CHAPTER III EXPERIMENTAL

3.1 General Procedures

All reactions were carried out either by use of 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 Physical measurements

^1H, ^{13}C, COSY, HMBC and HMQC NMR spectra were measured on a JEOL Lambda 400 MHz spectrometer or JEOL ECA 400 MHz spectrometer. The chemical shifts for ^1H and ^{13}C NMR spectra were referenced to residual C_6H_6 in benzene-d_6, to $(CH_3)_4Si$ in toluene-d_8 or to $CHCl_3$ in chloroform-d_1. ^{31}P NMR spectra were measured on the JEOL ECA 400 MHz spectrometer and the chemical shifts were referenced to the external standard 85% H_3PO_4. IR spectra in Nujol mulls were measured in the range of 4000–500 cm^{-1} by means of a Perkin-Elmer 2000 FTIR instrument. Elemental analyses were performed by the analytical unit of the Research School of Chemistry, Australian National University, the analytical unit of the CMMAC of the National University of Singapore and in-house microanalytical laboratory using a Perkin–Elmer 2400 Series II CHNS/O System except for Cr which was determined as CrO_4^{2-} according to the method by Haupt in our own laboratory [125]. Mass spectrometric measurements, performed by direct injection using electrospray ionization (ESI), were made on an Agilent 6230 LCMS instrument. Electrospray (high resolution) mass spectrometric measurements were obtained on an Accurate Mass Q-Tof spectrometer. Single crystal X-ray diffractometry services were performed by the X-ray Crystallography Laboratory in the University of Malaya, University of Christchurch in New Zealand and the CMMAC Laboratory of the National University of Singapore.

3.1.2 Solvents and reagents

All solvents used are of AR grade and distilled from sodium/benzophenone prior to use. Chromatographic materials were silica gel (Merck Kieselgel 60, 35-70 and 230-400 Mesh ASTM); florisil (BDH, 60 and 230-400 Mesh ASTM), Celite (Fluka AG) and Kieselgel 60 F_{254} TLC plates were dried at 140 ^{o}C overnight before chromatographic use. Chromium or molybdenum hexacarbonyl (99% purity) was purchased from Sigma-Aldrich Chemical Company; cyclopentadiene was purchased from Fluka. The ligands, bibenzyl trisulfide, bibenzyl disulfide and 2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide (Woollins' Reagent), were purchased from Sigma Aldrich Chemical Company; 2,4-bis(p-tolylthio)1,3-dithia-2,4-diphosphetane-2,4-disulfide (Davy's reagent) was purchased from TCI (Tokyo) Chemical; organic reagents for syntheses of thioarylphosphine series ligands: 1.6M *n*-butyllithium in *n*-hexane, *ortho*-bromothioanisole, *para*-bromothioanisole, and *p*-chlorodiphenylphosphine (98% purity) were purchased from Sigma Aldrich and used without further purification; phosphorus trichloride (99% purity) and *P*,*P*-dichlorophenylphosphine (99% purity) were purchased from Merck Chemical Company.

3.2 Preparation of starting complexes

3.2.1 Preparation of Dicyclopentadienylhexacarbonyldichromium and Dicyclopentadienylhexacarbonyldimolybdenum, $[CpM(CO)_3]_2$ [M = Cr(1) or Mo(2)]

The procedure was adapted from Manning *et al.* [126] as follows :

To a stirred suspension of thinly sliced sodium metal (0.39 g, 0.017 mol) in diglyme (120 mL) and *n*-hexane (30 mL) in a 3-necked 500 mL round-bottomed flask was added freshly cracked cyclopentadiene (4 mL) *via* a syringe over a period of 30 minutes. Stirring was continued until all the sodium has reacted giving a pink colour solution. $M(CO)_6$ (M = Cr (4.00 g, 0.018mol) or Mo (4.75 g, 0.018 mol)) was then added and the yellow mixture refluxed with stirring for *ca.* 4 h, using an oil bath maintained at 175 °C. The $M(CO)_6$ sublimate on the condenser walls was occasionally washed down by *n*-hexane and returned 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 which was coated with some remaining sublimed $M(CO)_6$, a solution of hydrated ferric sulphate, (14.539 g, 0.036 mol) in water (182 mL) and acetic acid (11 mL) was slowly added with stirring over a period of *ca.* 0.5 h. Later, the deep green suspension was continuously stirred inside an ice bath. The fine deep green solid material of Dicyclopentadienylhexacarbonyldichromium and the fine purple solid material of Dicyclopentadienyl-hexacarbonyldimolybdenum were filtered off under nitrogen using a 200 mL coarse sintered filter funnel layered with celite (1 cm). The collected precipitate was dried overnight in *vacuo*. For M = Cr, further purification can be done by sublimation at *ca.* 120 °C / 0.1 mm Hg to give the dark green crystalline product (2.41 g, *ca.* 60% yield). When M = Mo, the purple precipitate was purified by recrystallization under nitrogen from tetrahydrofuran (4.36 g, 98.8%yield). Dicyclopentadienylhexacarbonyldichromium were stored in the Dribox at -28 °C and dicyclopentadienylhexacarbonyldimolybdenum were stored in the Dribox at ambient tempetature.

3.2.2 Preparation of Dicyclopentadienyltetracarbonyldichromium, $[CpCr(CO)_2]_2$

The procedure which was adapted from Hackett *et al.* [5] is as follows :

A deep green suspension of $[CpCr(CO)_3]_2$ (200 mg, 0.497 mmol) in toluene (15 mL) was refluxed 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 layered with *n*-hexane (*ca.* 1 mL). Cooling at -30 °C for 1 h yielded fine deep green crystals of $[CpCr(CO)_2]_2$ (163 mg, 0.471 mmol, *ca.* 95% yield).

3.2.3 Preparation of Dicyclopentadienyltetracarbonyldimolybdenum, $[CpMo(CO)_2]_2$

The procedure which was adapted from Curtis *et al*. [11] is as follows :

A reddish purple suspension of $[CpMo(CO)_2]_3$ (1.0 g, 2.04 mmol) in toluene (~25 mL) was heated at 120 °C together with vigorous stirring for 24 h. The resultant dark brown solution was chromatographed on a silica gel column (2 cm x 6 cm) prepared in *n*-hexane. The eluate in toluene (35 mL) was then evaporated to dryness under *vacuo* yielding dark brown crystalline solids of $[CpMo(CO)_2]_2$ (0.869 g, 2.00 mmol, *ca.* 98.04% yield).

