

### III EXPERIMENTAL

#### 3.1 General Procedures

All reactions were carried out using conventional Schlenk techniques under an inert atmosphere of nitrogen or argon. Work-up procedures and products isolation were mainly done in a Vacuum Atmospheres Dribox equipped with a Model HE 493 Dri-Train under argon.

##### 3.1.1 Elemental analyses

Elemental P, Se, S, As, and W analyses were performed by the Analytical Unit of the Research School of Chemistry, Australian National University. Elemental C and H analyses were performed by the Industrial Research & Consultancy Unit of Universiti Sains Malaysia. Elemental chromium was analysed spectrophotometrically after oxidation to chromate,  $\text{CrO}_4^{2-}$ , in an alkaline medium by the method of Haupt ( $\epsilon_{\text{max}}^{372\text{nm}} = 4.815 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ ).

##### 3.1.2 Physical measurements

N.M.R. samples were prepared in the Dribox and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a JEOL FX100 100 FT MHz, JEOL GSX 270 270 FT MHz and Varian VXR300 300 FT spectrometers at the Research School of Chemistry, Australian National University, Canberra. Proton and carbon chemical shifts were referenced to residual  $\text{C}_6\text{H}_6$  in benzene- $d_6$  or to  $(\text{CH}_3)_4\text{Si}$  in toluene- $d_8$  respectively.  $^{31}\text{P}$  NMR spectra were measured on the JEOL FX90Q FT, 36.23-Mhz spectrometer and chemical shifts referenced to external  $\text{H}_3\text{PO}_4$ . IR spectra in nujol mulls or solution were measured in the range  $4000\text{--}200 \text{ cm}^{-1}$  by means of a Perkin-Elmer 1600 FT-IR and JASCO IR REPORT-100 spectrophotometer. The EI mass spectra were run on a VG ProSpec spectrometer and the FAB mass spectra were measured per kindness of Dr. J. MacLeod of the Research School of Chemistry, Australian National University,

Canberra. The VISIBLE spectrum of  $\text{CrO}_4^{2-}$  (for Cr analysis) was measured on a Beckmann DU-7 spectrometer.

### 3.1.3 Solvents and reagents

All solvents used are of AR grade and distilled before use. Hexane and toluene are distilled over sodium/benzophenone. Tetrahydrofuran and ether were dried over sodium hydroxide pellets and distilled over sodium/ benzophenone. Acetonitrile was distilled over calcium hydride. Chromatographic materials were silica gel, (Merck Kieselgel 60, 35-70 and 230-400 Mesh ASTM); florisil (Sigma, 100-200 Mesh); aluminium oxide (Standardised, Merck), Celite (Fluka AG) and Kieselgel 60 F<sub>254</sub> TLC plates were dried at 150°C overnight before chromatographic use. Chromium hexacarbonyl (99% purity) was purchased from Aldrich Chemical Company. Yellow phosphorus was used as supplied by BDH Chemicals Ltd., without further purification. Tetraphosphorus trisulfide,  $\text{P}_4\text{S}_3$ , was purchased from Fluka AG and used after recrystallization from benzene.  $\text{As}_4\text{S}_4$  was purchased from Alfa Inorganics.

## 3.2 Preparation of starting complexes

### 3.2.1 Preparation of Dicyclopentadienylhexacarbonyldichromium, $[\text{CpCr}(\text{CO})_3]_2$

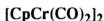
The procedure was adapted from Manning *et al.*<sup>110</sup> as follows :

To a stirred suspension of thinly sliced sodium metal (0.39 g, 0.017 mol) in diglyme (67 mL) in a 3-necked 250 mL round-bottomed flask was added freshly cracked cyclopentadiene (4 mL) *via* a syringe over a period of 30 min. Stirring was continued until all the sodium has reacted giving a pink coloured solution. Hexacarbonyl chromium (4.54 g, 0.033 mol) was then added and the yellow mixture refluxed with stirring for *ca.* 4 h, using an oil bath maintained at 175°C. The hexacarbonyl chromium sublimate on the condenser walls was occasionally dislodged with a glass rod and returned back to the reaction flask. When the reaction was complete, the



resultant greenish yellow product mixture was cooled to room temperature. After carefully removing the reflux condenser coated with some remaining sublimed hexacarbonyl chromium, a solution of hydrated ferric sulphate (6.6 g, 0.013 mol) in water (80 mL) and acetic acid (5 mL) was slowly added with stirring over a period of *ca.* 0.5 h. Fine deep green solids of dicyclopentadienylhexacarbonyl<sup>dichromium</sup> were precipitated. The suspension was transferred via a cannula tubing into a 200 mL coarse sintered filter funnel layered with Celite (1 cm). The collected precipitate was washed with distilled water (3 x 10 mL) followed by 50% methanol-water mixture (3 x 5 mL) and dried overnight in vacuo. Purification by sublimation at *ca.* 120°C/ 0.1 mm Hg gave a dark green crystalline product (2.41 g, *ca.* 60% yield) which was stored in the Dribox at ambient temperature.

### 3.2.2 Preparation of Dicyclopentadienyltetracarbonyldichromium,



The procedure was adapted from Hackett *et al.*<sup>61</sup> as follows :

A deep green suspension of  $[\text{CpCr}(\text{CO})_3]_2$  (200 mg, 0.497 mmol) in toluene (15 mL) was heated to reflux for 6 h. The resultant green solution was chromatographed on a silica gel column (1.5 cm x 4 cm) prepared in toluene. The eluate in toluene (30 mL) was then concentrated to *ca.* 5 mL and *n*-hexane (*ca.* 1 mL) was added. Cooling at -30°C for 1 h yielded fine deep green crystals of  $[\text{CpCr}(\text{CO})_2]_2$  (163 mg, 0.471 mmol, *ca.* 95% yield).

### 3.2.3 Synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}$

The compound  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}$  was synthesized by a modification of the literature procedure.<sup>111</sup> To a yellow suspension of  $\text{Na}[\eta^5\text{-CpCr}(\text{CO})_3]$  (400 mg, 1.785 mmol) in hexane (8 mL), glacial acetic acid (0.114 mL) dissolved in hexane (1 mL) was introduced via a syringe. The mixture was stirred for 2 h under an ice bath maintained at 0°C. The resultant greenish yellow mixture was concentrated to dryness

to gave a greenish yellow residue (*ca.* 400 mg). The residue was extracted with *n*-hexane-toluene (5:1, 5 x 15 mL), leaving behind fine yellow solids of unreacted  $\text{Na}[\text{CpCr}(\text{CO})_3]$  (*ca.* 135 mg, 0.603 mmol, 33.8% recovered). The greenish yellow extracts was concentrated to *ca.* 2 mL and loaded onto a silica gel column (2 cm x 5 cm) prepared in *n*-hexane. Two fractions were eluted :

Fraction (i) : a yellow eluate in hexane (75 mL) which yielded fine yellow crystalline solids of  $\eta^5\text{-CpCr}(\text{CO})_3\text{H}$  (150 mg, 0.743 mmol, 41.8% yield).

Fraction (ii) : a deep green eluate in toluene (50 mL) which yielded dark green crystalline solids of  $[\eta^5\text{-CpCr}(\text{CO})_3]_2$  (73 mg, 0.182mmol, 20.3% yield).

### 3.2.4 Preparation of Metal Carbonyl fragments, $\text{M}(\text{CO})_5\text{THF}$

A colourless solution of  $\text{Cr}(\text{CO})_6$  (70 mL, 1.54 g/mL) was irradiated with an ultra-violet light from a 125 W mercury high pressure lamp in a Hanovia photochemical reactor. The solution was magnetically stirred, and cooled with running water during irradiation. The progress of the reaction was followed by monitoring the I.R. spectrum of the solution in the carbonyl region at 0.5 hourly intervals. A gradual disappearance of the strong characteristic band of the  $\text{M}(\text{CO})_6$  compounds was observed [ $\nu_{\text{CO}}(\text{THF})$  :  $\text{Cr}(\text{CO})_6$ , 1972  $\text{cm}^{-1}$  and  $\text{W}(\text{CO})_6$ , 1969  $\text{cm}^{-1}$ ]. The complete conversion to  $\text{M}(\text{CO})_5(\text{THF})$  took 4-5 h, yielding an orange yellow solution.

### 3.2.5 Preparation of Tetraphosphorus Triselenide, $\text{P}_4\text{Se}_3$

The procedure was adapted from K. Irgolic, R.A. Zingaro and M. Kudchadker<sup>112</sup> as follows :

A suspension of yellow phosphorus (2.5 g, 0.081 mol P), finely powdered gray selenium (5 g, 0.063 mol Se) and powdered charcoal (7.5 g) in *n*-heptane (85 mL) placed in a three-necked 250 mL flask with a distilling head, was refluxed for 1 h under stirring, after which time 38 mL of tetralin was added through the third neck. The temperature was slowly raised over a period of *ca.* 45 min. until it reached 207°C,

at this point most of the *n*-heptane was removed by distillation through the distilling head. The hot mixture was allowed settled and the clear supernatant was decanted into a coarse sintered funnel. The residue remaining in the flask, consisting of charcoal, selenium and phosphorus selenide, was extracted with hot tetralin (3 x 15 mL). The combined supernatant filtrate and washings were cooled in ice and the tetraphosphorus triselenide crystallised out as fine yellow orange crystalline powder (4.15 g, 0.012 mol, 56.8% yield).

### 3.2.6 Preparation of Diiron Enneacarbonyl, $\text{Fe}_2(\text{CO})_9$

A mixture of iron pentacarbonyl (20 mL, 29.2 g, 0.149 mol) and glacial acetic acid (40 mL) was irradiated with an ultra-violet light source using a 125W mercury high pressure lamp in a Hanovia photochemical reactor. The solution was magnetically stirred, and cooled with running water during irradiation. The photochemical reactor was placed in a container carefully lined on sides and bottom with aluminium foil and the temperature maintained between 20-25°C by means of running water. After 24 h of irradiation, the precipitated diiron enneacarbonyl was filtered out of solution. The orange crystalline product (22.5 g, 0.062 mol, 83% yield) was first washed with ethanol and then with ether, and was dried *in vacuo*.

### 3.2.7 Preparation of $\text{Cp}_2\text{Cr}_2(\text{CO})_4\text{Se}$

The procedure was adapted from L.Y. Goh *et al.*<sup>14a</sup> as follows :

A deep green suspension of  $[\text{CpCr}(\text{CO})_3]_2$  (800 mg, 1.990 mmol) and grey  $\text{Se}_8$  (157 mg, 1.99 mmol) in tetrahydrofuran (35 mL) was allowed to stir for *ca.* 15 min at ambient temperature. The resultant reddish brown homogeneous solution was filtered *via* a sintered filter funnel layered with Celite (2 cm). The filtrate was concentrated to dryness to give dark reddish brown crystalline solids of  $\text{Cp}_2\text{Cr}_2(\text{CO})_4\text{Se}$  (795 mg, 1.871 mmol, 94% yield).

### 3.3 Cothermolysis of $[\text{CpCr}(\text{CO})_3]_2$ with elemental Phosphorus - isolation and characterisation of $[\text{CpCr}(\text{CO})_2]_5\text{P}_{10}$

#### 3.3.1 Isolation of $[\text{CpCr}(\text{CO})_2]_5\text{P}_{10}$

A deep green suspension of  $[\text{CpCr}(\text{CO})_3]_2$  (1.0 g, 2.488 mmol) and yellow  $\text{P}_4$  (617 mg, 4.976 mmol) in toluene (50 mL) was stirred at  $85^\circ\text{C}$  for 3.5 h. The resultant reddish brown solution was cooled to room temperature before filtering through Celite (1.5 cm x 4 cm). The filtrate was concentrated, absorbed onto Celite (*ca.* 2 g) and evacuated to dryness. It was then loaded onto an alumina column (2.0 cm x 15 cm) prepared in *n*-hexane. Elution gave four fractions :

Fraction (i) : a yellow eluate in *n*-hexane (65 mL) which upon concentration to dryness yielded yellowish brown platelets of  $\text{CpCr}(\text{CO})_2\text{P}_3$  (375 mg, 1.410 mmol, 28.3% yield).

Fraction (ii) : a deep green eluate in *n*-hexane-toluene (2:1, 55 mL) which gave fine dark green crystalline of  $[\text{CpCr}(\text{CO})_2]_2$  (145 mg, 0.419 mmol, 16.8% yield).

Fraction (iii) : a magenta eluate in *n*-hexane-toluene (1:1, 45 mL) followed by toluene (35 mL) which gave dark magenta crystalline solids of  $[\text{CpCr}(\text{CO})_2]_2\text{P}_2$  (323 mg, 0.803 mmol, 31.8% yield).

Fraction (iv) : a reddish brown eluate in ether-toluene (1:1, 60 mL) followed by ether (45 mL), which on concentration to *ca.* 15 mL with *n*-hexane (*ca.* 1 mL) added and slow crystallisation at  $-28^\circ\text{C}$  overnight, gave fine brown solids of  $[\text{CpCr}(\text{CO})_2]_5\text{P}_{10}$  (155 mg, 0.132 mmol, 13.3% yield) as the first crop and recrystallisation of the mother liquor gave a second crop (50 mg, 0.043 mmol, 4.2% yield).

### 3.4 Reactions with elemental Arsenic

#### 3.4.1 Reactions of $[\text{CpCr}(\text{CO})_3]_2$

##### 3.4.1.1 Isolation of products

##### (a) Cothermolysis at $110^\circ\text{C}$ for 1.5 h : isolation of $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$ , $\text{CpCr}(\text{CO})_2\text{As}_3$ and $\text{Cp}_2\text{Cr}_2\text{AsO}_5$

A suspension of finely ground gray arsenic (1.223 g , 16.4 mmol) in a deep green solution of  $[\text{CpCr}(\text{CO})_3]_2$  (400 mg, 0.995 mmol) in toluene (*ca.* 20 mL) was stirred under gentle reflux for *ca.* 1 h. The resultant reaction mixture had changed to purplish black. The mixture was concentrated to *ca.* 2 mL, absorbed onto silica gel (*ca.* 2.5 g), and evacuated to dryness. It was then loaded onto a silica gel column (1.5 cm x 15 cm) prepared in *n*-hexane. Elution gave five fractions :

Fraction (i) : a yellow eluate in *n*-hexane (15 mL) followed by *n*-hexane-toluene (9:1, 15 mL) which upon concentration to dryness yielded fine orange yellow flakes of  $\text{CpCr}(\text{CO})_2\text{As}_3$  (112 mg, 0.281 mmol, 14.2% yield). Anal. Calcd. for  $\text{C}_7\text{H}_5\text{CrO}_2\text{As}_3$  : C, 21.13; H, 1.27; Cr, 13.06; As, 56.49%. Found : C, 21.23; H, 1.28; Cr, 13.29; As, 56.49%.

