{S}$ (**10**), suggests that the complex **3** is capable of abstracting S from the P_4S_3 cage, creating reactive P_nS_m ($n = 1-4$, $m = 0-2$) fragments which must have reacted with **3** to form the Cr–P–Se complex (**4**). However, we have not been able to detect any reaction between the complex **3** and white elemental P_4 under similar thermal conditions. The high affinity of **3** for S has been earlier demonstrated in its facile reaction with elemental sulfur.¹⁹ Indeed, the high reactivity of the $\text{Cr}=\text{Se}=\text{Cr}$ bond in **3** is also manifested in insertions of a Se atom from elemental selenium,^{4b} of an $\text{Fe}(\text{CO})_3$ fragment from $\text{Fe}_2(\text{CO})_9$, and of CR_2 from CR_2N_2 .^{2j}

The variation of the isolated product composition with reaction conditions, as given in Table 2, shows that **8** is derived from the degradation of **4**, although this does not preclude/exclude its concurrent formation with **4** from the reaction of **1** with P_4Se_3 . The former route is supported by the thermolysis of **4** at 60 °C, which has resulted in decarbonylation together with loss of P and Se atoms followed by rearrangement to produce **8** in 54% yield after 4 h. Evidence for the subsequent degradation to **6**, **7**, and $\text{Cp}_4\text{Cr}_4\text{Se}_4$ (**9**) is provided by the thermolytic study of **8** (Scheme 3). There is also evidence for the formation of $[\text{CpCr}(\text{CO})_2]_2\text{Se}$ (**3**) (ca. 4%) from the NMR spectral monitoring of the thermolysis of **8**. The failure to isolate this low-yield product is consistent with its facile conversion to **9**.^{4b,18} These observations suggest that **3** (19.4%) and **9** (3.5%), isolated from the reaction of **1** with P_4Se_3 at 60 °C, arise from thermolytic degradation of **8**. This, indeed, is in agreement with the total absence of **3** from the ambient-temperature reaction, as discussed above.

Properties and Spectral Characteristics. Both the complexes $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{Se}_3)$ (**4**) and $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)$ (**8**) exist as dark brown crystals, stable for several days in air at ambient temperature. They are soluble in most organic solvents, except *n*-hexane, giving yellowish brown and reddish brown solutions, respectively. The solutions are slightly air-sensitive but fairly stable at room temperature under an inert atmosphere for several days.

The ^1H NMR spectrum of **4** in benzene- d_6 shows two sets of Cp resonances with relative intensity ca. 4:1, viz., the major signals at δ 4.56, 4.47 (with a shoulder at 4.45), and 4.26 (relative intensity 1:2:1) and the weaker signals at δ 4.79, 4.69, and 4.13 (relative intensity 1:2:1). In the ^{13}C NMR spectrum in benzene- d_6 , the Cp resonances are seen as high-intensity signals at δ 91.97,

Scheme 3



90.66 (with a slight shoulder at ca. 90.7), and 90.40 and lower intensity peaks at δ 93.91, 92.42, 92.34, and 91.32. Thus both the ^1H and ^{13}C NMR spectra are indicative of the presence of two isomers, each possessing four Cp rings, two of which are in almost identical magnetic environment, as was also observed before for the S analogue.⁸ The ^{31}P NMR spectrum in benzene- d_6 shows a predominant singlet peak at δ 300.87, together with a very weak broad singlet at δ 357.4 and a myriad of weak signals between δ -10 and 200, appearing as ill-defined multiplets centered at δ ca. 189, 169, 158, 137, 75, 69, and -0.7 and with total intensity approximately equal to that of the main peak. The main signal is accompanied by two pairs of ^{77}Se satellites (7.8% of main peak) with $J(\text{Se},\text{P})$ 515.3 and 343.5 Hz, respectively). No appreciable difference was observed between spectra measured at ambient temperature and at -80 °C in toluene- d_8 . Despite various attempts, we have not been able to obtain an assignment of the signals to the P atoms of the P_4Se_3 moiety in the complex, as was possible for the P_4S_3 analogue.⁸ The IR spectrum in Nujol shows $\nu(\text{CO})$ 1947vs, 1923vs, 1886vs, 1848s and $\nu(\text{others})$ 1063w, 1011w, 828s, 728w, 634s, 580s, 554s, 525w cm^{-1} .