3.2.4 Preparation of Tris(*o*-thiomethylphenyl)phosphine, $P(C_6H_4SMe\text{-}o)_3$

The procedure which was adapted from D.W.Meek *et al.* [127] is as follows :

Liquid *o*-bromothioanisole (2.50 g, 0.0123 mol) was added into the sodium dried ether (13 mL) in a 100 mL three-necked round bottomed flask fitted with a water-cooled condenser and a pressure-equalizing dropping funnel. The ether solution was cooled to

0 °C in an ice bath. Then, it was treated dropwise over a period of 2 h with 1.6M *n*-butyllithium in *n*-hexane (8 mL) at 0 °C under nitrogen *via* a pressure equalizing dropping funnel and stirred vigorously. A white precipitate started to form when one-half of the *n*-butyllithium was added in. When addition of *n*-butyllithium is complete, the resulting mixture was further stirred for another 1 h at 0 °C. Subsequently, phosphorus trichloride (0.56 g, 0.0041 mol) in ether (8 mL) was added in dropwise over 3 h at 0 °C. After that, the reaction mixture was warmed up to room temperature and was hydrolyzed with 8 mL of 0.2N hydrochloric acid. At this juncture, the white suspension was further stirred to ensure all the inorganic salts have dissolved and the white precipitate was then filtered by a Buchner funnel and washed thoroughly with distilled water, ethanol and followed by ether. The resultant white precipitate was dried under air (yield: $P(C_6H_4SMe\text{-}o)_3$ = 1.285 g, 78.00 %). The product was then recrystallized from toluene/ether to give colorless crystalline solids.

3.2.5 Synthesis of Bis(*o*-thiomethylphenyl)phenylphosphine, $PPh(C_6H_4SMe\text{-}o)_2$

The procedure which was adapted from D.W.Meek [127] is as follows: Liquid *o*-bromothioanisole (2.50 g, 0.0123 mol) was treated as described in Sec. 3.2.4. Phenyl phosphorus dichloride (1.10 g, 0.0031 mol) in ether (7 mL) was added dropwise with stirring. When the addition of phosphine solution was complete, the resulting two-phase mixture was stirred at room temperature for 2 h. 5 mL of distilled water followed by 8 mL of 0.2N hydrochloric acid was added to hydrolyze the excess inorganic salts. The white solid was filtered through a Buchner funnel, washed with a small amount of cold ethanol, and dried under air. (yield: 1.00 g, 0.0028 mol, 90.32 %).

3.2.6 Synthesis of (*o*-thiomethylphenyl)diphenyl phosphine, $PPh_2(C_6H_4SMe\text{-}o)$

The procedure which was adapted from D.W.Meek [127] is as follows: Liquid *o*-bromothioanisole (2.50 g, 0.0123 mol) was treated as described in Sec. 3.2.4. Then, diphenyl phosphorus chloride (2.44 g, 0.0111 mol) in ether (9 mL) was added dropwise with stirring for 3 h. When the addition of phosphine solution was complete, the resulting white precipitate was then hydrolyzed with 0.2N hydrochloric acid (8 mL). After a short period of stirring to ensure that all the inorganic salts have dissolved, the white solid was filtered through a Buchner funnel, washed with water, ethanol and ether, and dried under air. (yield: 1.39 g, 0.0045 mol, 40.73 %).

3.2.7 Preparation of Tris(*p*-thiomethylphenyl)phosphine, $P(C_6H_4SMe\text{-}p)_3$

The procedure which was adapted from D.W.Meek [127] is as follows:

4-Bromothioanisole (5.00 g, 0.0246 mol) and diethyl ether (30 mL) was treated with 1.6M *n*-butyllithium in *n*-hexane (15.5 mL) as described in Sec. 3.2.4. Subsequently, phosphorus trichloride (1.13 g, 0.0082 mol) in ether (15 mL) was added in dropwise over 2.5 h at 0 °C and a yellow precipitate was formed during this addition. When the addition was complete, the reaction mixture was warmed up to room temperature and was slowly hydrolyzed with 18 mL of 0.2N hydrochloric acid. At this juncture, the yellow precipitate immediately dissolved and a colorless suspension was obtained. The suspension was further stirred overnight and the white precipitate was filtered through a Buchner funnel and washed thoroughly with distilled water, methanol and followed by ether. The resultant white precipitate was dried under air (1.78 g) and further analyzed *via* ^1H NMR and a mixture of $P(C_6H_4SMe\text{-}p)_3$ and $P(O)(C_6H_4SMe\text{-}p)_3$ was found. Subsequently, the mixture of products was dissolved in toluene (~5 mL) and then loaded onto a prepared silica gel column in *n*-hexane (2 cm x 6 cm). The following fractions were eluted:

(i) A pale yellow fraction was eluted with *n*-hexane-toluene (2:1, 65 mL). The solution was evaporated to dryness under *vacuo* and a white precipitate of $P(C_6H_4SMe\text{-}p)_3$ was formed, (0.99 g, 0.0025 mol, 39.9% yield). ^1H NMR ($CDCl_3$): δ 2.47 (s, CH_3), δ 7.20 - 7.19 (m, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 15.48 (CH_3), δ 140.07, 134.25, 134.06, 133.43, 133.33, 126.31, 126.23 (C_6H_4). ^{31}P NMR ($CDCCl_3$): δ -8.41. The white precipitate was redissolved in a minimum volume of THF followed by layering with ether and was left to recrystallize at -28 °C. After 1 week, fine crystalline white solids were formed.

(ii) A light yellowish fraction was eluted with THF (50 mL). The solution was evaporated to dryness under *vacuo* and a yellowish white precipitate of $P(O)(C_6H_4SMe\text{-}p)_3$ was formed, (0.67 g, 0.0016 mol, 25.7% yield). ^1H NMR ($CDCl_3$): δ 2.49 (s, CH_3), δ 7.28 - 7.27, 7.57 - 7.49 (m, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 14.98 (CH_3), δ 144.62, 144.59, 132.51, 132.40, 125.48, 125.34 (C_6H_4). ^{31}P NMR ($CDCl_3$): δ 28.74. The yellowish white precipitate was redissolved in a minimum volume of THF followed by layering with ether and was left to recrystallize at -28 °C. After 3 days, white crystalline crystals suitable for single crystal X-ray diffractometry analyses were formed.

3.2.8 Preparation of Diiron Enneacarbonyl, $Fe_2(CO)_9$

The procedure which was adapted from R. B. King [128] is as follows:

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 the sides and bottom with aluminium foil and the temperature was 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 followed by ether, and then dried in *vacuo*.