Fraction (ii) : a dirty green eluate in *n*-hexane-toluene (1:1, 10 mL) which gave green solids (21 mg, dried residue), the  $^1\text{H}$  NMR spectrum of which showed the presence of a 1: 6 molar mixture of  $\text{CpCr}(\text{CO})_2\text{As}_3$  (0.4% yield) and  $[\text{CpCr}(\text{CO})_2]_2(\text{Cr}=\text{Cr})$  (5.3% yield), identified by its  $^1\text{H}$  NMR in benzene- $d_6$  ( $\delta$  4.23) and TLC against an authentic sample [ $R_f$  = 0.51 with *n*-hexane-toluene (3:2) as eluent] (Table 43).

Fraction (iii) : a purple eluate in toluene (40 mL) from which was obtained fine dark purple crystalline solids of  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$  (100 mg, 0.202 mmol, 20.4% yield). Anal. Calcd. for  $\text{C}_{14}\text{H}_{10}\text{Cr}_2\text{O}_4\text{As}_2$  : C, 33.90; H, 2.03; Cr, 20.97; As, 30.21%. Found : C, 33.92; H, 1.92; Cr, 20.75; As, 30.36%.

Fraction (iv) : a brown eluate in ether (5 mL) and THF (5 mL) which gave an unidentified dark brown oily residue (*ca.* 10 mg), the  $^1\text{H}$  NMR spectrum of which showed Cp resonances at  $\delta$  7.73, 7.66 and 5.48 (broad).

Table 43. R.F. values on silica gel 60F<sub>254</sub> plate

	Complex	Color	R.F. Value	Eluent
1.	[CpCr(CO) <sub>2</sub> ] <sub>2</sub> As <sub>2</sub> (2)	Purple	0.27	a
2.	CpCr(CO) <sub>2</sub> As <sub>3</sub> (3)	Yellow	0.51	a
3.	[CpCr(CO) <sub>2</sub> ] <sub>2</sub> (4)	Green	0.56	a
4.	Cp <sub>2</sub> Cr <sub>2</sub> As <sub>5</sub> (5)	Orange	0.58	a
5.	Cp <sub>4</sub> Cr <sub>4</sub> (CO) <sub>9</sub> P <sub>4</sub> S <sub>3</sub> (9)	Brown	0.10	a
6.	[CpCr(CO) <sub>2</sub> ] <sub>2</sub> S (10)	Greenish yellow	0.59	a
7.	CpCr(CO) <sub>3</sub> H (11)	Pale yellow	0.69	a
8.	Cp <sub>4</sub> Cr <sub>4</sub> (CO) <sub>9</sub> P <sub>4</sub> Se <sub>3</sub> (12)	Brown	0.08	a
9.	Cp <sub>4</sub> Cr <sub>4</sub> (CO) <sub>8</sub> P <sub>2</sub> Se <sub>2</sub> (13)	Reddish brown	0.28	a
10.	CpCr(CO) <sub>2</sub> P <sub>3</sub> (14)	Yellow	0.65	a
11.	[CpCr(CO) <sub>2</sub> ] <sub>2</sub> P <sub>2</sub> (15)	Magenta	0.41	a
12.	Cp <sub>2</sub> Cr <sub>2</sub> P <sub>5</sub> (16)	Orange yellow	0.67	a
13.	[CpCr(CO) <sub>2</sub> ] <sub>2</sub> Se (17)	Orange brown	0.59	a
14.	Cp <sub>4</sub> Cr <sub>4</sub> S <sub>4</sub> (18)	Green	0.52	b
15.	Cp <sub>4</sub> Cr <sub>4</sub> Se <sub>4</sub> (19)	Green	0.49	b
16.	[CpCr(CO) <sub>2</sub> ] <sub>2</sub> As <sub>2</sub> S <sub>2</sub> (20)	Orange	0.79	c
17.	[CpCr(CO) <sub>2</sub> ] <sub>2</sub> As <sub>2</sub> [Cr(CO) <sub>5</sub> ] <sub>2</sub> (21)	Purplish brown	0.08	a
18.	[CpCr(CO) <sub>2</sub> ] <sub>2</sub> As <sub>2</sub> [W(CO) <sub>5</sub> ] <sub>2</sub> (22)	Brown	0.07	a
19.	[CpCr(CO) <sub>2</sub> ] <sub>2</sub> P <sub>2</sub> [Fe(CO) <sub>4</sub> ] (23)	Brownish magenta	0.27	b
20.	[CpCr(CO) <sub>2</sub> ] <sub>2</sub> P <sub>2</sub> [Fe(CO) <sub>4</sub> ] <sub>2</sub> (24)	Greenish brown	0.16	b

a - *n*-hexane : toluene (3 : 2); b - *n*-hexane : toluene : ether (3 : 2 : 2); c - toluene : THF (1 : 1).

Fraction (v) : a light green eluate in  $\text{CH}_3\text{CN}$  (20 mL) which gave an unidentified green oily residue (*ca.* 10 mg), the  $^1\text{H}$  NMR spectrum of which showed Cp resonances at  $\delta$  7.26, 4.31, 4.11 and 3.95.

Fraction (vi) : a Prussian blue eluate in methanol (20 mL) which gave a paramagnetic dark blue crystalline solid (53 mg, 13.6% yield based on its Cr content) with the empirical formula  $\text{Cp}_2\text{Cr}_2\text{AsO}_5$ .

**(b) Cothermolysis at 110°C for 16 h : isolation of  $\text{Cp}_2\text{Cr}_2\text{As}_5$**

A deep green suspension of  $[\text{CpCr}(\text{CO})_3]_2$  (200mg, 0.498 mmol) and finely ground arsenic (615 mg, 8.20 mmol) in toluene (15 mL) was refluxed under stirring for 16 h. The reaction mixture had changed to a dark blue suspension. The mixture was filtered through Celite (1.5 cm x 1 cm disc) and concentrated to *ca.* 1.5 mL. It was loaded onto a silica gel column (1.5 cm x 10 cm) prepared in *n*-hexane. Elution gave four fractions :

Fraction (i) : a yellow eluate in *n*-hexane (5 mL) followed by *n*-hexane-toluene (9:1, 5 mL) which was concentrated to dryness to yield yellowish orange flakes of  $\text{CpCr}(\text{CO})_2\text{As}_3$  (19 mg, 0.048 mmol, 4.8% yield).

Fraction (ii) : a golden yellow eluate in *n*-hexane-toluene (1:1, 35mL) which gave fine black crystalline solids of  $\text{Cp}_2\text{Cr}_2\text{As}_5$  (65 mg, 0.107 mmol, 21.5% yield).

Fraction (iii) : a brown eluate in toluene-ether (1:1, 15 mL) which gave brown solids (9 mg, 3% yield based on Cr content) which the  $^1\text{H}$  NMR showed a Cp resonance at  $\delta$  14.8. Elemental analyses indicated the approximate molecular formula  $\text{Cp}_5\text{Cr}_5\text{As}_4\text{O}_8$ , but this could not be structurally confirmed due to lack of a single diffraction quality crystal.

Fraction (iv) : a Prussian blue eluate in THF (25mL) followed by THF-methanol (20 mL) which gave dark blue solids of  $\text{Cp}_2\text{Cr}_2\text{AsO}_5$  (78 mg, 0.168 mmol, 33.8% yield).

(c) **Cothermolysis at 140°C for 6 h : isolation of  $\text{Cp}_5\text{Cr}_5\text{As}_4\text{O}_8$**

A suspension of finely ground gray arsenic (600 mg, 8.0 mmol) in a deep green solution of  $[\text{CpCr}(\text{CO})_3]_2$  (200 mg, 0.453 mmol) in xylene (10 mL) was refluxed with stirring for 6 h. The resultant dark mixture was concentrated to *ca.* 1 mL and loaded onto a silica gel column (1 cm x 10 cm) prepared in *n*-hexane. Elution gave two fractions :

Fraction (i) : a yellow fraction in *n*-hexane-toluene (1:1, 5 mL) from which when concentrated to dryness yielded orange yellow flaky solids of  $\text{CpCr}(\text{CO})_2\text{As}_3$  (12 mg, 0.03 mmol, 3% yield), identified by its  $^1\text{H}$  NMR in benzene- $d_6$  ( $\delta$  3.94) and TLC against an authentic sample [ $R_f$  = 0.51 with *n*-hexane-toluene (3:2) as eluent].

Fraction (ii) : a brown fraction in toluene (5 mL) followed by ether (5 mL) and finally a ether-THF (1:1, 5 mL) which gave dark brown crystalline solids (50 mg), the  $^1\text{H}$  NMR spectrum of which showed the presence of two broad peaks centered at  $\delta$  15.5 and 14.8. Rechromatography of this brown product on a silica gel column (1 cm x 6 cm) prepared in *n*-hexane gave : (a) a light brown fraction in *n*-hexane-toluene (1:1, 10 mL) which was obtained as brown solids (11 mg) which the  $^1\text{H}$  NMR spectrum showed the presence of two broad peaks centered at  $\delta$  14.8 and 11.3. (b) a brown fraction in toluene-ether (1:1, 15 mL) which gave dark brown solids of  $\text{Cp}_5\text{Cr}_5\text{As}_4\text{O}_8$  (29 mg, 15% yield based on its Cr content). (c) a yellowish brown fraction in ether-THF (1:1, 10 mL) which gave a brown residue (12 mg.), the  $^1\text{H}$  NMR spectrum of which showed the presence of  $\delta$  15.5 and 14.8.

### 3.4.1.2 Thermolysis of products

(a) **Thermolysis of  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$**

A deep purple solution of  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$  (70 mg, 0.141 mmol) in toluene (10 mL) was stirred under nitrogen at reflux temperature for *ca.* 16.h. Filtration of the resultant brown solution yielded dark brown amorphous solids of  $\text{Cp}_2\text{Cr}_2\text{As}_5$  (*ca.* 25 mg, 0.041 mmol, 29% yield).  $^1\text{H}$  NMR (benzene- $d_6$ ) :  $\delta(\text{Cp})$  23.5. Anal. Calcd. for



$C_{10}H_{10}Cr_2As_5$  : C, 19.73; H, 1.66, Cr, 17.08%. Found : C. 20.13; H. 1.67; Cr. 17.31%. The filtrate was concentrated to *ca.* 1 mL and loaded on a silica gel column (1.5 cm x 7 cm) prepared in *n*-hexane. Elution gave two fractions :

Fraction (i) : a golden yellow eluate in *n*-hexane-toluene (1:1, 10 mL) which upon concentration to dryness yielded fine lustrous black crystalline solids of  $Cp_2Cr_2As_5$  (15 mg, 0.025 mmol, 17.5% yield).

Fraction (ii) : a brown eluate in toluene-ether (1:1, 15mL) which gave dark brown solids of  $Cp_5Cr_5As_4O_8$  (15 mg, 28% yield based on Cr content), identified by its  $^1H$  NMR in benzene- $d_6$  ( $\delta$  14.8).

#### (b) Thermolysis of $CpCr(CO)_2As_3$

A yellow solution of  $CpCr(CO)_2As_3$  (40 mg, 0.101 mmol) in toluene (4 mL) was thermolysed with stirring under reflux. No colour change was observed up to 7 h. After 21 h, the solution had turned slightly brownish with some dark precipitate. Filtration removed fine black crystalline solids of  $Cp_2Cr_2As_5$  (3 mg, 0.005 mmol, 5% yield), identified its  $^1H$  NMR in benzene- $d_6$  ( $\delta$  23.5) and TLC against an authentic sample [ $R_f$  = 0.579 in *n*-hexane-toluene (3:2) as eluent]. The concentrated filtrate (*ca.* 1 mL) was loaded on a silica gel column prepared in *n*-hexane. Elution gave two fractions:

Fraction (i) : a yellow eluate in *n*-hexane (15 mL) which when concentrated to dryness yielded yellowish brown flakes of unreacted  $CpCr(CO)_2As_3$  (27 mg, 0.068 mmol, 67.5% recovery).

Fraction (ii) : a golden yellow eluate in toluene (10 mL) which gave fine lustrous black crystalline solids of  $Cp_2Cr_2As_5$  (8 mg, 0.013 mmol, 13% yield). A dark layer remained immovable at the top of the column.

### 3.4.2 Reactions of $[\text{CpCr}(\text{CO})_2]_2$

#### 3.4.2.1 Isolation of products

##### (a) Cothermolysis at $110^\circ\text{C}$ for 1 h : isolation of $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$ ,

##### $\text{CpCr}(\text{CO})_2\text{As}_3$ and $\text{Cp}_2\text{Cr}_2\text{AsO}_5$

A suspension of finely ground arsenic (215 mg, 2.867 mmol) in a deep green solution of  $[\text{CpCr}(\text{CO})_2]_2$  (60 mg, 0.173 mmol) in toluene (4 mL) was stirred under reflux for 1 h. The resultant dark purplish blue reaction mixture was allowed to cooled to room temperature and a 2 mL aliquot of the supernatant solution was removed *via* a syringe. It was filtered through a disc of Celite (1.5 cm x 1 cm) and eluted with THF (*ca.* 3 mL). The filtrate/eluate was concentrated to dryness and the residue (33 mg) redissolved in toluene (*ca.* 1 mL) and loaded onto a column (1.5 cm x 2.5 cm) of silica gel prepared in *n*-hexane. Elution gave three fractions :

Fraction (i) : a yellow solution in *n*-hexane (15 mL) which yielded yellowish brown flakes of  $\text{CpCr}(\text{CO})_2\text{As}_3$  (11 mg, 0.028 mmol, 31.9% yield).

Fraction (ii) : a purple solution in *n*-hexane-toluene (1:1, 10 mL) followed by toluene (5 mL) from which was obtained fine purplish black crystalline solids of  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$  (8 mg, 0.016 mmol, 18.5% yield), identified by its  $^1\text{H}$  NMR in benzene- $d_6$  ( $\delta$  4.12) and TLC against an authentic sample [  $R_f$  = 0.27 with *n*-hexane-toluene (3:2) as eluent].

Fraction (iii) : a Prussian blue solution in THF (20 mL) which gave dark blue crystalline solids of  $\text{Cp}_2\text{Cr}_2\text{AsO}_5$  (13 mg, 38.3% yield based on its Cr content).

##### (b) Cothermolysis at $110^\circ\text{C}$ for 5 h : isolation of $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$ and $\text{Cp}_2\text{Cr}_2\text{As}_2\text{O}_5$

The remaining aliquot (2 mL) from the above experiment was allowed to reflux for a further 4 h. The resultant dark blue reaction mixture was filtered and chromatographed on a silica gel column (1.5 cm x 2.5 cm) prepared in *n*-hexane.

Elution gave three fractions :

Fraction (i) : a purple solution in *n*-hexane-toluene (1:1, 10 mL) followed by toluene (5 mL), which when concentrated to dryness yielded  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$  (8 mg, 0.002 mmol, 18.6% yield).

Fraction (ii) : a greenish brown solution in toluene-ether (1:1, 15 mL) which gave an unidentified brown residue (2 mg).

Fraction (iii) : a Prussian blue solution in ether (5 mL) followed by THF (10 mL), which gave fine dark blue crystalline solids of  $\text{Cp}_2\text{Cr}_2\text{AsO}_5$  (15 mg, 44.2% yield based on its Cr content). A blue immovable band remained at the top of the column.