The proton NMR spectrum of **8** in benzene- d_6 shows two Cp resonances at δ 4.69 and 4.12, which are observed at δ 4.71 and 4.14 in toluene- d_8 . The Cp resonances are observed at δ 93.10 and 89.91 in the ^{13}C NMR spectrum in benzene- d_6 and the P atoms at δ 333.24 in the ^{31}P NMR spectrum in toluene- d_8 . The IR spectrum shows $\nu(\text{CO})$ 1943vs, 1889s cm^{-1} in toluene and 1968s sh, 1946vs sh, 1928vs, 1904vs, 1892vs, 1870s sh, 1852s cm^{-1} in Nujol.

Crystal Structures. $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{Se}_3)$ (**4**)- $1/2\text{-C}_6\text{H}_6$. The molecular structure is shown in Figure 1. Selected bond lengths and bond angles are given in Table 4. The structure, very similar to that of its S analogue,⁸ contains one $\text{CpCr}(\text{CO})_3$ and three $\text{CpCr}(\text{CO})_2$ fragments coordinated to the four P atoms of a five-membered P_4Se ring, which forms the central component of an opened-up conformation of the P_4Se_3 cage. In fact, the only difference in the structures of these S and Se analogous complexes lies in the difference in bond distances dictated by the difference (0.14 Å) in the covalent radii of Se and S.

Besides its S analogue,⁸ **4** is the only other instance

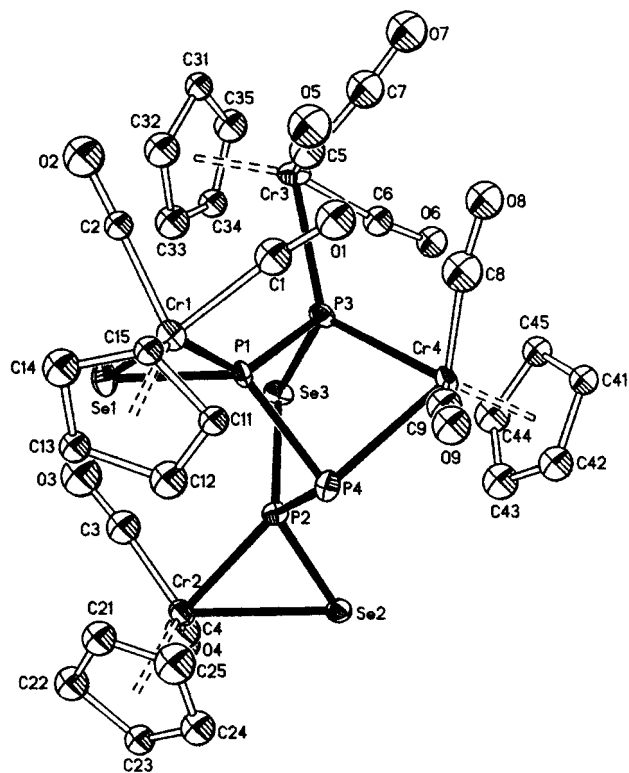


Figure 1. ORTEP plot (at 20% probability level) for the molecular structure of **4**.

of complexes formed from multiple bond cleavage without fragmentation of the P₄E₃ cage molecule by a transition metal complex. Earlier examples from Stopponi's work contain either the intact P₄Se₃ cage¹¹ or fragments of P₄Se₃, e.g., P₃Se₃¹⁰ or P₂Se,¹² as ligands.