3.3 Reactions of $[CpCr(CO)_3]_2$ with Bibenzyl Trisulfide, Bz_2S_3

3.3.1 Reactivity studies of $[CpCr(CO)_3]_2$ with equimolar Bibenzyl Trisulfide at ambient temperature

To a deep green solution of $[CpCr(CO)_3]_2$ (**1**) (200 mg, 0.497 mmol) in toluene (15 mL) was added Bz_2S_3 (138 mg, 0.497 mmol). The dirty green mixture was allowed to stir at ambient temperature for 2 h. The resultant yellowish brown reaction mixture was concentrated to *ca.* 2 mL under *vacuo* and then loaded onto a silica gel column (1.5 cm x 10 cm) prepared in *n*-hexane. The following fractions were eluted as follows:

(i) A yellowish brown fraction in *n*-hexane-toluene (2:1, 35mL) which when concentrated and recrystallized from suitable solvents to yield deep green crystalline solids of $[CpCr(CO)_2]_2S$ (**5**) (108 mg, 0.286 mmol, 57.4% yield).

(ii) A dark brown fraction in toluene (25 mL) which when concentrated to dryness yielded dark brown crystalline solids of $[CpCr(CO)_2(SBz)]_2$ (**6**) (98 mg, 0.166 mmol, 33.3% yield). Data : ^1H NMR (benzene-d_6): δ4.16 (s, Cp). ^{13}C NMR (benzene-d_6) : δ 89.61 (Cp). IR:ν(CO) at 1986s, 1954m, 1901vs cm^{-1} (nujol) ; other bands at 1066vw, 1025vw, 840w, 722w cm^{-1} (nujol). Anal. Calcd. for $C_{28}H_{24}Cr_2O_4S_2$: C, 56.15; H, 4.35; Cr, 17.25; O, 10.37; S, 10.59. Found: C, 56.76; H, 4.05; Cr, 17.57; S, 10.81; O, 10.81.

(iii) A purple fraction in ether (10 mL) which when concentrated and recrystallized from suitable solvents to yield dark purple crystalline solids of $[CpCrSBz]_2S$ (**7**) (11 mg, 0.021 mmol, 4.3% yield). Data : ^1H NMR (benzene-d_6): δ13.89 (br, Cp, $\nu_{½}$ = 57 Hz). ^{13}C NMR (benzene-d_6): δ101.03 (Cp), δ 135.60, 133.14 (C_6H_5). IR:ν at 1063vw, 1015vw, 840w, 732w cm^{-1} (nujol). Anal. Calcd. for $C_{24}H_{24}Cr_2S_3$: C, 56.25; H, 4.68; Cr, 20.31; S, 18.75. Found: C, 56.57; H, 4.15; Cr, 19.59; S, 18.31. A greenish blue fraction remained uneluted at the top of the column.

3.3.2 Reactivity studies of $[CpCr(CO)_3]_2$ with equimolar Bibenzyl Trisulfide at 60 °C

To a deep green solution of $[CpCr(CO)_3]_2$ (200 mg, 0.498 mmol) in toluene (20 mL) was added Bibenzyl Trisulfide (139 mg, 0.498 mmol) and was stirred for 5 h at 60 °C. The resultant dark brown reaction mixture was concentrated to *ca.* 2 mL and loaded onto a silica gel column (1.5 cm x 8 cm) prepared in *n*-hexane. Elution gave two fractions:

(i) A dirty green solution in *n*-hexane-toluene (1:1, 45 mL) which yielded dark green crystalline solids of $[CpCr(CO)_2]_2S$ (**5**) (152 mg, 0.402 mmol, 80.8% yield).

(ii) A deep purple solution in toluene-ether (3:1, 25 mL) which yielded dark purple crystalline solids of $[CpCr(SBz)]_2S$ (**7**) (35 mg, 0.068 mmol, 13.7% yield).

A greenish blue layer remained uneluted at the top rim of the column.

3.3.3 Reactivity studies of $[CpCr(CO)_2]_2$ with equimolar Bibenzyl Trisulfide at ambient temperature

A deep green solution of $[CpCr(CO)_2]_2$ (**2**) (200 mg, 0.578 mmol) in toluene (20 mL) containing Bibenzyl Trisulfide (161 mg, 0.578 mmol) was stirred for 72 h at ambient temperature. The resultant dirty brown reaction mixture was filtered through Celite, concentrated and loaded onto a silica gel column (1.5 cm x 10 cm) prepared in *n*-hexane. Two fractions were eluted as follows :

(i) A dirty green solution in *n*-hexane-toluene (1:1, 45 mL) which gave dark green crystalline solids of $[CpCr(CO)_2]_2S$ (**5**) (5 mg, 0.008 mmol, 5.1% yield).

(ii) A deep purple solution in toluene-ether (3:1, 35 mL) which gave dark purple crystalline solids of $[CpCr(SBz)]_2S$ (**7**) (135 mg, 0.264 mmol, 15.8% yield).

3.3.4 Thermolysis of $[CpCr(CO)_2(SBz)]_2$ (6)

A stirred dark brown solution of $[CpCr(CO)_2(SBz)]_2$ (**6**) (100 mg, 0.169 mmol) in toluene (10 mL) was maintained at 80 °C for *ca.* 1 h. The resultant dirty brown solution was filtered through Celite (1 cm disc), concentrated (*ca.*1 mL) and loaded onto a silica gel column (1.5 cm x 6 cm) prepared in *n*-hexane. Two fractions were eluted:

(i) A dirty green fraction in *n*-hexane-toluene (2:1, 25 mL) which gave dark green crystalline solids of $[CpCr(CO)_2]_2S$ (**5**) (39 mg, 0.103 mmol, 36.0% yield).

(ii) A deep purple solution in ether (25 mL) which gave dark purple crystalline solids of $[CpCr(SBz)]_2S$ (40 mg, 0.078 mmol, 27.4% yield).

3.3.5 Thermolysis of $[CpCr(SBz)]_2S$ (7)

A stirred deep purple solution of $[CpCr(SBz)]_2S$ (100 mg, 0.195 mmol) in toluene (10 mL) was maintained at 100 °C for 20 h. The resultant dirty purple solution was filtered through Celite (1 cm disk), concentrated (*ca.* 1 mL) and loaded onto a silica gel column (1.5 cm x 6 cm) prepared in *n*-hexane-toluene (1:1). Two fractions were eluted:

(i) A grayish green solution in toluene (20 mL) which gave dark green crystalline solids of $Cp_4Cr_4S_4$ (**8**) (25 mg, 0.042 mmol, 22.0% yield).

(ii) A deep purple solution in toluene-ether (3:1, 25 mL) which gave dark purple crystalline solids of $[CpCr(SBz)]_2S$ (**7**) (35 mg, 0.059 mmol, 35% recovery).

A greenish blue layer remained uneluted at the top rim of the column.