### 3.5 Reaction with Tetraphosphorus Trisulphide, $\text{P}_4\text{S}_3$

#### 3.5.1 Reaction of $[\text{CpCr}(\text{CO})_3]_2$

##### (a) At ambient temperature

A deep green mixture of  $[\text{CpCr}(\text{CO})_3]_2$  (100 mg, 0.249 mmol) and  $\text{P}_4\text{S}_3$  (55 mg, 0.249 mmol) in toluene (15 mL) was stirred at ambient temperature for 13 days. The resultant yellowish brown reaction mixture was filtered through Celite (1 cm x 1 cm disc, *ca.* 1 g). The mixture was absorbed onto silica gel (*ca.* 2 g), concentrated to dryness and loaded onto a silica gel column (1.5 cm x 10 cm) prepared in *n*-hexane. Elution gave three fractions :

Fraction (i) : a yellow eluate in *n*-hexane (50 mL). Concentration to about 2 mL and cooling at  $-28^\circ\text{C}$  overnight precipitated fine pale yellow solids of unreacted  $\text{P}_4\text{S}_3$  (18 mg, 0.082 mmol, 32.7% recovery) which were filtered. Rechromatography of the mother liquor on a silica gel column (1.5 cm x 5 cm) gave a greenish yellow fraction in *n*-hexane (35 mL) which when concentrated to dryness yielded fine yellow crystalline solids (43 mg) consisting of a 3 : 1 : 8 molar mixture of  $\text{P}_4\text{S}_3$  (11 mg, 0.05 mmol, 20% unreacted),  $\text{CpCr}(\text{CO})_2\text{P}_3$  (4 mg, 0.015 mmol, 3% yield) and  $\text{CpCr}(\text{CO})_3\text{H}$  (28 mg, 0.139 mmol, 27.9% yield). Further elution with toluene (15 mL)

gave a light brown solution which when dried <sup>gave</sup> pale yellow solids of  $P_4S_3$  (3 mg, 0.014 mmol, 5.5% recovery).

Fraction (ii) : a dirty green eluate in *n*-hexane-toluene (2:1, 35 mL). Concentration to dryness yielded deep green crystalline solids of  $[CpCr(CO)_2]_2S$  (12 mg, 0.032 mmol, 12.8% yield), identified by its  $^1H$  NMR in benzene- $d_6$  [ $\delta(Cp)$  4.36] and TLC against an authentic sample [ $R_f$  = 0.59 with *n*-hexane-toluene (3:2) as eluent].

Fraction (iii) : a reddish brown eluate in *n*-hexane-toluene (1:2, 45 mL). Concentration to dryness yielded dark brown crystalline solids of  $Cp_4Cr_4(CO)_9P_4S_3$  (58 mg, 0.062 mmol, 49.6% yield). Anal. Calcd. for  $C_{29}H_{20}Cr_4O_9P_4S_3$  : C, 37.03; H, 2.14; Cr, 22.11; P, 13.17; S, 10.23%. Found : C, 36.03; H, 1.75; Cr, 22.40; P, 12.45; S, 10.20%

### (b) Cothermolysis at 60°C

A deep green mixture of  $[CpCr(CO)_3]_2$  (500 mg, 1.244 mmol) and  $P_4S_3$  (330 mg, 1.50 mmol) in toluene (30 mL) was stirred at 60°C for 3 h. The resultant greenish brown mixture was allowed to cool down to room temperature and filtered through Celite (2cm x 1cm disc, *ca.* 2 g). The mixture was absorbed onto silica gel (*ca.* 5g), concentrated to dryness and loaded onto a silica gel column (1.5 cm x 15 cm) prepared in *n*-hexane. Five fractions were eluted:

Fraction (i) : a yellow eluate in *n*-hexane (20 mL) followed by *n*-hexane-toluene (9:1, 25 mL). Cooling of the concentrate (3 mL) at -28°C overnight, yielded pale yellow needles of  $P_4S_3$  (45 mg, 0.205 mmol, 0.090 13.6% recovery). The mother liquor was rechromatographed on a silica gel column (1.5 cm x 8 cm) prepared in *n*-hexane. Elution with *n*-hexane-toluene (8:2, 50 mL) yielded a yellowish brown residue (60 mg) consisting of a 16 : 6 : 1 molar mixture of  $P_4S_3$  (42 mg unreacted),  $CpCr(CO)_3H$  (3% yield) and  $CpCr(CO)_2P_3$  (0.4% yield), respectively, estimated from its  $^{31}P$  NMR and  $^1H$  NMR spectra.

Fraction (ii) : a dirty green eluate in *n*-hexane-toluene (7:3, 40 mL) which when concentrated to dryness yielded deep green crystals of  $[\text{CpCr}(\text{CO})_2]_2\text{S}$  (170 mg, 0.450 mmol, 36.2% yield).

Fraction (iii) : a magenta fraction in *n*-hexane-toluene (1:1, 30 mL) which was obtained as fine dark crystalline solids of  $[\text{CpCr}(\text{CO})_2]_2\text{P}_2$  (5mg, 0.012 mmol, 1% yield), identified by its  $^1\text{H}$  NMR in benzene- $d_6$  [ $\delta(\text{Cp})$  4.15] and TLC against an authentic sample [ $R_f = 0.41$  with *n*-hexane -toluene ( 3:2 ) as eluent].

Fraction (iv) : a reddish brown fraction in toluene (40 mL) which yielded dark brown solids of  $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{S}_3)$  (130 mg, 0.138 mmol, 22.2 % yield).

Fraction (v) : a greenish brown fraction in ether (40 mL) which gave a dirty brown residue (85 mg) consisting of a mixture of  $\text{Cp}_4\text{Cr}_4\text{S}_4$ , identified by its  $^1\text{H}$  NMR in benzene- $d_6$  [ $\delta(\text{Cp})$  4.91)]<sup>95</sup> and TLC against an authentic sample [ $R_f = 0.52$  with *n*-hexane : toluene : ether (3 : 2 : 2) as eluent] together with  $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{S}_3)$  and an unidentified Cp-containing compound [ $\delta(\text{Cp})$  5.13]. This fraction was rechromatographed on a silica gel column (1.5 cm x 10 cm) prepared in *n*-hexane-ether (1:1). Two fractions were obtained : (a) a brown eluate in toluene (35 mL) which yielded a brown residue of  $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{S}_3)$  (45 mg, 0.048 mmol, 7.7 % yield) when the solvent was removed. (b) a dirty green eluate in toluene-ether (9:1, 35 mL) which gave fine dark green solids of  $\text{Cp}_4\text{Cr}_4\text{S}_4$  (25 mg, 0.042 mmol, 6.7% yield).

### 3.5.3 Reaction of $[\text{CpCr}(\text{CO})_3]_2$ with $\text{P}_4\text{S}_3$ in the presence of isoprene

A deep green mixture of  $[\text{CpCr}(\text{CO})_3]_2$  (80 mg, 0.199 mmol) and  $\text{P}_4\text{S}_3$  (44 mg, 0.200 mmol) in toluene (10 mL) was allowed to stir in a stoppered 100 mL Schlenk flask at ambient temperature. Approximately 0.01 mL of isoprene was introduced into the flask *via* a microsyringe. After stirring for 9 days, the resultant dark brown reaction mixture was filtered, absorbed onto silica gel (*ca.* 3 g) and evacuated to dryness before loading onto a silica gel column (1.5 cm x 10 cm) prepared in *n*-hexane. Elution gave five fractions :

Fraction (i) : a pale yellow eluate in *n*-hexane (30 mL) which when concentrated to dryness yielded brownish yellow solids (16 mg). The solids were extracted with *n*-hexane (2 x 5 mL) leaving behind unreacted  $P_4S_3$  (18 mg, 0.082 mmol, 40.9% recovered). Concentration of the extracts to dryness gave yellow flakes of  $CpCr(CO)_2P_3$  (ca. 2 mg, 0.007 mmol, 2% yield).

Fraction (ii) : a dirty green eluate in *n*-hexane-toluene (4:1, 25 mL) which gave deep green crystalline solids of  $[CpCr(CO)_2]_2S$  (4 mg, 0.010 mmol, 5.3% yield).

Fraction (iii) : a deep green eluate in *n*-hexane-toluene (3:1, 15 mL) which gave dark green solids of  $[CpCr(CO)_2]_2$  (ca. 3 mg, 0.009 mmol, 4.4% yield).

Fraction (iv) : a light magenta eluate in *n*-hexane-toluene (2:1, 15 mL) which gave dark magenta solids of  $[CpCr(CO)_2]_2P_2$  (ca. 2 mg, 0.005 mmol, 2.5% yield).

Fraction (v) : a reddish brown eluate in *n*-hexane-toluene (1:3, 40 mL) which gave fine dark brown crystalline solids of  $Cp_4Cr_4(CO)_9(P_4S_3)$  (55 mg, 0.059 mmol, 58.9% yield). A greenish blue immovable band remained at the top of the column.

### 3.5.2 Reaction of $[CpCr(CO)_2]_2$

A deep green suspension of  $[CpCr(CO)_2]_2$  (50 mg, 0.145 mmol) and  $P_4S_3$  (32 mg, 0.145 mmol) in toluene (10 mL) was stirred at ambient temperature. No reaction was observed after stirring for 24 h at this temperature. The reaction was continued at 60°C and the reaction allowed to proceed to completion in ca. 18 h. The resultant dirty brown mixture was filtered through Celite (1.5 cm x 2 cm disc). The filtrate was concentrated, absorbed on silica gel (1.5 g) which was evacuated to remove solvent and loaded onto a silica gel column (1.5 cm x 12 cm) prepared in *n*-hexane. Elution gave five fractions :

Fraction (i) : a yellow eluate in *n*-hexane-toluene (4:1, 15 mL) which when concentrated to dryness yielded brownish yellow solids (41 mg). The solid was extracted with *n*-hexane (3 x 5 mL) leaving behind unreacted  $P_4S_3$  (13 mg, 0.059 mmol, 41% recovery). Concentration of the extracts yielded a brownish yellow

residue (28 mg) consisting of a 1:2.7 molar mixture of  $\text{CpCr(CO)}_2\text{P}_3$  (8 mg, 0.03 mmol, 10% yield) and  $\text{CpCr(CO)}_3\text{H}$  (20 mg, 0.099 mmol, 34% yield), estimated from its  $^1\text{H}$  NMR spectrum.

Fraction (ii) : a green eluate in *n*-hexane-toluene (3:1, 20 mL) which gave dark green solids of  $[\text{CpCr(CO)}_2]_2$  (4 mg, 0.011 mmol, 8% recovered).

Fraction (iii) : a magenta eluate in *n*-hexane-toluene (1:1, 15mL) which gave dark crystalline magenta solids of  $[\text{CpCr(CO)}_2]_2\text{P}_2$  (8 mg, 0.02 mmol, 14% yield).

Fraction (iii) : a dirty brown eluate in toluene-ether (1:1, 35 mL) which gave dark green solids of  $\text{Cp}_4\text{Cr}_4\text{S}_4$  (13 mg, 0.022 mmol, 30 % yield).

Fraction (iv) : a dark brown eluate in THF (20 mL) which gave an unidentified dark brown oily residue (9 mg).

### 3.5.3 NMR Tube Reactions

The following reactions were studied in  $\text{C}_6\text{D}_6$  in 5-mm NMR tubes under argon *via* proton NMR spectral analysis :-

#### (a) Reaction of $[\text{CpCr(CO)}_3]_2$ (1) with $\text{P}_4\text{S}_3$

A deep green 2.4 mM mixture of **1** with 0.5 mole equivalent of  $\text{P}_4\text{S}_3$  was maintained at  $60^\circ\text{C}$  and the reaction was followed by its  $^1\text{H}$  NMR spectrum recorded at intervals. A similar reactions with one mole equivalent of  $\text{P}_4\text{S}_3$  was similarly studied at  $80^\circ\text{C}$ . The results for the reactions were tabulated in Table 12 and 13.

#### (b) Reaction of $[\text{CpCr(CO)}_2]_2$ (4) with $\text{P}_4\text{S}_3$

A deep green 2.8 mM mixture of **4** with 0.5 mole and 1 mole equivalent, respectively of  $\text{P}_4\text{S}_3$  was allowed to react at  $60^\circ\text{C}$ . Its  $^1\text{H}$  NMR spectra were examined at intervals of 1, 2, 4, 6 and 18 h. The results for the reactions were tabulated in Table 14.

(c) Cothermolysis of  $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{S}_3)$  (**9**) with  $\text{P}_4\text{S}_3$

A reddish brown 1mM mixture of **9** with 1 mole equivalent of  $\text{P}_4\text{S}_3$  was maintained at  $60^\circ\text{C}$ . Its spectra was examined at intervals of 1, 3, 4, 5 and 18 h. The thermolysis of **9** was similarly examined. The results for both the reactions were presented together in Table 15.

3.5.4 Thermolysis of  $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{S}_3)$  (**9**)

A stirred reddish brown solution of  $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{S}_3)$  in toluene (15 mL) was maintained at  $80^\circ\text{C}$  for 3.5 h. The resultant yellowish brown solution was concentrated to *ca.* 2 mL followed by addition of *n*-hexane (0.5 mL). Cooling at  $-28^\circ\text{C}$  overnight yielded fine dark green solids of  $\text{Cp}_4\text{Cr}_4\text{S}_4$  (5 mg, 0.008 mmol, 9.6% yield) which was filtered. The mother liquor was concentrated to *ca.* 1 mL and loaded onto a silica gel column (1.5 cm x 17 cm) prepared in *n*-hexane. Four fractions were eluted :

Fraction (i) : a yellow eluate in *n*-hexane-toluene (9:1, 35 mL) which when concentrated to dryness yielded brownish yellow crystals of  $\text{CpCr}(\text{CO})_2\text{P}_3$  (9 mg, 0.039 mmol, 9.9 % yield), identified by its  $^1\text{H}$  NMR in benzene- $d_6$  [ $\delta(\text{Cp})$  3.94] and TLC against an authentic sample [ $R_f$  = 0.65 with *n*-hexane-toluene (3:2) as eluent].

Fraction (ii) : a dirty green eluate in *n*-hexane-toluene (3:1, 35 mL) which gave deep green crystals of  $[\text{CpCr}(\text{CO})_2]_2\text{S}$  (15 mg, 0.039 mmol, 23.3 % yield).

Fraction (iii) : a magenta eluate in *n*-hexane-toluene (1:3, 30 mL) which gave fine dark magenta solids of  $[\text{CpCr}(\text{CO})_2]_2\text{P}_2$  (7 mg, 0.017 mmol, 10.1 % yield).

Fraction (iv) : a dirty brown eluate in ether (30 mL) which gave fine dark brown solids of  $\text{Cp}_4\text{Cr}_4\text{S}_4$  (25 mg, 0.042 mmol, 49.3% yield).