Cp₄Cr₄(CO)₈(P₂Se₂) (8**).** The compound crystallized in the chiral space group C₂₂2₁; its absolute molecular structure is shown in Figure 2. Selected bond lengths and bond angles are given in Table 5. The P–P bond distance of 2.233(3) Å is very close to those in the P₄Se₃ cage (mean 2.25 Å).³² Known values of P–P bond lengths average 2.22 Å in the P₁₀ core of [CpCr(CO)₂]₅P₁₀⁵ and 2.21 Å in P₄ vapor.³³ The P–Se distance of 2.250(3) Å is very close to that in the intact P₄Se₃ cage (mean 2.24 Å).³² The Cr–P distances (2.340(3) and 2.393(3) Å) fall within the range 2.341–2.494 Å observed for other CpCr complexes with phosphorus ligands.^{5,6} The Cr–Se distances (2.566(2) and 2.575(2) Å) are longer than those observed in the (μ-η²-Se₂) complex [CpCr(CO)₂]₂Se₂ (2.538–2.551 Å)^{4b} or in the cubanes Cp₄Cr₄Se₂(CO)₂ (2.317–2.400 Å) and Cp₄Cr₄Se₂O₂ (2.441–2.462 Å).¹⁸

The molecule possesses 2-fold symmetry with the symmetry axis passing through the midpoint of the P–P bond. This bond forms the backbone of an unusual "open-book" framework and joins two CrP₂Se trapezoidal planes separated by a dihedral angle of 119.4°. The PSe edges of the trapezoids are each η²-bonded to a CpCr(CO)₂ fragment. Thus each of the Cr atoms assumes a four-legged piano stool configuration. Each of the P atoms is tetrahedrally coordinated, while the Se atoms are each three-coordinate. It is noted in compari-

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) of **4**

Se(1)–P(1)	2.162(8)	Cr(3)–C(7)	1.80(4)
Se(1)–Cr(1)	2.636(6)	Cr(3)–C(5)	1.80(4)
Se(2)–P(2)	2.173(8)	Cr(3)–C(6)	1.86(3)
Se(2)–Cr(2)	2.635(6)	Cr(3)–Cp(3) ^a	1.85(3)
Se(3)–P(2)	2.256(8)	Cr(3)–P(3)	2.506(9)
Se(3)–P(3)	2.315(8)	Cr(4)–C(8)	1.80(4)
Cr(1)–C(2)	1.81(3)	Cr(4)–C(9)	1.91(3)
Cr(1)–C(1)	1.91(4)	Cr(4)–Cp(4) ^a	1.84(3)
Cr(1)–Cp(1) ^a	1.81(3)	Cr(4)–P(3)	2.397(9)
Cr(1)–P(1)	2.298(9)	Cr(4)–P(4)	2.490(9)
Cr(2)–C(3)	1.79(4)	P(1)–P(4)	2.185(11)
Cr(2)–C(4)	1.79(4)	P(1)–P(3)	2.195(11)
Cr(2)–Cp(2) ^a	1.84(3)	P(2)–P(4)	2.201(11)
Cr(2)–P(2)	2.282(9)		
P(1)–Se(1)–Cr(1)	56.2(2)	C(8)–Cr(4)–P(4)	129.2(12)
P(2)–Se(2)–Cr(2)	55.7(2)	C(9)–Cr(4)–P(4)	79.4(10)
P(2)–Se(3)–P(3)	93.7(3)	P(3)–Cr(4)–P(4)	74.5(3)
C(2)–Cr(1)–C(1)	81.6(13)	Se(1)–P(1)–P(4)	123.9(4)
C(2)–Cr(1)–P(1)	106.9(9)	Se(1)–P(1)–P(3)	118.4(4)
C(1)–Cr(1)–P(1)	89.9(10)	P(4)–P(1)–P(3)	84.9(4)
C(2)–Cr(1)–Se(1)	84.5(9)	Se(1)–P(1)–Cr(1)	72.4(3)
C(1)–Cr(1)–Se(1)	132.3(10)	P(4)–P(1)–Cr(1)	123.7(4)
P(1)–Cr(1)–Se(1)	51.4(2)	P(3)–P(1)–Cr(1)	139.0(4)
C(3)–Cr(2)–C(4)	83(2)	Se(2)–P(2)–P(4)	112.1(4)
C(3)–Cr(2)–P(2)	83.0(11)	Se(2)–P(2)–Se(3)	115.8(3)
C(4)–Cr(2)–P(2)	112.8(12)	P(4)–P(2)–Se(3)	104.2(4)
C(3)–Cr(2)–Se(2)	119.5(11)	Se(2)–P(2)–Cr(2)	72.5(3)
C(4)–Cr(2)–Se(2)	81.2(2)	P(4)–P(2)–Cr(2)	125.5(4)
P(2)–Cr(2)–Se(2)	51.9(2)	Se(3)–P(2)–Cr(2)	122.9(4)
C(7)–Cr(3)–C(5)	80(2)	P(1)–P(3)–Se(3)	99.1(4)
C(7)–Cr(3)–C(6)	79(2)	P(1)–P(3)–Cr(4)	89.5(3)
C(5)–Cr(3)–C(6)	118.5(14)	Se(3)–P(3)–Cr(4)	109.2(3)
C(7)–Cr(3)–P(3)	126.0(12)	P(1)–P(3)–Cr(3)	121.6(4)
C(5)–Cr(3)–P(3)	76.1(11)	Se(3)–P(3)–Cr(3)	100.1(3)
C(6)–Cr(3)–P(3)	71.4(9)	Cr(4)–P(3)–Cr(3)	133.1(4)
C(8)–Cr(4)–C(9)	80(2)	P(1)–P(4)–P(2)	93.7(4)
C(8)–Cr(4)–P(3)	80.7(12)	P(1)–P(4)–Cr(4)	87.4(4)
C(9)–Cr(4)–P(3)	114.6(10)	P(2)–P(4)–Cr(4)	108.1(4)