3.3.6 NMR Tube Reactions

(a) Reaction of $[CpCr(CO)_2]_2S$ (5) with Bz_2S_3 at 60 °C

A dirty green mixture of $[CpCr(CO)_2]_2S$ (**5**) (20 mg, 0.05 mmol) and Bz_2S_3 (15 mg, 0.05 mmol) in benzene-d_6 (0.6 mL) in a 5 mm NMR tube, suspended in an oil bath at 60 °C and its ^{1}H NMR spectra were monitored at intervals (30, 60, 120 min and 24 h). From the spectra, $[CpCr(CO)_2]_2S$ (**5**) (74.4% recovery), $[CpCr(SBz)]_2S$ (**7**) (1.1% yield) and $Cp_4Cr_4S_4$ (**8**) (2.5% yield) were found after 24 h.

(b) Reaction of $[CpCr(CO)_2(SBz)]_2$ (6) with Bz_2S_3 at ambient temperature

A dark brown mixture of $[CpCr(CO)_2(SBz)]_2$ (**6**) (15 mg, 0.03 mmol) and Bz_2S_3 (7 mg, 0.03 mmol) in benzene-d_6 (0.6 mL) in a 5 mm NMR tube was clamped to a mechanical shaker, and its ^{1}H NMR spectra were monitored at a regular intervals. From the spectra, $[CpCr(CO)_2]_2S$ (**5**) (27.5% yield) and $[CpCr(CO)_2(SBz)]_2$ (**6**) (33.4% recovery) were found after 26 h of reaction.

3.4 Reaction Of $[CpMo(CO)_3]_2$ With Bibenzyl Trisulfide

3.4.1 Reactivity studies of $[CpMo(CO)_3]_2$ with equimolar Bibenzyl Trisulfide at 60 °C

To a reddish purple solution of $[CpMo(CO)_3]_2$ (**3**) (200 mg, 0.41 mmol) in toluene (*ca.* 20 mL) was added Bz_2S_3 (114 mg, 0.41 mmol). The reaction mixture was stirred under nitrogen at 60 °C for 3.5 h. The resultant reddish brown solution was filtered through a disk of Celite (1 cm x 1.5 cm) and concentrated to *ca*. 2-3 mL, and then loaded onto a silica gel column (10 cm x 1.5 cm) which was prepared in *n*-hexane. The following fractions were eluted:

(i) A reddish brown fraction in a 2:1 *n*-hexane/toluene mixture (90 mL) which upon concentrated under *vacuo* and recrystallized from suitable solvents to yield dark brown crystalline solids of $[CpMo(CO)_2(SBz)]_2$ (**9**) (46 mg, 0.067 mmol, 16.3% yield). Data : ^{1}H NMR (C_6D_6): δ4.61 (s, C_5H_5), δ3.69 (s, CH_2), δ7.72 - 7.03 (m, C_6H_5). ^{13}C NMR (C_6D_6): δ38.85 (CH_2), δ96.79, 96.76, 96.72, 96.67 (C_5H_5), δ141.15, 130.32, 128.73, 127.72 ($S\text{-}CH_2\text{-}C_6H_5$), δ(CO) 256.67. IR: ν(CO) at 1944vs, 1918sh, 1849vs, 1831sh cm^{-1}; other bands, 1067vw, 1029vw, 1009w, 842w, 808m, 700m cm^{-1} (nujol). Anal. Calcd. for $C_{28}H_{24}Mo_2O_4S_2$: C, 49.4 ; H, 3.5 ; Mo, 28.2; S, 9.4. Found : C, 49.5 ; H, 3.6; Mo, 28.5; S, 9.3%.

(ii) A pink fraction in a 4:1 toluene/ether mixture (30 mL) which upon concentrated under *vacuo* and recrystallized from suitable solvents to yield fine dark pink crystalline solids of $[CpMo(SBz)(S)]_2$ (**10a**) (53 mg, 0.084 mmol, 20.5% yield). Data : ^{1}H NMR (C_6D_6): δ2.72 (s, CH_2), δ5.89 (s, C_5H_5), δ7.72 - 7.01 (m, C_6H_5). ^{13}C NMR (C_6D_6): δ38.8 (CH_2), δ98.22, 98.19, 98.14, 98.07 (C_5H_5), δ142.26, 129.79, 129.62 (S-CH_2-C_6H_5). IR: v at 1667m, 1599w, 1317w, 1277m, 1008w, 808m, 698s cm^{-1} (nujol). Anal. Calcd. for $C_{24}H_{24}Mo_2S_4$: C, 45.6; H, 3.8; Mo, 30.4; S, 20.3. Found : C, 45.6; H, 3.4; Mo, 30.7; S, 19.8%.

(iii) A brownish pink fraction in a 2:1 toluene/ether mixture (25 mL) which gave fine dark pink crystalline solids of $[CpMo(SBz)(S)]_2$ (**10b**) (102 mg, 0.161 mmol, 39.3% yield) when concentrated to dryness. Data : ^{1}H NMR (C_6D_6): δ2.78 (s, CH_2), δ5.84 (s, C_5H_5), δ 7.72 - 6.89 (m, C_6H_5). ^{13}C NMR (C_6D_6): δ41.57 (CH_2), δ97.95 (C_5H_5), δ142.05, 130.32, 129.37 (S-CH_2-C_6H_5). IR: v at 1667m, 1599w, 1317w, 1276m, 1011w, 800m, 698s cm^{-1} (nujol). Anal. Calcd. for $C_{24}H_{24}Mo_2S_4$: C, 45.6; H, 3.8; Mo, 30.4; S, 20.3. Found : C, 45.0; H, 3.5; Mo, 30.4; S, 20.5%.

(iv) A pinkish brown fraction in ether (7 mL) which upon concentrated under *vacuo* and recrystallized from suitable solvents to yield pinkish brown crystalline solids of $[CpMo(CO)(SBz)]_2S$ (**11**) (8 mg, 0.012 mmol, 2.9% yield). Data : ^{1}H NMR (C_6D_6): δ 4.02(s, CH_2), δ4.83 (s, C_5H_5), δ7.42 - 7.01 (m, C_6H_5). ^{13}C NMR (C_6D_6): δ49.37 (CH_2), δ 91.56, 91.24, 91.03, 90.71, 90.38 (C_5H_5), δ143.10, 128.74 (S-CH_2-C_6H_5), δ244.10 (CO). IR: v(CO) at 1925vs, 1869s, 1846sh cm^{-1}; other bands, 1061vw, 1031vw, 1011vw, 813m, 760m, 700m cm^{-1} (nujol). Anal. Calcd. for $C_{26}H_{24}Mo_2O_2S_3$: C, 47.6; H, 3.7; Mo, 29.3; S, 14.6. Found : C, 47.5; H, 3.8; Mo, 30.2; S, 14.9%.