### 3.6 Reaction with tetraphosphorus triselenide, $P_4Se_3$

#### 3.6.1 Reaction of $[CpCr(CO)_3]_2$

##### (a) At ambient temperature for 6 days : isolation of $Cp_4Cr_4(CO)_9(P_4Se_3)$

A deep green suspension of  $[CpCr(CO)_3]_2$  (200 mg, 0.498 mmol) and  $P_4Se_3$  (180 mg, 0.498 mmol) in toluene (25 mL) was stirred at ambient temperature for 6 days until all the dimer has reacted. The resultant dark brown reaction mixture was concentrated to dryness and the residue extracted with THF (3 x 15 mL) leaving behind an orange yellow film of  $P_4Se_3$  (ca. 75 mg, 0.208 mmol, 41.7% recovery) on the walls of the flask. The combined extracts was concentrated, absorbed onto Celite (ca. 1.5 g) which was evacuated to dryness and then loaded onto a silica gel column (1.5 cm x 15 cm) prepared in *n*-hexane-toluene (1:1). Elution gave six fractions :

Fraction (i) : a yellow solution in *n*-hexane-toluene (2:1, 15 mL) which yielded yellow crystalline solids (20 mg), consisting of a 5 : 2 molar mixture of  $CpCr(CO)_3H$  (7% yield) and  $CpCr(CO)_2P_3$  (2.3% yield), respectively, estimated from its  $^{31}P$  NMR and  $^1H$  NMR spectra.

Fraction (ii) : an orange solution in *n*-hexane-toluene (2:1, 10 mL) which gave fine light brownish orange solids of unreacted  $P_4Se_3$  (10 mg, 0.028 mmol, 5.6% recovery).

Fraction (iii) : a magenta solution in *n*-hexane-toluene (2:3, 25 mL) which gave fine dark magenta crystalline solids of  $[CpCr(CO)_2]_2P_2$  (33 mg, 0.081 mmol, 16.3% yield), identified by its  $^1H$  NMR in benzene- $d_6$  [ $\delta(Cp)$  4.15] and TLC against an authentic sample [ $R_f$  = 0.41 with *n*-hexane-toluene (3:2) as eluent].

Fraction (iv) : a reddish brown solution in *n*-hexane-toluene (2:3, 30 mL) which when evaporated to dryness yielded fine dark brown solids of  $Cp_4Cr_4(CO)_8(P_2Se_2)$  (30 mg, 0.033 mmol, 13.2% yield). Anal. Calcd. for  $C_{28}H_{20}Cr_4O_8P_2Se_2$  : 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%.

Fraction (v) : a yellowish brown solution in *n*-hexane-toluene (1:3, 45 mL) from which was as obtained dark brown solids of  $Cp_4Cr_4(CO)_9(P_4Se_3)$  (130 mg, 0.120 mmol,

48.3% yield). Anal. Calcd. for  $C_{29}H_{20}Cr_4O_9P_4Se_3$  : C, 32.19; H, 1.85; Cr, 19.24; P, 11.47; Se, 21.92%. Found : C, 32.61; H, 2.30; Cr, 19.13; P, 12.97; Se, 21.91%.

Fraction (vi) : a greenish brown solution in ether (20 mL) which gave an uncharacterisable dirty brown oily residue (ca. 25 mg).

**(b) At ambient temperature for 12 days : isolation of  $Cp_4Cr_4(CO)_8(P_2Se_2)$**

A deep green suspension of  $[CpCr(CO)_3]_2$  (500 mg, 1.244 mmol) and  $P_4Se_3$  (449 mg, 1.244 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 x 25 mL) leaving behind an orange yellow film of  $P_4Se_3$  (ca. 120 mg, 0.332 mmol, 26.7% recovery) on the walls of the flask. The combined extracts were concentrated, absorbed onto Celite (ca. 1.5 g) which was evacuated to dryness and loaded onto a silica gel column (2 cm x 15 cm) prepared in *n*-hexane-toluene (1:1). Elution gave five fractions :

Fraction (i) : a yellow solution in *n*-hexane-toluene (2:1, 45 mL) which when evaporated to dryness yielded yellow crystalline solids (90 mg), consisting of a mixture of a 1.6 : 1 molar mixture of  $CpCr(CO)_3H$  (6.9% yield) and  $CpCr(CO)_2P_3$  (8.4% yield), respectively, estimated from its  $^{31}P$  NMR and  $^1H$  NMR spectra.

Fraction (ii) : an orange solution in *n*-hexane-toluene (1:1, 40 mL) which gave brownish orange crystalline solids of  $P_4Se_3$  (25 mg, 0.069 mmol, 5.6% recovery).

Fraction (iii) : a reddish brown solution in *n*-hexane-toluene (2:3, 60 mL) which gave dark brown solids of  $Cp_4Cr_4(CO)_8(P_2Se_2)$  (190 mg, 0.21 mmol, 33.5% yield).

Fraction (iv) : a yellowish brown solution in *n*-hexane-toluene (1:3, 60 mL) which gave dark brown solids of  $Cp_4Cr_4(CO)_9(P_4Se_3)$  (130 mg, 0.12 mmol, 19.4% yield).

Fraction (v) : a greenish brown solution in ether (30 mL) followed by THF (30 mL) which yielded a greenish brown oily residue (100 mg). Rechromatograph of this residue on a silica gel column (2 x 10 cm) prepared in *n*-hexane-toluene (1:1), gave a

yellowish brown fraction in *n*-hexane-toluene (1:3, 45 mL) which when concentrated yielded dark brown solids of  $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{Se}_3)$  (51 mg, 0.049 mmol, 7.6% yield).

**(c) Cothermolysis at 60°C**

A deep green solution of  $[\text{CpCr}(\text{CO})_3]_2$  (250 mg, 0.622 mmol) in toluene (20 mL), containing  $\text{P}_4\text{Se}_3$  (225 mg, 0.622 mmol) was stirred at 60°C for 2 h. The resultant dark brown reaction mixture was concentrated to dryness. The residue was extracted out using THF (3 x 15 mL) leaving behind a film of orange yellow precipitate of  $\text{P}_4\text{Se}_3$  (ca. 55 mg, 0.152 mmol, 24.4% recovery) on the walls of the flask. The combined extracts were concentrated, absorbed onto Celite (ca. 2 g) which was evacuated to dryness and then loaded onto a silica gel column (1.5 cm x 17 cm) prepared in *n*-hexane-toluene (1:1). Seven fractions were eluted :

Fraction (i) : a yellow solution in *n*-hexane-toluene (2:1, 20 mL) which upon concentration to dryness yielded brownish yellow solids (32 mg), the  $^1\text{H}$  NMR spectrum of which showed a 5.9:1 molar mixture of  $\text{CpCr}(\text{CO})_2\text{P}_3$  (8.2% yield) and  $\text{CpCr}(\text{CO})_3\text{H}$  (2% yield).

Fraction (ii) : an orange solution in *n*-hexane-toluene (1:1, 15 mL) which gave fine light brown solids of unreacted  $\text{P}_4\text{Se}_3$  (15 mg, 0.042 mmol, 6.7% recovered).

Fraction (iii) : an orange brown solution in *n*-hexane-toluene (7:3, 35 mL) which gave deep green crystals of  $[\text{CpCr}(\text{CO})_2]_2\text{Se}$  (51 mg, 0.12 mmol, 19.4% yield).

Fraction (iv) : a magenta solution in *n*-hexane-toluene (2:3, 20 mL) which gave fine dark magenta crystals of  $[\text{CpCr}(\text{CO})_2]_2\text{P}_2$  (22 mg, 0.054 mmol, 8.7% yield).

Fraction (v) : a reddish brown solution in *n*-hexane-toluene (2:3, 45 mL) which gave fine dark brown crystalline solids of  $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)$  (45 mg, 0.049 mmol, 15.9% yield).

Fraction (vi) : a yellowish brown solution in *n*-hexane-toluene (1:3, 60 mL) which gave dark brown solids of  $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{Se}_3)$  (123 mg, 0.114 mmol, 36.6% yield).

Fraction (vii) : a dirty brown solution in toluene (10 mL) followed by toluene-ether (1:1, 20 mL) which gave dark brown solids of  $\text{Cp}_4\text{Cr}_4\text{Se}_4$  (8.5 mg, 0.011 mmol, 3.5% yield), identified by its  $^1\text{H}$  NMR in benzene- $d_6$  [ $\delta(\text{Cp})$  5.13] and TLC against an authentic sample [ $R_f = 0.493$  with *n*-hexane : toluene : ether (3 : 2 : 2) as eluent].

### 3.6.2 Reaction of $[\text{CpCr}(\text{CO})_2]_2$

A deep green suspension of  $[\text{CpCr}(\text{CO})_2]_2$  (100 mg, 0.289 mmol) with  $\text{P}_4\text{Se}_3$  (104 mg, 0.289 mmol) in toluene (15 mL) was stirred for at ambient temperature. No reaction was observed after 24 h. The temperature was therefore raised to  $60^\circ\text{C}$ , the reaction continued until all of **4** had reacted (*ca.* 18 h). The resultant dirty brown suspension containing some dark insoluble solids was filtered through Celite (1.5 cm x 2 cm disc). The filtrate was concentrated, absorbed onto silica gel (*ca.* 5g) which was evacuated to dryness and loaded onto a silica gel column (5 cm x 15 cm) prepared in *n*-hexane. Elution gave three fractions :

Fraction (i) : a yellow eluate in *n*-hexane-toluene (9:1, 15 mL) which when dried yielded brownish orange solids (53 mg) The solids were extracted with *n*-hexane (3 x 10 mL) leaving behind unreacted  $\text{P}_4\text{Se}_3$  (15 mg, 0.042 mmol, 14.4% recovery). Concentration of the extracts yielded a brownish yellow residue (38 mg) consisting of a 3.2:1 molar mixture of  $\text{CpCr}(\text{CO})_3\text{H}$  (28.9% yield) and  $\text{CpCr}(\text{CO})_2\text{P}_3$  (6.8% yield) estimated from its  $^1\text{H}$  NMR spectrum.

Fraction (ii) : a magenta eluate in *n*-hexane-toluene (1:1, 20 mL) which gave dark magenta solids of  $[\text{CpCr}(\text{CO})]_2\text{P}_2$  (13 mg, 0.032 mmol, 11.1% yield).

Fraction (iii) : a dirty brown eluate in toluene (10 mL) followed by toluene-ether (1:1, 15 mL) which gave dark brown solids of  $\text{Cp}_4\text{Cr}_4\text{Se}_4$  (37 mg, 0.047 mmol, 32.5% yield).

### 3.6.3 Reaction of $\text{Cp}_2\text{Cr}_2(\text{CO})_4\text{Se}$

#### 3.6.3.1 Isolation of products

##### (a) From a reaction with $\text{P}_4\text{Se}_3$

An orange brown mixture of  $\text{Cp}_2\text{Cr}_2(\text{CO})_4\text{Se}$  (100 mg, 0.236 mmol) and  $\text{P}_4\text{Se}_3$  (62 mg, 0.172 mmol) in toluene was stirred at ambient temperature for 6 days. The resultant reddish brown mixture was filtered through Celite (2 cm x 1 cm disc, *ca.* 1.5 g). The filtrate was then absorbed onto silica gel (*ca.* 3 g), evacuated to dryness and loaded onto a silica gel column (1.5 cm x 10 cm) prepared in *n*-hexane. Four fractions were eluted :

Fraction (i) : a pale yellow solution with *n*-hexane (35 mL) which when concentrated to dryness yielded fine greenish yellow crystalline solids (*ca.* 8 mg) consisting of a 3:1 molar mixture of  $\text{CpCr}(\text{CO})_3\text{H}$  (6% yield) and  $\text{CpCr}(\text{CO})_2\text{P}_3$  (2% yield), estimated from its  $^1\text{H}$  NMR spectrum.

Fraction (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  $\text{Cp}_2\text{Cr}_2(\text{CO})_4\text{Se}$  (8 mg, 0.018 mmol, 8% recovery).

Fraction (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  $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)$  (82 mg, 0.090 mmol, 81.8% yield).

Fraction (iv) : a dark brown solution with *n*-hexane-toluene (1:2, 30 mL) which when concentrated to dryness yielded dark brown solids of  $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{Se}_3)$  (5 mg, 0.005 mmol, 4.2% yield).

##### (b) From a reaction with $\text{P}_4\text{S}_3$

An orange brown mixture of  $\text{Cp}_2\text{Cr}_2(\text{CO})_4\text{Se}$  (400 mg, 0.941 mmol) and  $\text{P}_4\text{S}_3$  (150 mg, 0.682 mmol) in toluene was stirred at ambient temperature for 6 days. The resultant greenish brown mixture was filtered and the recovered yellow precipitate was washed with toluene then evacuated dry. Its mass spectrum showed the fragmentation pattern of a mixture of  $\text{P}_7$  and  $\text{CpCr}(\text{CO})_2\text{P}_3$  [ $m/z$  62 ( $\text{P}_2$ ), 93 ( $\text{P}_3$ ), 124

(P<sub>4</sub>), 155 (P<sub>5</sub>), 217 (P<sub>7</sub>), 238 (CpCr(CO)P<sub>3</sub>), 266 (CpCr(CO)<sub>2</sub>P<sub>3</sub>)]. The filtrate was then absorbed onto silica gel (*ca.* 5 g), evacuated to dryness and loaded onto a silica gel column (2 cm x 15 cm) prepared in *n*-hexane-toluene (2:1). Five fractions were eluted :

Fraction (i) : a pale yellow solution in *n*-hexane (45 mL) which when concentrated to dryness yielded fine greenish yellow crystalline solids (*ca.* 22 mg) consisting of a 3.4:1 molar mixture of CpCr(CO)<sub>3</sub>H (5% yield) and CpCr(CO)<sub>2</sub>P<sub>3</sub> (1% yield), estimated from its <sup>1</sup>H NMR spectrum.

Fraction (ii) : a greenish brown solution in *n*-hexane-toluene (2:1, 45 mL) which when concentrated to dryness yielded fine deep green crystalline solids of Cp<sub>2</sub>Cr<sub>2</sub>(CO)<sub>4</sub>S (55 mg, 0.146 mmol, 15.5% yield).

Fraction (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 Cp<sub>4</sub>Cr<sub>4</sub>(CO)<sub>8</sub>(P<sub>2</sub>Se<sub>2</sub>) (215 mg, 0.235 mmol, 50.1% yield).

Fraction (iv) : a dark brown solution in *n*-hexane-toluene (2:3, 50 mL) which when concentrated to dryness yielded fine dark brown solids of Cp<sub>4</sub>Cr<sub>4</sub>(CO)<sub>9</sub>(P<sub>4</sub>Se<sub>3</sub>) (35 mg, 0.032 mmol, 6.9% yield).

Fraction (v) : a dark brown solution in toluene-ether (2:1, 20 mL) followed by (1:1, 30 mL) which when concentrated to dryness yielded an unidentified Cp-containing (δ 7.76, 7.69) dark brown oily residue (35 mg).