^a Cp(1), Cp(2), Cp(3), and Cp(4) are centroids of respective Cp rings.

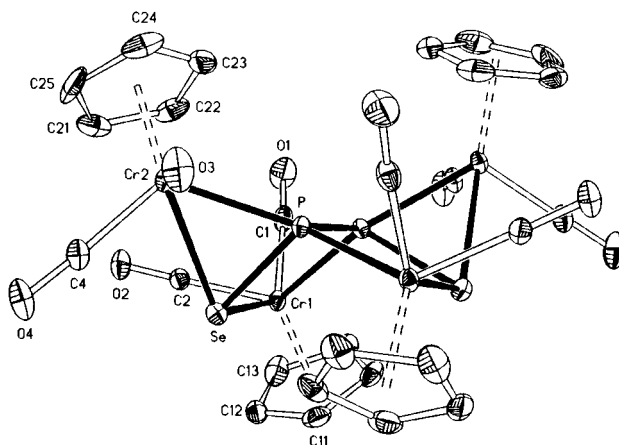


Figure 2. ORTEP plot (at 20% probability level) for the molecular structure of **8**.

son that in **4**, whereas three of the P atoms are also four-coordinate, the fourth P atom is three-coordinate, and all three Se atoms are two-coordinate. The approximately Z-shaped configuration of the Se–P–P–Se four-atom aggregate and its manner of bonding to the CpCr(CO)₂ fragments is an unusual feature not observed before in complexes arising from reactions of transition metal compounds with the P₄X₃ (X = S, Se) molecules. Scherer had obtained the complexes Cp₄Fe₄–(P₂X₂)₂ (X = S, Se) from the oxidation of the P₂ units of

(32) Keulen, E.; Vos, A. *Acta Crystallogr.* **1959**, *12*, 323.