A dark brown band remained uneluted on the top of the column.

3.4.2 Thermolysis of [CpMo(CO)$_2$(SBz)]$_2$ (9)

A stirred reddish brown solution of [CpMo(CO)$_2$(SBz)]$_2$ (**9**) (100 mg, 0.147mmol) in toluene (15 mL) was maintained at 60 °C for *ca.* 14.5 h. The resultant dark yellowish brown solution was filtered through Celite (1 cm disk), concentrated (*ca.* 2 mL) and then loaded onto a silica gel column (1.5 cm x 10 cm) prepared in *n*-hexane. Two fractions were eluted:

(i) A deep pink fraction in a 2:1 toluene/ether mixture (20 mL) which when concentrated to dryness gave deep pink crystalline solids of [CpMo(SBz)(S)]$_2$ (**10a**) (15 mg, 0.024 mmol, 16.3% yield).

(ii) A pinkish brown fraction in ether (15 mL) which when concentrated and recrystallized from suitable solvents to yield dark reddish brown crystalline solids of [CpMo(CO)(SBz)]$_2$S (**10b**) (25 mg, 0.038 mmol, 25.9% yield).

3.4.3 Thermolysis of [CpMo(CO)(SBz)]$_2$S (11)

A pinkish brown solution of [CpMo(CO)(SBz)]$_2$S (**11**) (100 mg, 0.152 mmol) in toluene (15 mL) was maintained at 110 °C for 18 h. The resultant dark yellowish brown solution was filtered through Celite (1 cm disk), concentrated (*ca.* 2 mL), and then loaded onto a silica gel column (1.5 cm x 10 cm) prepared in *n*-hexane-toluene (1:1). Only one fraction was eluted as a pink solution in 2:1 toluene/ether mixture (35 mL) which when concentrated to dryness gave deep pink crystalline solids of [CpMo(SBz)(S)]$_2$ (**10**) (24 mg, 0.038 mmol, 25.0% yield). A dark brown layer remained uneluted at the top rim of the column.

3.4.4 NMR tube reactions

(a) Thermolysis of [CpMo(CO)$_2$(SBz)]$_2$ (9) with Bz$_2$S$_3$

A reddish brown solution of [CpMo(CO)$_2$(SBz)]$_2$ (**9**) (20 mg, 0.029 mmol) in C$_6$D$_6$ (0.6 mL) placed in a 5 mm NMR tube was heated with an equivalent of Bz$_2$S$_3$ (8 mg, 0.029 mmol) at 60 °C for 9.5 h. Its ^{1}H NMR spectrum showed that the resultant yellowish brown solution consists of [CpMo(CO)(SBz)]$_2$S (**11**) (31% yield) and [CpMo(SBz)(S)]$_2$ (**10**) (49% yield) together with an uncharacterized dark brown precipitate.

(b) Thermolysis of [CpMo(CO)(SBz)]$_2$S (11) with Bz$_2$S$_3$

A pinkish brown solution of [CpMo(CO)(SBz)]$_2$S (**11**) (20 mg, 0.030 mmol) in d_8-toluene (0.6 mL) in a 5 mm NMR tube was heated with an equivalent of Bz$_2$S$_3$ (8 mg, 0.030 mmol) at 110 °C for 15 h. Its ^{1}H NMR spectrum showed that the resultant solution consists of [CpMo(SBz)(S)]$_2$ (**10**) (47% yield) together with an uncharacterized dark brown precipitate.

3.5 Reactions of [CpCr(CO)$_3$]$_2$ with Bibenzyl Disulfide, Bz$_2$S$_2$

3.5.1 Reactivity studies of [CpCr(CO)$_3$]$_2$ with equimolar Bibenzyl Disulfide at ambient temperature

To a deep green suspension of [CpCr(CO)$_3$]$_2$ (**1**) (200 mg, 0.498 mmol) in toluene (~20 mL) was added in an equimolar amount of Bz$_2$S$_2$ (122 mg, 0.498 mmol). The reaction mixture was allowed to stir at room temperature for 13.5 h until the color had changed to dirty brown. The resultant product mixture was filtered through a sintered-glass funnel to remove the excess ligand. Subsequently, the filtrate was evacuated to dryness and redissolved again in THF (~3 mL) followed by adsorption onto silica gel (~1.0 g). The brown color slurry was pumped under *vacuo* until completely dry and loaded onto a prepared silica gel column (1.5 cm x 10 cm) in *n*-hexane. The following fractions were eluted:

(i) A yellowish brown fraction in *n*-hexane-toluene (2:1) (35 mL) which when concentrated and recrystallized from suitable solvents to yield deep green crystalline solids of $[CpCr(CO)_2]_2S$ (**5**) (54 mg, 0.143 mmol, 28.8 % yield).

(ii) A dark brown fraction in toluene (15 mL) which when concentrated to dryness yielded dark brown crystalline solids of $[CpCr(CO)_2(SBz)]_2$ (**6**) (104 mg, 0.212 mmol, 42.6 % yield).

(iii) A purple fraction in ether (10 mL) which when concentrated to dryness yielded purple crystalline solids of $[CpCr(SBz)]_2S$ (**7**) (30 mg, 0.0584 mmol, 11.8 % yield). Further recrystallization from THF/ether solution yielded single crystals suitable for X-ray diffraction analysis.

A blue band remained uneluted on top of the column.

3.5.2 Reactivity studies of $[CpCr(CO)_3]_2$ with equimolar of Bibenzyl Disulfide at 110 ˚C

To a deep green suspension of $[CpCr(CO)_3]_2$ (**1**) (200 mg, 0.497 mmol) in toluene (~15 mL) was added in an equimolar amount of Bz_2S_2 (122 mg, 0.497 mmol). The reaction mixture was allowed to stir at 110 ˚C for 1 h. The resultant dark brown reaction mixture was filtered through celite to remove the excess ligand. The filtrate was concentrated to *ca.* 8 mL and was then absorbed onto celite (~3.5 g). The slurry was evacuated to dryness and chromatographed onto a silica gel column (1.5 cm x 11 cm) prepared in *n*-hexane. The following fractions were eluted:

(i) A yellowish brown fraction in *n*-hexane-toluene (6:1) (50 mL) which when concentrated and recrystallized from suitable solvents to yield deep green crystalline solids of $[CpCr(CO)_2]_2S$ (**5**) (101 mg, 0.267 mmol, 53.7% yield).

(ii) A dark brown fraction in toluene (15 mL) which when concentrated and recrystallized from suitable solvents to yield the known dark brown crystalline solids of $Cp_4Cr_4S_4$ (**8**) (46 mg, 0.076 mmol, 15.4% yield).