### 3.6.3.2 NMR Tube Reactions

#### (a) Reaction of [CpCr(CO)<sub>3</sub>]<sub>2</sub> with P<sub>4</sub>Se<sub>3</sub>

A deep green mixture of [CpCr(CO)<sub>3</sub>]<sub>2</sub> (5 mg, 0.012 mmol) and P<sub>4</sub>Se<sub>3</sub> (5 mg, 0.014 mmol) in *d*<sub>6</sub>-benzene was ultrasonicated at ambient temperature. Its <sup>1</sup>H NMR spectrum was recorded at intervals. After 9 h, the reaction mixture was reddish brown.

**(b) Reaction of  $\text{Cp}_2\text{Cr}_2(\text{CO})_4\text{Se}$  with an equimolar equivalent of  $\text{P}_4\text{X}_3$  ( $\text{X} = \text{S}, \text{Se}$ ) at ambient temperature**

An orange brown 2 mM mixture of  $\text{Cp}_2\text{Cr}_2(\text{CO})_4\text{Se}$  with an equimolar equivalent of  $\text{P}_4\text{Se}_3$  in  $\text{C}_6\text{D}_6$  in a serum-capped 5-mm tube under argon was at ambient temperature on a mechanical shaker vigorously agitated. The reaction was monitored at 24 h intervals for 4 days. A similar reaction was performed using  $\text{P}_4\text{S}_3$ . A time-dependent variation of the  $^1\text{H}$  NMR spectral changes for the reactions was illustrated in Figures 46 and 47, respectively.

**(c) Variable temperature NMR measurement of  $\text{Cp}_4\text{Cr}_4(\text{CO})_8\text{P}_2\text{Se}_2$**

The  $^1\text{H}$  NMR spectrum of an approximately 2 mM solution of  $\text{Cp}_4\text{Cr}_4(\text{CO})_8\text{P}_2\text{Se}_2$  in  $\text{C}_6\text{D}_6$  in a serum-capped 5-mm tube under argon was recorded at 28, 50, 70 and  $90^\circ\text{C}$ , respectively. The temperature-dependent variation of the  $^1\text{H}$  NMR spectral changes was presented in Figure 51.

### 3.6.3 Thermolysis of products

**(a) Thermolysis of  $\text{Cp}_4\text{Cr}_4(\text{CO})_9\text{P}_4\text{Se}_3$**

A stirred brown solution of  $\text{Cp}_4\text{Cr}_4(\text{CO})_9\text{P}_4\text{Se}_3$  (80 mg, 0.074 mmol) in toluene (15 mL) was maintained at  $60^\circ\text{C}$  for 4 h. The resultant reddish brown solution was concentrated to *ca.* 2 mL followed by addition of *n*-hexane (0.5 mL). Overnight cooling at  $-28^\circ\text{C}$  yielded dark magenta crystalline solids of  $[\text{CpCr}(\text{CO})_2]_2\text{P}_2$  (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 x 20 cm) prepared in *n*-hexane. Four fractions were eluted:

Fraction (i): an orange yellow solution in *n*-hexane-toluene (3:1, 25 mL) which when concentrated to dryness yielded brownish yellow crystals of  $\text{CpCr}(\text{CO})_2\text{P}_3$  (5 mg, 0.019 mmol, 6.3% yield), identified by its  $^1\text{H}$  NMR in benzene- $d_6$  [ $\delta(\text{Cp})$  3.94] and TLC against an authentic sample [ $R_f = 0.65$  with *n*-hexane-toluene (3:2) as eluent].

Fraction (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 mg, 0.017 mmol, 11.6% yield).

Fraction (iii) : a brown solution in *n*-hexane-toluene (1:2, 35 mL) which gave dark brown solids of  $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)$  (35 mg, 0.038 mmol, 51.9% yield).

Fraction (iv) : a dirty brown solution in ether (20 mL) which gave fine dark brown solids of  $\text{Cp}_4\text{Cr}_4\text{Se}_4$  (7 mg, 0.09 mmol, 12.1% yield).

**(b) Thermolysis of  $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)$**

A stirred reddish brown solution of  $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)$  (60 mg, 0.066 mmol) in toluene (15 mL) was maintained at 80°C for 3 h. The resultant magenta brown solution was concentrated to *ca.* 2 mL and chromatographed as described above. Four fractions were eluted :

Fraction (i) : an orange yellow solution in *n*-hexane-toluene (3:1, 20 mL) which when evaporated to dryness yielded brownish yellow crystals of  $\text{CpCr}(\text{CO})_2\text{P}_3$  (3mg, 0.011 mmol, 3.3% yield).

Fraction (ii) : a magenta solution in *n*-hexane-toluene (1:1, 35 mL) which gave fine dark magenta crystals of  $[\text{CpCr}(\text{CO})_2]_2\text{P}_2$  (30 mg, 0.074 mmol, 55.9% yield).

Fraction (iii) : a greenish brown solution in toluene (10 mL) followed by ether (20 mL) which gave fine dark brown solids of  $\text{Cp}_4\text{Cr}_4\text{Se}_4$  (19 mg, 0.024 mmol, 36.8% yield).

Fraction (iv) : a brown solution in ether-THF (1:1, 15 mL) which gave a dark brown oily uncharacterisable residue (5 mg).



### 3.7 Reactions with realgar, $\text{As}_4\text{S}_4$

#### 3.7.1 Reactions of $[\text{CpCr}(\text{CO})_3]_2$

##### 3.7.1.1 Isolation of products

###### (a) At ambient temperature : isolation of $[\text{CpCr}(\text{CO})_2]\text{As}_2\text{S}_2$

An orange green suspension of  $[\text{CpCr}(\text{CO})_3]_2$  (300 mg, 0.746 mmol) and  $\text{As}_4\text{S}_4$  (450 mg, 1.051 mmol) in toluene (35 mL) was ultrasonicated at ambient temperature for 25 h. The resultant greenish orange reaction mixture was allowed to settle and the supernatant mother liquor carefully decanted leaving behind a yellowish orange precipitate (550 mg). The supernatant mother liquor was concentrated to *ca.* 2 mL, mixed with *n*-hexane (0.5 mL) and left overnight at  $-28^\circ\text{C}$ . Dirty brown solids (95 mg) were precipitated. Its  $^1\text{H}$  NMR spectrum showed a 7:0.5:1:1.5:1:1 molar mixture of unreacted  $[\text{CpCr}(\text{CO})_3]_2$  (*ca.* 55 mg, 0.137 mmol, 18.3% recovery),  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$  (2) (4 mg, 0.008 mmol, 1% yield),  $[\text{CpCr}(\text{CO})_2]_2$  (4) (8 mg, 0.023 mmol, 3.8% yield) [ $\delta(\text{Cp})$  4.23],  $\text{Cp}_4\text{Cr}_4\text{S}_4$  (18) (12 mg, 0.020 mmol, 6.7% yield) [ $\delta(\text{Cp})$  4.91],  $[\text{CpCr}(\text{CO})_2]_2\text{S}$  (10) (8 mg, 0.021 mmol, 3.5% yield) [ $\delta(\text{Cp})$  4.36] and an unidentified Cp-containing species [ $\delta(\text{Cp})$  5.13], respectively. The dirty green mother liquor which was concentrated to *ca.* 3 mL, layered with *n*-hexane (0.5 mL) and left overnight at  $-28^\circ\text{C}$  yielded deep green crystals of  $[\text{CpCr}(\text{CO})_2]_2\text{S}$  (53 mg, 0.140 mmol, 23.3% yield), identified by its  $^1\text{H}$  NMR in benzene- $d_6$  [ $\delta(\text{Cp})$  4.36] and TLC against an authentic sample [ $R_f = 0.59$  with *n*-hexane-toluene (3:2) as eluent]. The bulk yellowish orange precipitate above (550 mg) was extracted with toluene-ether (1:1) (5 x 30 mL) to give a dirty green solution which when concentrated to dryness yield deep green crystals of  $[\text{CpCr}(\text{CO})_2]_2\text{S}$  (30 mg, 0.080 mmol, 13.2% yield) with a trace of  $\text{Cp}_4\text{Cr}_4\text{S}_4$  indicated by TLC [ $R_f = 0.52$  with *n*-hexane-toluene-ether (3:2:2) as eluent]. Subsequent extraction with THF (10 x 20 mL) followed by concentration of the extracts to dryness yielded reddish orange solids of  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2\text{S}_2$  (69 mg, 0.123 mmol, 20.5% yield). Anal. Calcd. for

$C_{14}H_{10}Cr_2O_4As_2S_2$  : C, 30.0 ; H, 1.78; Cr, 18.57 ; As, 26.79; S, 11.43%. Found : C, 29.83 ; H, 1.65; Cr, 18.68 ; As, 25.62 S, 11.10%.

### (b) Cothermolysis at 60°C

An orange green suspension of  $[CpCr(CO)_3]_2$  (200 mg, 0.498 mmol) and  $As_4S_4$  (300 mg, 0.701 mmol) in toluene (35 mL) was stirred for 8 h at 60°C. The resultant greenish orange reaction mixture was allowed to settle and the supernatant mother liquor carefully decanted leaving behind a greenish orange precipitate (390 mg). The  $^1H$  NMR spectrum of the supernatant solution showed an approximate 1: 5: 2: 1: 4: 2: 1 molar mixture of  $CpCr(CO)_2As_3$  (7 mg, 0.018 mmol, 1.8% yield) [ $\delta(Cp)$  3.94],  $Cp_4Cr_4S_4$  (34 mg, 0.057 mmol, 22.9% yield) [ $\delta(Cp)$  4.91],  $[CpCr(CO)_2]_2S$  (14 mg, 0.037 mmol, 7.4% yield) [ $\delta(Cp)$  4.36],  $[CpCr(CO)_2]_2As_2S_2$  (7 mg, 0.013 mmol, 2.5% yield) [ $\delta(Cp)$  4.26],  $[CpCr(CO)_2]_2$  (28 mg, 0.081 mmol, 16.3% yield) [ $\delta(Cp)$  4.23],  $[CpCr(CO)_2]_2As_2$  (14 mg, 0.028 mmol, 5.7% yield) [ $\delta(Cp)$  4.12] and an unidentified Cp-containing species [ $\delta(Cp)$  5.13], respectively. The bulk greenish orange precipitate above (390 mg) was initially washed with toluene (3 x 30 mL) followed by 1:1 toluene-ether (2 x 25 mL) to give a dirty green solution. The extract was concentrated to ca. 2 mL, layered with *n*-hexane (0.5 mL) and left overnight at -28°C yielded deep green crystals of  $[CpCr(CO)_2]_2S$  (35 mg, 0.093 mmol, 18.6% yield), leaving behind a reddish orange residue (325 mg).

Subsequent extraction with THF (6 x 20 mL) followed by concentration of the extracts to dryness gave reddish orange solids of  $[CpCr(CO)_2]_2As_2S_2$  (35 mg, 0.063 mmol, 12.6% yield).

### 3.7.2 Reaction of $[CpCr(CO)_2]_2$

An orange green suspension of  $[CpCr(CO)_2]_2$  (100 mg, 0.289 mmol) and  $As_4S_4$  (185 mg, 0.433 mmol) in toluene (15 mL) was ultrasonicated for 24 h at ambient temperature. No reaction was observed and the reaction was continued by stirring at 60°C for 7 h until all of **4** has reacted. The dirty green reaction mixture

was filtered through Celite (1.5 cm x 2 cm disc) and the filtrate concentrated to *ca.* 2 mL. It was loaded onto a silica gel column (1.5 cm x 15 cm) prepared in *n*-hexane.

Elution gave four fractions :

Fraction (i) : a yellow eluate in *n*-hexane-toluene (9:1, 25 mL) which when concentrated to dryness yielded brownish yellow platelets of  $\text{CpCr(CO)}_2\text{As}_3$  (35 mg, 0.088 mmol, 15.2% yield)

Fraction (ii) : a dirty green eluate in *n*-hexane-toluene (3:1, 30 mL) which gave deep green crystalline solids of  $[\text{CpCr(CO)}_2]_2\text{S}$  (15mg, 0.039 mmol, 13.7% yield).

Fraction (iii) : a dirty brown eluate in toluene (40 mL) which gave dark brown solids of  $\text{Cp}_4\text{Cr}_4\text{S}_4$  (33 mg, 0.055 mmol, 38.3% yield).

Fraction (iv) : a greenish brown eluate in ether-toluene (1:1, 15 mL) which gave an unidentified Cp-containing species ( $\delta$  5.13) oily dark brown residue (5 mg).

### 3.7.1.3 Thermolysis of $[\text{CpCr(CO)}_2]_2\text{As}_2\text{S}_2$

A stirred reddish orange solution of  $[\text{CpCr(CO)}_2]_2\text{As}_2\text{S}_2$  (30 mg, 0.054 mmol) in toluene (30mL) was maintained at 50°C for 7 h. The resultant dirty green mixture was concentrated to *ca.* 1 mL and chromatographed on silica gel column (1cm x 10 cm) prepared in *n*-hexane. Four fractions were eluted :

Fraction (i) : a yellow eluate in *n*-hexane-toluene (9:1, 15 mL) which upon concentration to dryness yielded brownish yellow solids of  $\text{CpCr(CO)}_2\text{As}_3$  (6 mg, 0.015 mmol, 14.1% yield), identified its  $^1\text{H}$  NMR in benzene- $d_6$  [ $\delta(\text{Cp})$  3.94] and TLC against an authentic sample [ $R_f$  = 0.51 in *n*-hexane-toluene (3:2) as eluent].

Fraction (ii) : a yellowish green eluate in *n*-hexane-toluene (3:1, 20 mL) which gave deep green solids of  $[\text{CpCr(CO)}_2]_2\text{S}$  (12 mg, 0.032 mmol, 59.3% yield).

Fraction (iii) : a dirty brown eluate in toluene-ether (2:1) (15 mL) which gave dark brown solids of  $\text{Cp}_4\text{Cr}_4\text{S}_4$  (3 mg, 0.005 mmol, 18.8% yield).

Fraction (iv) : a greenish brown eluate in ether-toluene (1:1, 10 mL) which gave dark brown solids (2 mg) of an unidentified Cp-containing species ( $\delta$  5.13).

### 3.8 Formation of some transition metal carbonyl fragments adducts of $[\text{CpCr}(\text{CO})_2]_2\text{E}_2$ (E = P, As)

#### 3.8.1 Reactions of $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$ with $\text{M}(\text{CO})_5(\text{THF})$ (M = Cr, W)

##### 3.8.1.1 Isolation of $[\text{CpCr}(\text{CO})_2\text{As}_2[\text{Cr}(\text{CO})_5]_2$

To a deep purple solution of  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$  (70 mg, 0.141 mmol) was injected in an orange yellow solution of  $\text{Cr}(\text{CO})_5(\text{THF})$  (41 mL, 0.287 mmol) and the mixture was stirred at ambient temperature. After 1 h, the reaction mixture had turned purplish brown. Stirring was continued for 3 h. The reaction mixture was concentrated to dryness and the residue redissolved in toluene (*ca.* 2 mL) and chromatographed on a silica gel column (1.5 cm x 15 cm) prepared in *n*-hexane. Two fractions were eluted:

Fraction (i) : a yellow solution in *n*-hexane (10 mL) which when concentrated to dryness yielded an uncharacterised oily yellowish brown residue (12 mg).