(33) Maxwell, L. R.; Hendricks, S. B.; Mosley, V. M. *J. Chem. Phys.* **1935**, *3*, 699.

Table 5. Selected Bond Lengths (Å) and Angles (deg) of **8^a**

Se–P	2.250(2)	C(1)–Cr(1)–P#1	82.3(2)
Se–Cr(2)	2.565(1)	C(2)–Cr(1)–P#1	123.8(2)
Se–Cr(1)	2.565(1)	C(1)–Cr(1)–Se	126.1(2)
Cr(1)–C(1)	1.823(8)	C(2)–Cr(1)–Se	76.5(2)
Cr(1)–C(2)	1.854(7)	P#1–Cr(1)–Se	74.03(5)
Cr(1)–Cp(1) ^b	1.845(8)	C(3)–Cr(2)–C(4)	82.6(3)
Cr(1)–P#1	2.386(2)	C(3)–Cr(2)–P	81.8(2)
Cr(2)–C(3)	1.824(8)	C(4)–Cr(2)–P	118.3(2)
Cr(2)–C(4)	1.843(8)	C(3)–Cr(2)–Se	110.9(3)
Cr(2)–Cp(2) ^b	1.844(8)	C(4)–Cr(2)–Se	77.3(2)
Cr(2)–P	2.346(2)	P–Cr(2)–Se	54.31(5)
P–P#1	2.233(3)	P#1–P–Se	83.48(8)
P–Cr(1)#1	2.386(2)	P#1–P–Cr(2)	117.13(10)
O(1)–C(1)	1.146(9)	Se–P–Cr(2)	67.81(5)
O(2)–C(2)	1.139(8)	P#1–P–Cr(1)#1	103.93(9)
O(3)–C(3)	1.154(8)	Se–P–Cr(1)#1	119.56(7)
O(4)–C(4)	1.142(8)	Cr(2)–P–Cr(1)#1	138.94(8)
⟨C–C⟩ _{cp}	1.37(1)	O(1)–C(1)–Cr(1)	173.6(7)
P–Se–Cr(2)	57.88(5)	O(2)–C(2)–Cr(1)	177.4(6)
P–Se–Cr(1)	97.98(5)	O(3)–C(3)–Cr(2)	175.5(6)
Cr(2)–Se–Cr(1)	117.09(4)	O(4)–C(4)–Cr(2)	177.1(7)
C(1)–Cr(1)–C(2)	78.0(3)	⟨C–C⟩ _{cp}	108.0(9)

^a Symmetry transformations used to generate equivalent atoms: #1 *x*, *–y*, *–z*. ^b Cp(1)–Cp(2) are centroids of the respective Cp rings.

Cp₄Fe₄(P₂)₂ with S₈ and gray Se, respectively; these Fe complexes also possess the X–P–P–X moiety in a

similar *cisoid* configuration, but without further η²-PX coordination as observed in **8**.³⁴

Acknowledgment. The authors gratefully acknowledge support from the University of Malaya, from the Malaysian IRPA R&D Grant No. 04-07-04-211 (L.Y.G.) and 09-02-03-0004 (C.W.), and presently, also Grant RP 3972673 from the National University of Singapore (L.Y.G.). They also thank Dr. K. Karaghiosoff (Universität München) for measurement of ³¹P NMR spectra, Dr. Z.-Y. Zhou of Academia Sinica, Chengdu, and Dr. H. K. Fun (Universiti Sains Malaysia) for crystal structure refinement of complex **8**, and finally the Research School of Chemistry, Australian National University, for access to its NMR facilities during a visiting research fellowship to L.Y.G.

Supporting Information Available: For structures of **4** and **8**, a listing of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and packing diagrams (16 pages). See any current masthead page for ordering information and Internet access instructions.

OM9806388

(34) Scherer, O. J.; Kemény, G.; Wolmershäuser, G. *Chem. Ber.* **1995**, *128*, 1145.