(iii) A dark brown fraction in ether-THF (1:1) (30 mL) which when concentrated to dryness yielded dark brown solids (119 mg) consisting of an inseparable mixture of two complexes in the proportion of 2:3 (estimated from TLC analysis). Despite repeated attempts, this mixture was not separated. ^1H NMR analysis of the mixture showed δ 4.94 (s, Cp) and δ 5.13 (s, Cp).

3.5.3 Reactivity studies of $[CpCr(CO)_2]_2$ with equimolar Bibenzyl Disulfide at 110 ˚C

To a deep green suspension of $[CpCr(CO)_2]_2$ (**2**) (150 mg, 0.433 mmol) in toluene (~10 mL) was added in an equimolar amount of Bz_2S_2 (107 mg, 0.433 mmol). The reaction mixture was allowed to stir at 110 ˚C for 1 h. The resultant dark brown reaction mixture was filtered through celite *via* a sintered-glass funnel. The filtrate was concentrated to *ca.* 3 mL left and was absorbed onto celite (~2.0 g). The slurry was evacuated to dryness and was chromatographed onto a silica gel column (1.5 cm x 10 cm) prepared in *n*-hexane. The following fractions were eluted:

(i) A yellowish brown fraction in *n*-hexane-toluene (1:2.5) (18 mL) which when concentrated to dryness gave deep green crystalline solids of $[CpCr(CO)_2]_2S$ (**5**) (66 mg, 0.175 mmol, 40.3 % yield).

(ii) A dark brown fraction in toluene (15 mL) which when concentrated to dryness gave dark brown crystalline solids of $Cp_4Cr_4S_4$ (**8**) (27.5 mg, 0.046 mmol, 10.6 % yield).

(iii) A dark brown fraction in ether-THF (1:1) (30 mL) which when concentrated to dryness gave dark brown solids (62 mg) consisting of an inseparable mixture of two complexes in the proportion of 2:3 (estimated from TLC analysis). Attempts to separate this mixture had resulted in failure.

3.5.4 NMR Tube Reaction

(a) Reaction of $[CpCr(CO)_2]_2$ (2) with equimolar Bibenzyl Disulfide at 60 ºC

A deep green solution of $[CpCr(CO)_2]_2$ (**2**) (20.0 mg, 0.058 mmol) with Bz_2S_2 (14 mg, 0.058 mmol) in C_6D_6 (~0.5 mL) was cothermolyzed at 60 °C. The reaction was monitored by recording its ^1H NMR spectrum at intervals. The final spectrum showed the presence of $[CpCr(CO)_2]_2S$ (**5**) (28.3% yield), $[CpCr(SBz)]_2S$ (**7**) (3.9% yield), $Cp_4Cr_4S_4$ (**8**) (19% yield) together with unreacted $[CpCr(CO)_2]_2$ (**2**) (9.7% recovery) after 6 h.

(b) Reaction of $[CpCr(CO)_2]_2S$ (5) with equimolar Bibenzyl Disulfide at 60 ºC

A dirty brown solution of $[CpCr(CO)_2]_2S$ (**5**) (20 mg, 0.053 mmol) with Bz_2S_2 (13 mg, 0.053 mmol) in C_6D_6 (~0.5 mL) was cothermolyzed at 110 °C The reaction was monitored by recording its ^1H NMR spectrum at intervals. The final spectrum showed only the presence of $Cp_4Cr_4S_4$ (**8**) (6.5 % yield) together with unreacted $[CpCr(CO)_2]_2S$ (**5**) (67.2% recovery) after 5 h.

3.6 Reactions of $[CpMo(CO)_2]_2$ with Bibenzyl Disulfide, Bz_2S_2

3.6.1 Reactivity studies of $[CpMo(CO)_2]_2$ with equimolar of Bibenzyl Disulfide at 70 °C

To a reddish brown solution of $[CpMo(CO)_2]_2$ (**4**) (200mg, 0.46mmol) in toluene (~20mL) was added Bz_2S_2 (114mg, 0.46mmol). The reaction mixture was stirred at 70 °C for 7.5 h. The resultant yellowish brown reaction mixture was filtered through a disc of Celite (1 cm x 1.5 cm). The filtrate was concentrated to dryness and redissolved in THF (~3 mL) and absorbed onto silica gel (~1.5 g). The dark brown slurry was evacuated to dryness under *vacuo* and chromatographed onto a silica gel column (9 cm x 1.5 cm) prepared in *n*-hexane. The following fractions were eluted:

(i) A yellowish brown fraction in *n*-hexane/toluene mixture (4:1, 20 mL) which upon concentrated under *vacuo* and recrystallized from suitable solvents to yield dark brown crystalline solids of $[CpMo(CO)(SBz)]_2$ (**12a**) (124 mg, 0.199 mmol, 43.3% yield). Data : ^1H NMR (C_6D_6): δ5.05, 4.69 (s, C_5H_5), δ3.64, 3.61 (d, CH_2), δ3.96, 3.93 (d, CH_2) δ7.50 - 7.08 (m, C_6H_5). ^{13}C NMR (C_6D_6): δ52.36(CH_2), δ91.58, 91.18 (C_5H_5), δ141.86, 129.79, 129.00, 127.31 ($S\text{-}CH_2\text{-}C_6H_5$), δ250.85, 246.50 (CO). IR: *v*(CO) at 1835vs, 1796s cm^{-1}; other bands, 800m, 763m, 721vw, 698s, 530w, 489sh, 474m cm^{-1} (nujol). Anal. Calcd. for $C_{26}H_{24}Mo_2O_2S_2$: C, 49.7 ; H, 3.8; Mo, 31.2; O, 5.1; S, 10.2. Found : C, 49.3; H, 3.5; Mo, 31.6; S, 10.6 %.

(ii) A yellowish green fraction in *n*-hexane/toluene mixture (1:1, 40 mL) which upon concentrated under *vacuo* and recrystallized from suitable solvents to yield green crystalline solids of *trans-anti* $[CpMo(CO)(SBz)]_2$ (**12b**) (98 mg, 0.158 mmol, 34.1%

yield). Data : ^{1}H NMR (C_6D_6): δ4.87 (s, C_5H_5), δ3.34, 3.31 (d, CH_2), δ 3.93, 3.90 (d, CH_2), δ7.72 - 7.01 (m, C_6H_5). ^{13}C NMR (C_6D_6): δ91.18 (C_5H_5), δ55.04 (CH_2), δ130.56, 129.71, 128.95, 127.26 (S-CH_2-C_6H_5), δ 249.41 (CO). IR: *v*(CO) at 1837vs, 1828sh, 1796.2sh cm^{-1}; other bands, 799m, 763m, 724vw, 698m, 535w, 490m, 474m cm^{-1} (nujol). Anal. Calcd. for $C_{26}H_{24}Mo_2O_2S_2$: C, 49.7; H, 3.8; Mo, 31.2; O, 5.1; S, 10.2. Found : C, 49.6; H, 3.7; Mo, 31.0; O, 5.1; S, 10.3 %.