Fraction (ii) : a purplish brown solution in toluene (20 mL) followed by toluene-ether (1:1, 20 mL), which on concentration to *ca.* 2.5 mL and slow crystallisation at  $-28^\circ\text{C}$  overnight, gave a first crop of  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2[\text{Cr}(\text{CO})_5]_2$  (53 mg, 0.060 mmol, 42.7% yield) as fine dark crystalline solids. Recrystallisation of the mother liquor yielded a second crop (21 mg, 0.024 mmol, 16.9% yield). Anal. Calcd. for  $\text{C}_{24}\text{H}_{10}\text{Cr}_4\text{O}_{14}\text{As}_2$ : C, 32.73; H, 1.14; Cr, 23.64; As, 17.05%. Found: C, 32.75; H, 0.92; Cr, 23.15; As, 16.70%.

##### 3.8.1.2 Isolation of $[\text{CpCr}(\text{CO})_2]_2\text{As}_2[\text{W}(\text{CO})_5]_2$

The procedure as described above was repeated for a solution of  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$  (70 mg, 0.141 mmol) in THF (5 mL) and  $\text{W}(\text{CO})_5(\text{THF})$  (41 mL, 0.287 mmol). A similar chromatography of the purplish brown reaction mixture solution on a silica gel column (1.5 cm x 15 cm) gave two fractions:

Fraction (i) : a yellow solution in *n*-hexane (12 mL) which when concentrated to dryness yielded an uncharacterised oily brown residue (13 mg).

Fraction (ii) : a brown solution in toluene (25 mL) followed by toluene-ether (1:1.20 mL) which was concentrated to *ca.* 2.5 mL and slow crystallisation at  $-28^{\circ}\text{C}$  overnight, yielded fine dark crystalline solids of  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2[\text{W}(\text{CO})_5]_2$  (66 mg, 0.058 mmol, 40.9% yield) as the first crop and recrystallisation of the mother liquor gave a second crop (23 mg, 0.020 mmol, 14.3% yield). Anal. Calcd. for  $\text{C}_{24}\text{H}_{10}\text{Cr}_2\text{W}_2\text{O}_{14}\text{As}_2$  : C, 25.17; H, 0.87; Cr, 9.09; As, 13.11; W, 32.17%. Found : C, 25.69; H, 1.05; Cr, 9.35; As, 12.93; W, 31.72%.

### 3.8.2 Reaction of $[\text{CpCr}(\text{CO})_2]_2\text{P}_2$ with $\text{Fe}_2(\text{CO})_9$ : isolation of $[\text{CpCr}(\text{CO})_2]_2\text{P}_2[\text{Fe}(\text{CO})_4]$ and $[\text{CpCr}(\text{CO})_2]_2\text{P}_2[\text{Fe}(\text{CO})_4]_2$

A deep magenta suspension of  $[\text{CpCr}(\text{CO})_2]_2\text{P}_2$  (150 mg, 0.368 mmol) and golden orange  $\text{Fe}_2(\text{CO})_9$  (134 mg, 0.366 mmol) in THF (10 mL) was stirred under an atmosphere of carbon monoxide at *ca.*  $0^{\circ}\text{C}$ . The reaction mixture had changed to a homogenous brownish magenta solution after *ca.* 15 min. The mixture was absorbed onto Celite (*ca.* 2 g) and concentrated to dryness. The dried residue was loaded onto a silica gel column (1.5 cm x 13 cm) prepared in *n*-hexane. Elution gave four fractions :  
 Fraction (i) : a yellowish green solution in *n*-hexane (20 mL) which yielded a minute amount of a dark green solid (*ca.* 5 mg) of an unidentifiable compound, possessing a cluster of Cp resonances at  $\delta$  4.48, 4.41, 4.31, and 4.21 in its proton NMR spectrum.  
 Fraction (ii) : a magenta solution in *n*-hexane-toluene (7:3, 30 mL) which when concentrated to dryness yielded fine dark magenta crystalline solids of unreacted  $[\text{CpCr}(\text{CO})_2]_2\text{P}_2$  (21 mg, 0.051 mmol, 13.9% yield).

Fraction (iii) : a brownish magenta solution in *n*-hexane-toluene (3:7, 45 mL), which was obtained as fine dark crystalline solids of  $[\text{CpCr}(\text{CO})_2]_2\text{P}_2[\text{Fe}(\text{CO})_4]$  (145 mg, 0.251 mmol, 68.5% yield). Anal. Calcd. : C, 37.76; H, 1.67; Cr, 17.20; P, 10.26; Fe, 9.26%. Found : C, 37.93; H, 1.62; Cr, 18.06; P, 10.78; Fe, 9.21%.

Fraction (iv) : a dirty green solution in toluene (20 mL), which gave dark crystalline solids of  $[\text{CpCr}(\text{CO})_2]_2\text{P}_2[\text{Fe}(\text{CO})_4]_2$  (45 mg, 0.060 mmol, 16.5% yield). Anal.

Calcd.: C, 35.55; H, 1.35; Cr, 13.98; P, 8.33; Fe, 15.02%. Found : C, 35.54; H, 1.43; Cr, 14.45; P, 7.44; Fe, 14.31%. The brown rim at the top of the column was eluted with ether (10 mL) and THF (25 mL). However, the residue showed a featureless proton NMR spectrum.

### 3.9 Crystal structure determinations

#### 3.9.1 Structure determinations of $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$ and $\text{CpCr}(\text{CO})_2\text{As}_3$

Single crystals of  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$  (2) were obtained as dark purple flat trapezoidal-shaped needles from toluene layered with *n*-hexane after 6 days at  $-30^\circ\text{C}$ .

Details of crystal parameters, data collection, and structure refinement are given in Table 44. Raw intensities collected on a Nicolet R3m/V four-circle diffractometer at room temperature (294 K) were processed with the profile-fitting procedure of Diamond<sup>113</sup> and corrected for absorption with use of the  $\psi$ -scan data of eight selected reflections over the range  $6^\circ < 2\theta < 23^\circ$ .<sup>114</sup> Patterson superposition yielded the positions of all non-hydrogen atoms except those of the cyclopentadienyl group, which were derived from successive difference Fourier syntheses. All non-hydrogen atoms were subjected to anisotropic refinement,

and the H atoms were generated geometrically (C-H bonds fixed at  $0.96 \text{ \AA}$ ) and assigned the same isotropic temperature factor of  $U = 0.12 \text{ \AA}^2$ . No extinction correction was applied. Computations were performed with use of the SHELTXL-PLUS program package<sup>115</sup> on a DEC Micro VAX-II computer. Analytical expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.<sup>116</sup>

The compound  $\text{CpCr}(\text{CO})_2\text{As}_3$  (3) was crystallized as golden brown plates from a saturated solution in toluene layered with hexane after 5-6 days at 245 K. The crystal used for data collection was coated in epoxy glue.

Details of crystal parameters, data collection, and structure refinement are given in Table 45. The structure was solved by direct methods with MULTAN80;<sup>117</sup> the H-atoms were generated with  $\text{C-H} = 0.95 \text{ \AA}$  and were allowed to ride on their parent atoms. Computer programs used for structure solution and refinement were from the MolEN<sup>118</sup> package and were run on a MicroVAX II minicomputer.

Table 44. Data Collection and Processing Parameters

mol formula	$[\text{C}_6\text{H}_5\text{Cr}(\text{CO})_2]_2\text{As}_2$
mol wt	496.07
color and habit	dark-purple flat needles with (100) well developed
unit-cell params	$a = 15.551(3) \text{ \AA}$ $b = 7.453(1) \text{ \AA}$ $c = 13.446(2) \text{ \AA}$ $\beta = 96.21(2)^\circ$ $V = 1549.4(4) \text{ \AA}^3$ $Z = 4$ $F(000) = 960$
density (calcd)	$2.127 \text{ g/cm}^3$
space group	$C2/c$ (No. 15)
radiation	graphite-monochromatized Mo $K\alpha$ , $\lambda = 0.71073 \text{ \AA}$
std rflns	(222), (422)
intens variation	$\pm 1\%$
$R_{\text{int}}$ (from merging of equiv rflns)	0.022
abs coeff	$56.13 \text{ cm}^{-1}$
cryst size	$0.40 \times 0.32 \times 0.04 \text{ mm}^3$
mean $\mu_r$	0.025
transmissn factors	0.347–0.839
scan type and rate	$\omega$ -2 $\theta$ ; 2.93–14.65 deg min $^{-1}$
scan range	0.65° below $K\alpha_1$ to 0.65° above $K\alpha_2$
bkgd counting	stationary counts for 1/5 of scan time at each end of scan range
$hkl$ collectn range	0–18, 0–8, –17 to +17; $2\theta_{\text{max}} = 50^\circ$
no. of unique data measured	1201
no. of obsd data with $ F_o  \geq 6\sigma( F_o )$ , $n$	893
no. of variables, $p$	100
$R_F = \sum   F_o  -  F_c   / \sum  F_o $	0.034
weighting scheme	$w = [\sigma^2(F_o) + 0.0006 F_o ^2]^{-1}$
$R_G = [\sum w( F_o  -  F_c )^2 / \sum w F_o ^2]^{1/2}$	0.040
$S = [\sum w( F_o  -  F_c )^2 / (n - p)]^{1/2}$	1.141
resid extrema in final diff map	+0.34 to –0.42 e $\text{\AA}^{-3}$



Table 45. Data Collection and Processing Parameters for  $\text{CpCr}(\text{CO})_2\text{As}_3$  (3)*Crystal data* $[\text{Cr}(\text{As}_3)(\text{C}_5\text{H}_5)(\text{CO})_2]$  $M_r = 397.88$ 

Monoclinic

 $P2_1/a$  $a = 7.537$  (2) Å $b = 10.992$  (1) Å $c = 12.670$  (2) Å $\beta = 100.59$  (1)° $V = 1031.7$  (3) Å<sup>3</sup> $Z = 4$  $D_x = 2.561$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation $\lambda = 0.71073$  Å

Cell parameters from 25 reflections

 $\theta = 14\text{--}16^\circ$  $\mu = 10.58$  mm<sup>-1</sup> $T = 300$  K

Plate

 $0.28 \times 0.28 \times 0.14$  mm

Brown

Enraf-Nonius CAD-4  
diffractometer $\theta$ -2 $\theta$  scans

Absorption correction:

empirical (North, Phillips  
& Mathews, 1968) $T_{\min} = 0.580$ ,  $T_{\max} =$   
0.999

2063 measured reflections

1804 independent reflections

1189 observed reflections

 $[I > 3\sigma(I)]$  $\theta_{\max} = 25^\circ$  $h = 0 \rightarrow 8$  $k = 0 \rightarrow 13$  $l = -15 \rightarrow 14$ 

3 standard reflections

monitored every 400

reflections

intensity variation:

0.026%

*Refinement*Refinement on  $F$  $R = 0.038$  $wR = 0.043$  $S = 0.658$ 

1189 reflections

118 parameters

H-atom parameters not  
refined $w = 1/[\sigma^2(F) + 0.0004F^2 + 1]$  $(\Delta/\sigma)_{\max} < 0.001$  $\Delta\rho_{\max} = 0.90$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -0.96$  e Å<sup>-3</sup>

Atomic scattering factors

from *International Tables*

for X-ray Crystallography

(1974, Vol. IV).

### 3.9.2 Structure determinations of $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{S}_3)$ , $\text{CpCr}(\text{CO})_3\text{H}$ and $\text{P}_4\text{S}_3$

Single crystals of  $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{S}_3)$  (**9**) were obtained as thick dark brown rectangular platelets from THF-ether after 3 weeks at  $-30^\circ\text{C}$ . Diffraction-quality single crystals of  $\text{CpCr}(\text{CO})_3\text{H}$  (**11**) (pale lemon yellow),  $\text{P}_4\text{S}_3$  (yellow) and  $\text{CpCr}(\text{CO})_2\text{P}_3$  (**14**) (brownish yellow) were selected from a bulk crystalline solid recrystallised from THF-*n*-hexane after a week at  $-30^\circ\text{C}$ .

The crystals used for unit cell determination and data collection for  $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{S}_3)$  (**9**) and  $\text{P}_4\text{S}_3$  were coated with epoxy glue while those of  $\text{CpCr}(\text{CO})_3\text{H}$  was sealed in glass capillaries to prevent decomposition in air. Details of the crystal parameters data collection and structure refinement are given in Table 46. Raw intensities were processed for Lorentz polarization effects, decay and corrected for absorption.<sup>119</sup> Structures of  $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{S}_3)$  (**9**),  $\text{CpCr}(\text{CO})_3\text{H}$  (**11**) and  $\text{P}_4\text{S}_3$  were solved by the direct method MULTAN.<sup>117</sup> All non hydrogen atoms were subjected to anisotropic refinement. Hydrogen atoms of the cyclopentadienyl rings were generated geometrically each with a distance of  $0.95 \text{ \AA}$  and was allowed to ride with  $B = 1.3$  times that of the parent atom. A disordered THF solvent molecule per molecule of **9** was found in the unit cell. The positional parameters for the five membered ring were fixed while their displacement parameters were all refined as carbon atoms. Residual peaks in the final difference map account mainly for peaks around the THF molecules. The hydrogen atom in **11** cannot be located from the difference map. The crystal structure of  $\text{CpCr}(\text{CO})_3\text{H}$  was solved by the heavy atom method from a Patterson synthesis and all the remaining atoms were located from subsequent difference Fourier maps except for the hydrogen atoms on the Cp ring which were generated geometrically with riding mode on their respective parent C atoms. Two peaks were located near the Cr atoms at about  $1.2 \text{ \AA}$  and were assigned as hydride and refined with occupancies of 0.5 each. The isotropic thermal parameters

Table 46. Data Collection and Processing Parameters

Molecular formula	$\text{Cp}_2\text{Cr}_2(\text{CO})_6\text{P}_2\text{S}_2\cdot\text{THF}$	$\text{CpCr}(\text{CO})_3\text{H}$	$\text{P}_4\text{S}_3$
$M_r$	1012.66	202.13	220.09
Crystal colour and habit	dark brown polyhedron	yellow polyhedron	brown thick needles
Crystal size (mm)	0.1 x 0.15 x 0.2	0.46 x 0.43 x 0.2	0.3 x 0.3 x 0.21
Unit cell parameters			
$a(\text{\AA})$ $\alpha(^{\circ})$	12.074(1) 73.05(2)	10.982(2) 90.0	10.596(2)
$b(\text{\AA})$ $\beta(^{\circ})$	12.880(3) 73.21(1)	7.284(1) 116.85(1)	9.6622(7)
$c(\text{\AA})$ $\gamma(^{\circ})$	14.451(5) 78.67(1)	11.844(2) 90.0	13.661(2)
$V(\text{\AA}^3)$ $Z$	2042.5(9) 2	845.3(2) 4	1398.7(6) 8
$D_x$ ( $\text{Mg m}^{-3}$ )	1.646	1.588	2.090
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$Pnma$
Radiation	$\text{MoK}_\alpha$	$\text{MoK}_\alpha$	$\text{MoK}_\alpha$
No. of reflections for lattice parameters	25	25	25
$\theta$ range for lattice parameters ( $^{\circ}$ )	12 - 15	15 - 16	14 - 16
Absorption coefficient ( $\text{mm}^{-1}$ )	1.365	1.312	1.806
Temperature (K)	300	300	300
Diffractometer type	CAD4	CAD4	CAD4
Collection method	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
Absorption correction type	$\psi$ -scan	$\psi$ -scan	$\psi$ -scan
Absorption correction ( $T_{\text{min}}$ , $T_{\text{max}}$ )	91.77, 99.76	89.40, 99.66	77.31, 98.45
No. of reflections measured	6208	1563	2478
No. of independent reflections	5788	1489	1302
$\theta_{\text{max}}(^{\circ})$	25 $^{\circ}$	25 $^{\circ}$	25 $^{\circ}$
No. of observed reflections	3221	1177	983
No. of standard reflections (and interval)	3(400)	3(200)	3(400)
Criterion for observed	$>3\sigma(I)$	$>2\sigma(I)$	$>3\sigma(I)$

(continued)

Variation of standards	$-3.27 \times 10^{-1} \%h^{-1}$	$-6.58 \times 10^{-1} \%h^{-1}$	$-1.10 \times 10^{-1} \%h^{-1}$
$h_{min}$ $h_{max}$	0 --> 12	-13 --> 11	0 --> 11
$k_{min}$ $k_{max}$	-15 --> 15	0 --> 8	0 --> 12
$l_{min}$ $l_{max}$	-16 --> 17	0 --> 14	-8 --> 0
$R$	0.048	0.052	0.044
$wR$	0.057	0.126	0.052
No. of parameters refined	447	117	73
No. of reflections used in refinement	3221	1177	983
$S$	0.455	1.198	1.509
Weighting scheme $w =$	$[\sigma(F)^2 + 0.0004F^2 + 1]^{-1}$	$[\sigma^2(F_o)^2 + (0.0600P)^2 + 0.4800P]^{-1*}$	$[\sigma(F)^2]^{-1}$
$(\Delta/\sigma)_{max}$	0	0.01	0.00
$(\rho)_{max}$ ( $e\text{\AA}^{-3}$ )	1.039	0.424	0.833

$$*P = (F_o^2 + 2F_c^2)/3$$

were reasonable and refinement concluded at  $R=0.052$ . Computations for **9**, **11** and  $P_4S_3$  were performed using the MolEN<sup>118</sup> package on a DEC Micro VAX-II computer, while SHELXL 93 programs were used for  $CpCr(CO)_3H$  on a IBM 486PC. Analytic expressions of atomic scattering factors were employed and anomalous dispersion corrections were incorporated.<sup>116</sup>

### 3.9.3 Structure determinations of $Cp_4Cr_4(CO)_9(P_4Se_3)$ and $Cp_4Cr_4(CO)_8(P_2Se_2)$

Diffraction-quality single crystals of **12** and **13** were obtained as black triangular prisms and tetrahedra, respectively, from *n*-hexane-toluene after 7 and 10 days, respectively, at  $-28^\circ C$ .

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 47 and 48. The raw data were processed and corrected for Lorentz-polarization effects as well as for absorption.<sup>119</sup>

The structure of **12** was solved by the direct method MULTAN 80<sup>117</sup> and refined by full-matrix least-squares refinement using the MolEN<sup>118</sup> package on a VAXII mini computer. Only the Cr and Se atoms were refined anisotropically while the C, P and O atoms were refined isotropically. A benzene ring was located on a two-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 1.3 times its respective carbon atoms. The poor crystal quality resulted in a high R-factor of 7.0% for  $I>3$  (I) reflections.

The absolute structure of **13** was solved by direct methods using the programs SHELXL86 and were refined by using SHELXL93 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 1.3 times that of its parent carbon atoms.

Table 47. Crystal Data and Structure Refinement for  $[\text{Cp}_4\text{Cr}_4(\text{CO})_8](\text{P}_4\text{Se}_3)$  (12)

Identification code	rw20y
Empirical formula	C32 H23 Cr4 O9 P4 Se3
Formula weight	1120.26
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 29.06(1) Å    alpha = 90 deg. b = 12.895(1) Å    beta = 104.23(2) deg. c = 21.377(7) Å    gamma = 90 deg.
Volume	7764(4) Å <sup>3</sup>
Z	8
Density (calculated)	1.915 Mg/m <sup>3</sup>
Absorption coefficient	4.06 mm <sup>-1</sup>
F(000)	4360
Theta range for data collection	1.45 to 25.00 deg.
Index ranges	-34<=h<=33, -15<=k<=0, 0<=l<=25
Reflections collected	7360
Independent reflections	6819 [R(int) = 0.1613]
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	6612 / 0 / 244
Goodness-of-fit on F <sup>2</sup>	1.503
Final R indices [I>2sigma(I)]	R1 = 0.070 , wR2 = 0.066
R indices (all data)	R1 = 0.3440, wR2 = 0.3926
Largest diff. peak and hole	0.88 and -1.553 e.Å <sup>-3</sup>

Table 48. Crystal Data and Structure Refinement for  $[\text{Cp}_4\text{Cr}_4(\text{CO})_8](\text{P}_2\text{Se}_2)$  (13)

Identification code	rw23
Empirical formula	$[\text{SePCr}_2\text{O}_4\text{C}_{14}\text{H}_{10}]_2$
Formula weight	912.34
Temperature	300(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$\text{C}222_1$
Unit cell dimensions	$a = 14.893(1)$ Å $\alpha = 90$ deg. $b = 14.894(4)$ Å $B = 90$ deg. $c = 13.670(2)$ Å $r = 90$ deg.
Volume	$3032.2(9)$ Å <sup>3</sup>
Z	4
Density (calculated)	$1.999$ Mg/m <sup>3</sup>
Absorption coefficient	$3.951$ mm <sup>-1</sup>
F(000)	1784
Crystal size	$0.2 \times 0.2 \times 0.2$ mm
Theta range for data collection	$1.93$ to $25.00$ deg.
Index ranges	$-17 \leq h \leq 0$ , $-17 \leq k \leq 0$ , $-16 \leq l \leq 16$
Reflections collected	2872
Independent reflections	2666 [ $R(\text{int}) = 0.0255$ ]
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	2666 / 0 / 199
Goodness-of-fit on $F^2$	1.015
Final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0386$ , $wR2 = 0.0830$
R indices (all data)	$R1 = 0.0477$ , $wR2 = 0.0880$
Absolute structure parameter	$0.00(2)$
Largest diff. peak and hole	$0.483$ and $-0.322$ e.Å <sup>-3</sup>

### 3.9.4 Structure determinations of $[\text{CpCr}(\text{CO})_2]_2\text{As}_2[\text{M}(\text{CO})_5]_2$ [ $\text{M} = \text{Cr}, \text{W}$ ]

Data collection and processing parameters for  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2[\text{M}(\text{CO})_5]_2$  [ $\text{M} = \text{Cr}$  (**21**),  $\text{W}$  (**22**)] are summarised in Table 49. The structures were solved by the direct method MULTAN.<sup>117</sup> Non hydrogen atoms were refined anisotropically by full matrix least squares refinement. H atoms were located from difference Fourier map and were refined isotropically. All computations were performed on a microVAX II minicomputer using the MolEN package.<sup>118</sup> Residual electron densities were observed near the W atoms in **22**. Atomic coordinates and their equivalent isotropic thermal parameters are given in Tables 50 and 51.

### 3.9.5 Structure determinations of $[\text{CpCr}(\text{CO})_2]_2\text{P}_2[\text{Fe}(\text{CO})_4]_m$ [ $m = 1, 2$ ]

Quality crystals of  $[\text{CpCr}(\text{CO})_2]_2\text{P}_2[\text{Fe}(\text{CO})_4]_m$  [ $m = 1$  (**23**),  $2$  (**24**)] were obtained from saturated solutions in toluene layered with hexane. Dark magenta brown rectangular plates of **23** and dark greenish brown trapezoidal shaped plates of **24** were collected after 3 and 7 days, respectively, at  $-28^\circ\text{C}$ .

Accurate cell dimensions and space group data were obtained from 25 strong reflections in the  $14^\circ < \theta < 16^\circ$  shell of the crystals with cell sizes of less than 0.3 mm in each dimension. Three standard reflections were used to monitor the intensity. The data were collected using the  $\omega$ -2 $\theta$  method with  $\text{MoK}\alpha$  radiation.

The parameters used in data collection and processing are summarized in Table 52. Lorentz-polarization, linear decay and absorption corrections were applied. An empirical Fourier Method (DIFABS)<sup>120</sup> was used for compound **23** while another empirical psi-scan method<sup>119</sup> was used for compound **24**.

Compound **23** was solved by the direct method SIMPEL<sup>121</sup> while compound **24** was solved by the direct method SIR.<sup>122</sup> All non-H atoms were refined anisotropically. Analytic expressions of neutral atom scattering factors were employed<sup>123</sup> and anomalous dispersion corrections were incorporated.<sup>124</sup>



Table 49. Data Collection and Processing Parameters of  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2[\text{Cr}(\text{CO})_5]_2$  (21) and  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2[\text{W}(\text{CO})_5]_2$  (22)

	(21)		(22)	
Molecular formula	$\text{C}_{24}\text{H}_{10}\text{O}_{14}\text{As}_2\text{Cr}_4$		$\text{C}_{24}\text{H}_{10}\text{O}_{14}\text{As}_2\text{Cr}_2\text{W}_2$	
$M_r$	880.17		1143.88	
Crystal colour and habit	black trigonal prism		black trigonal prism	
Crystal size (mm)	0.14 x 0.18 x 0.22		0.1 x 0.2 x 0.3	
Unit cell parameters				
$a(\text{\AA})$ $\alpha(^{\circ})$	18.590(2)	90	18.7689(7)	90
$b(\text{\AA})$ $\beta(^{\circ})$	10.4405(4)	110.088(7)	10.6810(8)	109.726(4)
$c(\text{\AA})$ $\gamma(^{\circ})$	16.633(2)	90	16.6130(8)	90
$V(\text{\AA}^3)$ $Z$	3031.9(8)	4	3135.0(5)	4
$D_x$ ( $\text{Mg m}^{-3}$ )	1.928		2.423	
Crystal system	monoclinic		monoclinic	
Space group	$C2/c$		$C2/c$	
Radiation	$\text{MoK}_{\alpha}$		$\text{MoK}_{\alpha}$	
No. of reflections for lattice parameters	25		25	
$\theta$ range for lattice parameters ( $^{\circ}$ )	12 - 14		13 - 14.5	
Absorption coefficient ( $\text{cm}^{-1}$ )	35.89		102.9	
Temperature (K)	299		300	
Diffractometer type	CAD4		CAD4	
Collection method	$\omega$ -2 $\theta$		$\omega$ -2 $\theta$	
Absorption correction type	$\psi$ -scan		$\psi$ -scan	
Absorption correction ( $T_{\min}$ , $T_{\max}$ )	82.167, 99.867		58.078, 99.825	
No. of reflections measured	5842		3016	
No. of independent reflections	2669		2752	
$\theta_{\max}(^{\circ})$	25		25	
No. of observed reflections	1628		1872	
No. of standard reflections (and interval)	3(400)		3(400)	
Criterion for observed	$> 3\sigma(I)$		$> 3\sigma(I)$	

(continued)

Variation of standards (% h <sup>-1</sup> )	2.07 x 10 <sup>-2</sup>		-9.79 x 10 <sup>-2</sup>	
$h_{\min}$ $h_{\max}$	0	22	-22	0
$k_{\min}$ $k_{\max}$	0	12	0	12
$l_{\min}$ $l_{\max}$	-19	18	-18	19
$R$	0.035		0.030	
$wR$	0.038		0.033	
No. of parameters refined	219		219	
No. of reflections used in refinement	1628		1872	
$S$	1.06		1.015	
Weighting scheme $w =$	$1/\sigma(F)^2$		$1/\sigma(F)^2$	
$(\Delta/\sigma)_{\max}$	0.01		0.11	
$(\Delta\rho)_{\max}$ (eÅ <sup>-3</sup> )	0.385		0.945	

Table 50. Atomic coordinates and equivalent isotropic temperature factors for  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2[\text{Cr}(\text{CO})_5]_2$ 

Atom	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
As	0.43843(3)	0.10112(6)	0.20323(4)	2.23(1)
Cr1	0.33550(5)	-0.0610(1)	0.14970(6)	2.95(2)
Cr2	0.51876(5)	0.25854(9)	0.16704(5)	2.45(2)
O1	0.2211(3)	0.0811(6)	0.2091(5)	9.9(2)
O2	0.2118(3)	-0.2572(6)	0.0797(3)	7.3(2)
O3	0.2824(4)	0.0794(7)	-0.0204(4)	8.2(2)
O4	0.3895(4)	-0.2086(6)	0.3167(4)	8.3(2)
O5	0.4406(3)	-0.2291(6)	0.0915(4)	7.2(2)
O6	0.5738(3)	0.0434(5)	0.0821(3)	5.3(1)
O7	0.6820(3)	0.3227(5)	0.2710(3)	5.1(1)
Cp1	0.5190(4)	0.4610(6)	0.1298(4)	4.2(2)
C1	0.2649(4)	0.0314(7)	0.1869(5)	5.4(2)
Cp2	0.4487(4)	0.4386(7)	0.1397(4)	4.4(2)
C2	0.2595(4)	-0.1817(8)	0.1060(4)	4.4(2)
Cp3	0.4100(4)	0.3442(7)	0.0810(4)	4.4(2)
C3	0.3024(4)	0.0264(8)	0.0438(5)	4.9(2)
C4	0.3690(4)	-0.1512(7)	0.2544(5)	4.4(2)
Cp4	0.4570(4)	0.3092(7)	0.0341(4)	4.4(2)
C5	0.4025(4)	-0.1640(7)	0.1133(4)	4.1(2)
Cp5	0.5248(4)	0.3799(7)	0.0645(4)	4.1(2)
C6	0.5537(3)	0.1239(6)	0.1158(4)	3.3(1)
C7	0.6197(3)	0.2952(6)	0.2331(4)	3.1(1)
H1	0.559(2)	0.516(4)	0.163(3)	1(1)*
H2	0.433(3)	0.479(5)	0.183(3)	3(1)*
H3	0.361(3)	0.307(5)	0.073(3)	3(1)*
H4	0.442(3)	0.248(5)	-0.010(3)	4(1)*
H5	0.561(4)	0.368(6)	0.046(4)	6(2)*

Starred atoms were refined isotropically.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$$(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos \gamma)*B(1,2) + ac(\cos \beta)*B(1,3) + bc(\cos \alpha)*B(2,3)]$$