(iii) A brownish pink fraction in toluene (40mL) which upon concentrated under *vacuo* and recrystallized from suitable solvents to yield pink solids of $[CpMo(SBz)S]_2$ (**10**) (16 mg, 0.025 mmol, 5.5% yield).

(iv) A reddish brown fraction in ether (8mL) which upon concentrated under *vacuo* and recrystallized from suitable solvents to yield reddish brown solids of $[CpMo(CO)(SBz)]_2S$ (**11**) (9 mg, 0.014 mmol, 3.1% yield).

3.6.2 Reactivity studies of $[CpMo(CO)_2]_2$ with equimolar Bibenzyl Disulfide at 110 °C

To a reddish brown suspension of $[CpMo(CO)_2]_2$ (**4**) (200 mg, 0.46 mmol) in toluene (~20 mL) was added an equimolar amount of Bz_2S_2 (114 mg, 0.46 mmol). The reaction mixture was refluxed with stirring for 2h. The resultant dark yellowish brown reaction mixture was filtered through a disc of celite (1 cm x 1.5cm) to remove the dark brown residue. The filtrate was concentrated to dryness and redissolved in THF (~3 mL) and absorbed onto silica gel (~1.5 g). The dark yellowish brown slurry was evacuated to dryness and chromatographed onto a silica gel column (7 cm x 1.5cm) prepared in *n*-hexane. The following fractions were eluted:

(i) A dark yellowish brown fraction in *n*-hexane/toluene mixture (4:1, 20 mL) which upon concentrated under *vacuo* and recrystallized from suitable solvents to yield dark brown crystalline solids of $[CpMo(CO)(SBz)]_2$ (**12a**) (125mg, 0.200mmol, 43.58% yield).

(ii) A yellowish green fraction in *n*-hexane/toluene mixture (1:1, 40 mL) which upon concentrated and recrystallized from suitable solvents to yield green crystalline solids of *trans-anti* $[CpMo(CO)(SBz)]_2$ (**12b**) (119 mg, 0.191 mmol, 41.4% yield).

(iii) A brownish pink fraction in toluene (40mL) which upon concentrated to *vacuo* and recrystallized from suitable solvents to yield pink solids of $[CpMo(SBz)S]_2$ (**10**) (15 mg, 0.024 mmol, 5.2% yield).

(iv) A reddish brown fraction in ether (8 mL) which upon concentrated under *vacuo* and recrystallized from suitable solvents to yield reddish brown solids of $[CpMo(CO)(SBz)]_2S$ (**11**) (16 mg, 0.024 mmol, 5.3% yield).

3.6.3 Solventless reaction at 110 °C for 2 h

$[CpMo(CO)_2]_2$ (**4**) (50 mg, 0.115 mmol) and an equimolar amount of Bz_2S_2 (28.3 mg, 0.115 mmol) were weighed. The two starting materials were ground with mortar and pestler inside the dribox to a fine powder. The neat reaction mixture was thermolyzed at 110 °C. After 3 minutes, the powder melted to become a paste. The reaction mixture was further thermolyzed for another 2 h. The resultant dark brown paste was dissolved in C_6D_6 for a ^1H NMR spectral scan. The yields of various products were estimated from the relative intensities of a Cp resonance. The following complexes were recorded:

(i) $[CpMo(CO)_2(SBz)]_2$ (**9**) (15.3% yield)

(ii) *trans-syn* $[CpMo(CO)(SBz)]_2$ (**12a**) (4.5% yield)

(iii) *trans-anti* $[CpMo(CO)(SBz)]_2$ (**12b**) (6.1% yield)

(iv) $[CpMo(CO)(SBz)]_2S$ (**11**) (1.3% yield)

(v) $[CpMo(SBz)S]_2$ (**10**) (2.4% yield)

3.6.4 Cothermolysis reaction of trans-syn[CpMo(CO)(SBz)]$_2$ (12a) with equimolar Bz$_2$S$_2$ at 110 °C for 2 h

To a yellowish brown solution of *trans-syn*$[CpMo(CO)(SBz)]_2$ (**12a**) (69 mg, 0.111 mmol) in toluene (~10 mL) was added Bz_2S_2 (27 mg, 0.111 mmol). The reaction mixture was stirred at reflux temperature for 2 h. The resultant dark yellowish brown reaction mixture was filtered through a sintered-glass funnel to remove any excess ligand. The filtrate was concentrated to *ca.* 2 mL land loaded onto a silica gel chromatographic column (8 cm x 1.5 cm) prepared in *n*-hexane. Four fractions were eluted:

(i) A yellowish brown fraction was eluted with *n*-hexane/toluene mixture (3:1, 8 mL) which upon concentration to dryness gave oily orange solids of $[Cp_2Mo_2(SBz)_4]$ (**13**) (30 mg, 0.037 mmol, 33.2% yield). Data : ^1H NMR (C_6D_6): δ4.92 (s, C_5H_5), δ3.42 (s, CH_2), δ 7.15 - 7.09, 7.24 - 7.18 (m, C_6H_5). ^{13}C NMR (C_6D_6): δ90.24 (C_5H_5), δ52.36 (CH_2), δ 139.07, 138.27, 130.33, 130.09, 129.71, 129.00, 127.88 and 127.45 ($S-CH_2-C_6H_5$). IR: v at 1261w, 1225m, 1199m, 1101sh, 1070s, 1029s, 913vw, 865m, 803w, 766s, 758s, 695vs, 661s, 570m, 564m, 467m, 391 w and 384w cm^{-1} (nujol). Anal. Calcd. for $C_{38}H_{38}Mo_2S_4$: C, 55.7; H, 4.6; Mo, 23.9; S, 15.6. Found : C, 55.4; H, 4.7; Mo, 24.1; S, 15.8%.

(ii) A yellowish brown fraction was eluted with *n*-hexane/toluene mixture (1:1.5, 18 mL) which when analyzed by ^1H NMR was confirmed as a mixture of *trans-syn* and *trans-anti* isomers of $[CpMo(CO)(SBz)]_2$ (**12b**) in 33.2% yield and 14.4% yield, respectively.

(iii) A brownish pink fraction was eluted with toluene (17 mL) which when concentrated to dryness gave a brownish pink precipitate of [CpMo(SBz)S]$_2$ (**10**) (15 mg, 0.024 mmol, 21.6% yield).