Table 51. Atomic coordinates and equivalent isotropic temperature factors for  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2[\text{W}(\text{CO})_5]_2$

Atom	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
----	-	-	-	-----
W	0.33372(2)	-0.05671(4)	0.14990(2)	2.898(7)
As	0.43918(4)	0.11182(8)	0.20348(5)	2.37(2)
Cr <sup>†</sup>	0.48136(7)	0.2650(1)	0.33318(7)	2.50(3)
O1	0.2134(4)	0.0886(9)	0.2099(7)	10.7(3)
O2	0.2075(4)	-0.2572(9)	0.0787(5)	7.7(2)
O3	0.2824(5)	0.082(1)	-0.0300(5)	9.4(3)
O4	0.3863(6)	-0.1978(9)	0.3270(5)	8.9(3)
O5	0.4444(5)	-0.233(1)	0.0945(6)	8.7(3)
O6 <sup>†</sup>	0.4293(4)	0.0547(7)	0.4198(4)	5.2(2)
O7 <sup>†</sup>	0.3188(3)	0.3232(8)	0.2314(4)	5.3(2)
C1	0.2586(5)	0.038(1)	0.1879(8)	6.0(3)
C2	0.2548(5)	-0.184(1)	0.1059(6)	4.7(2)
C3	0.3006(5)	0.030(1)	0.0341(7)	5.0(3)
C4	0.3684(5)	-0.143(1)	0.2641(6)	4.9(3)
C5	0.4056(5)	-0.167(1)	0.1140(7)	5.0(3)
C6 <sup>†</sup>	0.4487(5)	0.1318(9)	0.3854(5)	3.4(2)
C7 <sup>†</sup>	0.3815(5)	0.2986(9)	0.2694(5)	3.3(2)
Cd1 <sup>†</sup>	0.4819(6)	0.4628(9)	0.3695(6)	4.5(2)
Cp2 <sup>†</sup>	0.5510(5)	0.439(1)	0.3601(6)	4.5(2)
Cd3 <sup>†</sup>	0.5894(5)	0.349(1)	0.4179(6)	4.5(2)
Cd4 <sup>†</sup>	0.5431(6)	0.315(1)	0.4660(6)	4.9(3)
Cd5 <sup>†</sup>	0.4758(5)	0.383(1)	0.4362(6)	4.7(2)
H1 <sup>†</sup>	0.441(4)	0.509(8)	0.333(5)	4(2)*
H2 <sup>†</sup>	0.567(4)	0.469(8)	0.319(5)	5(2)*
H3 <sup>†</sup>	0.634(5)	0.309(9)	0.432(5)	6(3)*
H4 <sup>†</sup>	0.560(3)	0.262(7)	0.508(4)	2(2)*
H5 <sup>†</sup>	0.431(5)	0.39(1)	0.451(5)	6(2)*

Starred atoms were refined isotropically.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$$(4/3) * [a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) + ab(\cos \gamma) * B(1,2) + ac(\cos \beta) * B(1,3) + bc(\cos \alpha) * B(2,3)]$$

Table 52. Data Collection and Processing Parameters for  $[\text{CpCr}(\text{CO})_2]_2[\text{Fe}(\text{CO})_4]$  (23) and  $[\text{CpCr}(\text{CO})_2]_2[\text{Fe}(\text{CO})_4]_2$  (24)

	Compound (23)	Compound (24)
Chemical formula	$[\text{Cp}_2\text{Cr}_2\text{P}_2(\text{CO})_4][\text{Fe}(\text{CO})_4]$	$[\text{Cp}_2\text{Cr}_2\text{P}_2(\text{CO})_4][\text{Fe}(\text{CO})_4]_2$
Molecular weight	576.06	743.95
Crystal system	Monoclinic	Triclinic
Space group	$P 2_1/c$	$P\bar{1}$
$a(\text{\AA})$	17.024(1)	10.209(2)
$b(\text{\AA})$	8.180(1)	10.212(2)
$c(\text{\AA})$	30.891(2)	15.989(3)
$\alpha(^{\circ})$	90.	106.93(1)
$\beta(^{\circ})$	100.953(5)	91.87(1)
$\gamma(^{\circ})$	90	119.50(1)
$V(\text{\AA}^3)$	4223.4(7)	1356.5(4)
$Z$	8	2
$D_c(\text{Mgm}^{-3})$	1.812	1.82
$\mu(\text{cm}^{-1})$	18.57	19.86
No. of unique reflections	6616	4765
$\theta$ max	$24^{\circ}$	$25^{\circ}$
No. observed reflections	3743	3489
$h_{\min} \rightarrow h_{\max}$	$0 \rightarrow 19$	$0 \rightarrow 12$
$k_{\min} \rightarrow k_{\max}$	$0 \rightarrow 9$	$-12 \rightarrow 10$
$l_{\min} \rightarrow l_{\max}$	$-35 \rightarrow 34$	$-18 \rightarrow 18$
No. of variables	639	401
$R_F$	0.033	0.029
$R_w(w = [\sigma^2(F) + 0.0004F^2 + 1])^{-1}$	0.038	0.034
$S$	0.389	0.491
$(\Delta/\sigma)_{\max}$	0.11	0.01
$(\Delta\rho)_{\min}/\max(e\text{\AA}^{-3})$	$-0.107/0.292$	$-0.098/0.320$

Data were collected on a four circle CAD4 diffractometer at 26°C and computer programs for structural solution and refinement are from the MolEN package<sup>118</sup> and performed on a Micro VAX-II mini-computer.

Positional parameters for the non-hydrogen atoms and their equivalent displacement parameters are presented in Table 53 and 54.

Table 53. Positional and Equivalent Displacement Parameters for the Non-Hydrogen Atoms of  $[\text{CpCr}(\text{CO})_2]_2\text{P}_2[\text{Fe}(\text{CO})_4]$  (23)

Atom	x	y	z	B( $\text{\AA}^2$ )
Fe1a	0.11424(5)	0.4424(1)	0.41739(3)	3.19(2)
Fe1b	0.60569(5)	0.3121(1)	0.91978(3)	3.21(2)
Cr1a	0.16305(6)	0.8164(1)	0.32429(3)	3.34(2)
Cr1b	0.66595(6)	0.6768(1)	0.82759(3)	3.25(2)
Cr2a	0.31259(5)	0.6605(1)	0.37490(3)	3.03(2)
Cr2b	0.81292(6)	0.5255(1)	0.88264(3)	3.17(2)
P1a	0.18292(9)	0.5854(2)	0.37468(5)	2.64(3)
P1b	0.68190(9)	0.4516(2)	0.88004(5)	2.84(3)
P2a	0.2085(1)	0.5492(2)	0.31309(5)	3.41(4)
P2b	0.7130(1)	0.4088(2)	0.81977(6)	3.65(4)
O1a	0.0217(3)	0.2515(9)	0.4689(2)	8.7(2)
O1b	0.4930(3)	0.1475(8)	0.9650(2)	7.8(2)
O2a	0.2588(3)	0.2619(8)	0.4560(2)	7.5(2)
O2b	0.7401(3)	0.1068(8)	0.9610(2)	6.7(1)
O3b	0.5885(4)	0.5912(8)	0.9766(2)	7.3(2)
O3a	0.0957(4)	0.7273(8)	0.4717(2)	7.1(2)
O4b	0.5160(3)	0.1787(8)	0.8368(2)	6.8(2)
O4a	0.0129(3)	0.3138(8)	0.3374(2)	7.3(2)
O5a	0.1225(3)	0.9626(7)	0.4063(2)	6.2(1)
O5b	0.6176(3)	0.8234(6)	0.9072(2)	5.4(1)
O6a	-0.0031(3)	0.6794(8)	0.3033(2)	7.9(2)
O6b	0.5003(3)	0.5377(8)	0.8014(2)	7.4(2)
O7a	0.3900(3)	0.6629(8)	0.2951(2)	7.1(1)
O7b	0.8949(3)	0.5149(8)	0.8038(2)	7.0(1)
O8a	0.3524(3)	0.3038(6)	0.3783(2)	5.8(1)
O8b	0.8545(3)	0.1687(7)	0.8914(2)	6.8(2)
C1a	0.0583(4)	0.328(1)	0.4487(2)	5.2(2)
C1b	0.5370(4)	0.212(1)	0.9471(2)	5.0(2)
C2a	0.2029(4)	0.332(1)	0.4399(2)	4.5(2)
C2b	0.6889(4)	0.1892(9)	0.9445(2)	4.2(2)
C3b	0.5955(4)	0.489(1)	0.9532(2)	4.6(2)
C3a	0.1018(4)	0.618(1)	0.4493(2)	4.4(2)
C4b	0.5507(4)	0.236(1)	0.8687(2)	4.3(2)
C4a	0.0525(4)	0.367(1)	0.3683(2)	4.5(2)
C5a	0.1391(4)	0.9001(8)	0.3757(2)	4.0(2)
C5b	0.6373(4)	0.7621(8)	0.8772(2)	3.7(1)
C6a	0.0619(4)	0.7313(9)	0.3115(3)	4.8(2)
C6b	0.5638(5)	0.588(1)	0.8117(3)	5.0(2)
C7a	0.3581(4)	0.665(1)	0.3247(2)	4.9(2)
C7b	0.8611(4)	0.522(1)	0.8332(3)	4.9(2)
C8a	0.3370(4)	0.4393(9)	0.3771(2)	3.8(1)
C8b	0.8375(4)	0.3051(9)	0.8881(2)	4.5(2)
C11a	0.1362(6)	0.911(1)	0.2571(3)	7.1(2)
C11b	0.6398(6)	0.768(1)	0.7594(2)	6.1(2)
C12a	0.2175(5)	0.880(1)	0.2670(2)	6.1(2)
C12b	0.7215(5)	0.737(1)	0.7704(2)	5.9(2)
C13a	0.2515(5)	0.984(1)	0.3012(3)	5.6(2)
C13b	0.7546(5)	0.839(1)	0.8050(2)	5.4(2)
C14a	0.1905(5)	1.0755(9)	0.3133(3)	5.4(2)
C14b	0.6926(5)	0.9334(9)	0.8160(2)	5.2(2)
C15a	0.1176(6)	1.031(1)	0.2864(3)	6.4(2)
C15b	0.6221(5)	0.891(1)	0.7877(2)	5.6(2)
C21a	0.3091(4)	0.777(1)	0.4385(2)	4.5(2)
C21b	0.8066(4)	0.645(1)	0.9459(2)	4.7(2)
C22b	0.8237(4)	0.7664(9)	0.9177(2)	4.3(2)
C22a	0.3288(4)	0.9004(9)	0.4111(2)	4.4(2)
C23b	0.8959(4)	0.7263(9)	0.9058(3)	5.4(2)
C23a	0.4000(4)	0.854(1)	0.3990(3)	5.4(2)
C24b	0.9248(4)	0.581(1)	0.9260(3)	5.3(2)
C24a	0.4258(4)	0.703(1)	0.4199(3)	5.3(2)
C25b	0.8692(5)	0.533(1)	0.9521(3)	5.5(2)
C25a	0.3680(4)	0.655(1)	0.4446(2)	4.3(2)

<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:  $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma) B_{12} + ac(\cos \beta) B_{13} + bc(\cos \alpha) B_{23}]$

Table 54. Positional and Equivalent Displacement Parameters for the Non-hydrogen Atoms of  $[\text{CpCr}(\text{CO})_2]_2[\text{Fe}(\text{CO})_4]_2$  (**24**)<sup>a</sup>

Atom	x	y	z	B(Å <sup>2</sup> )
Fe1	-0.21591(5)	0.31432(6)	0.71859(4)	3.35(1)
Fe2	0.09568(6)	0.06556(5)	0.78142(4)	3.36(1)
Cr1	0.22538(6)	0.41769(6)	0.65136(4)	2.65(1)
Cr2	0.26641(6)	0.57412(6)	0.84861(4)	2.64(1)
P1	0.03258(9)	0.39830(9)	0.74695(6)	2.55(2)
P2	0.15136(9)	0.28570(9)	0.75313(6)	2.55(2)
O1	-0.3269(4)	0.3113(5)	0.5476(3)	9.3(1)
O2	-0.4127(4)	0.2035(5)	0.8410(2)	7.9(1)
O3	-0.1522(4)	0.6360(4)	0.8214(3)	7.9(1)
O4	-0.2934(5)	-0.0186(4)	0.6370(3)	7.9(1)
O5	-0.1556(4)	0.0699(5)	0.8631(3)	8.0(1)
O6	0.2637(5)	0.1256(4)	0.9532(3)	9.2(1)
O7	-0.1365(5)	-0.2538(4)	0.6596(3)	7.6(1)
O8	0.3151(4)	0.0267(4)	0.6788(3)	7.9(1)
O9	0.1052(4)	0.6165(3)	0.6149(2)	6.00(9)
O10	-0.0535(4)	0.1315(4)	0.5182(2)	6.1(1)
O11	0.1133(4)	0.4284(4)	0.9823(2)	6.2(1)
O12	0.5011(3)	0.4907(4)	0.8852(3)	5.93(9)
C1	-0.2811(5)	0.3165(6)	0.6150(3)	5.5(1)
C2	-0.3331(5)	0.2494(5)	0.7944(3)	4.8(1)
C3	-0.1750(4)	0.5129(5)	0.7795(3)	4.9(1)
C4	-0.2618(5)	0.1115(6)	0.6679(3)	5.1(1)
C5	-0.0568(5)	0.0704(5)	0.8329(3)	5.0(1)
C6	0.2013(6)	0.1039(5)	0.8864(4)	5.5(1)
C7	-0.0452(5)	-0.1271(5)	0.7059(3)	4.7(1)
C8	0.2336(5)	0.0453(5)	0.7199(4)	4.9(1)
C9	0.1499(4)	0.5411(4)	0.6308(3)	3.8(1)
C10	0.0514(4)	0.2395(5)	0.5701(3)	3.8(1)
C11p	0.3456(5)	0.4343(6)	0.5421(3)	5.4(1)
C11	0.1696(5)	0.4811(4)	0.9303(3)	3.9(1)
C12p	0.3452(4)	0.3181(6)	0.5716(3)	5.5(1)
C12	0.4104(4)	0.5192(4)	0.8694(3)	3.8(1)
C13p	0.4294(4)	0.3923(5)	0.6596(3)	4.6(1)
C14p	0.4835(4)	0.5567(5)	0.6832(3)	4.3(1)
C15p	0.4302(4)	0.5817(5)	0.6118(3)	4.5(1)
C21p	0.3748(5)	0.8006(4)	0.8170(3)	4.3(1)
C22p	0.4696(5)	0.8195(5)	0.8887(3)	4.6(1)
C23p	0.3921(6)	0.8026(5)	0.9583(3)	5.3(1)
C24p	0.2470(5)	0.7736(5)	0.9282(3)	5.4(1)
C25p	0.2344(5)	0.7705(4)	0.8408(3)	4.5(1)

<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:  $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma) B_{12} + ac(\cos \beta) B_{13} + bc(\cos \alpha) B_{23}]$ .