3.6.5 NMR Tube Reactions

(a) Thermolysis studies of *trans-anti*[CpMo(CO)(SBz)]$_2$

The green solution of *trans-anti*[CpMo(CO)(SBz)]$_2$ (**12b**) (20 mg, 0.03 mmol) in C_6D_6 (~0.5 mL), was thermolyzed at 110 °C and changes was monitored by hourly scan ^{1}H NMR spectrum. The results of these studies are shown in Table 13.

(b) Co-thermolysis of *trans-syn*[CpMo(CO)(SBz)]$_2$ (12a) with equimolar Bz$_2$S$_2$ at 110 °C

The complex *trans-syn*[CpMo(CO)(SBz)]$_2$ (**12a**) (16 mg, 0.026 mmol) together with Bz$_2$S$_2$ (6 mg, 0.026 mmol) was dissolved in C_6D_6 (~0.5 mL) in a 5 mm NMR tube. The reaction mixture was thermolyzed at 110 °C and the reaction was monitored at regular intervals *via* ^{1}H NMR spectra. The final spectrum showed the presence of *trans-anti*[CpMo(CO)(SBz)]$_2$ (**12b**) (8.1% recovery), *trans-syn*[CpMo(CO)(SBz)]$_2$ (**12a**) (7.0% recovery), [CpMo(CO)(SBz)]$_2$S (**11**) (4.6% yield) and [CpMo(SBz)S]$_2$ (**10**) (30.9% yield) after 13 h. The time-dependent spectra of these studies are illustrated in Figure 24.

(c) Reaction of [CpMo(CO)$_3$]$_2$ (3) with equimolar Bz$_2$S$_2$ at 60 °C

A reddish purple solution of [CpMo(CO)$_3$]$_2$ (**3**) (20.0 mg, 0.04 mmol) with Bz$_2$S$_2$ (10 mg, 0.04 mmol) in C_6D_6 (~0.5 mL) was cothermolyzed at 60 °C. The reaction was followed by recording its ^{1}H NMR spectrum at intervals. No reaction was observed after 21 h.

3.7 Reaction of $[CpMo(CO)_3]_2$ with 2,4-bis(*p*-tolylthio)1,3-dithia-2,4-diphosphetane-2,4-disulfide (Davy's reagent)

3.7.1 Reaction of $[CpMo(CO)_3]_2$ with equimolar Davy's reagent at 110 °C.

A stirred suspension of $[CpMo(CO)_3]_2$ (**3**) (400 mg, 0.82 mmol) with an equimolar amount of 2,4-bis(*p*-tolylthio)1,3-dithia-2,4-diphosphetane-2,4-disulfide (356 mg, 0.80 mmol) in toluene (20 mL) was refluxed for 4 h. The resultant dark orange brown reaction mixture was absorbed onto *ca.* 2 g of silica gel and evaporated under *vacuo* to dryness. It was loaded onto a silica gel column (1.5 cm x 16.0 cm) prepared in *n*-hexane. The following fractions were eluted by chromatography:

(i) A dark brown fraction in *n*-hexane (68 mL) which when concentrated to dryness yielded unreacted $[CpMo(CO)_2]_2$ (**2**) (206 mg, 0.475 mmol, 58% yield).

(ii) A greenish brown fraction in *n*-hexane-toluene (1:2) (45 mL) which when concentrated to dryness yielded dark brown crystalline solids of $[CpMo(CO)_2(S_2P(SC_6H_4Me)_2)]$ (**14**) (51 mg, 0.09 mmol, 11% yield). Data : ^1H NMR (benzene-d_6): δ 1.92 (s, CH_3), δ 4.50 (s, Cp), δ 7.73 - 6.80 (m, C_6H_4). ^{13}C NMR (benzene-d_6): δ 21.55, 21.34 (CH_3), δ 95.98 (Cp), δ 137.36, 137.33, 137.15, 137.11, 130.84, 130.82, 130.38, 130.35 (C_6H_4), δ 256.39, 256.46 (CO). ^{31}P NMR (benzene-d_6): δ 125.18. IR ν(CO): 1949vs, 1904sh, 1861vs, 1833sh cm^{-1}, (PS) 806s, 600s cm^{-1} (nujol). Anal. Calcd. for C21H19MoO2PS4: C, 45.16; H, 3.43; Mo, 17.18; O, 5.73; P, 5.55; S, 22.96. Found: C, 45.56; H, 3.15; Mo, 17.57; O, 5.25; P, 6.01; S, 22.15.

(iii) A purple fraction in *n*-hexane-toluene (1:3) (50 mL) which when concentrated to dryness yielded fine dark purple crystals of $[Cp_2Mo_2(\mu\text{-}S)(\mu\text{-}S_2)(SC_6H_4Me)]$ (**16**) (57 mg, 0.10 mmol, 13% yield). Data : ^1H NMR (benzene-d_6): δ 2.03 (s, CH_3), δ 5.91 (s, Cp), δ 7.52 - 6.75 (m, C_6H_4). ^{13}C NMR (benzene-d$_6$): δ 98.55 (Cp). IR: ν at 1299vw, 1261vw, 1156vw, 1101w, 1062w, 1009w, 836vw, 803 w 733vw, 721vw cm^{-1} (nujol). Anal. Calcd.

for $C_{17}H_{17}Mo_2S_4$: C, 37.71; H, 3.16; Mo, 35.44; S, 23.69. Found: C, 37.86; H, 3.05; Mo, 35.57; S, 22.81%.

A brown layer remained uneluted at the top rim of the column.

3.7.2 Reaction of $[CpMo(CO)_2]_2$ with equilmolar Davy's reagent at 70 °C

A solution of $[CpMo(CO)_2]_2$ (**4**) (400 mg, 0.92 mmol) in toluene (25 mL) was reacted with an equimolar amount of Davy's reagent (402 mg, 0.92 mmol) under stirring for 18 h at 70 ^{o}C. The resultant dark pinkish brown reaction mixture was filtered *via* a sintered glass funnel to remove an uncharacterized insoluble dark brown residue (128 mg). The filtrate was then absorbed onto celite and evaporated under *vacuo* until dryness. It was loaded onto a florisil column (2 cm x 8 cm) prepared in *n*-hexane. The following fractions were eluted :

(i) A greenish brown fraction in *n*-hexane-toluene (2:1) (65 mL) from which when concentrated to dryness gave dark brown crystalline solids of **14** (133 mg, 0.24 mmol, 26% yield).

(ii) A pinkish brown fraction in *n*-hexane-toluene (1:1.5) (72 mL) in which when concentrated to dryness gave fine deep pink solids of $Cp_2Mo_2(CO)_5(S_2P(SC_6H_4Me))$ (**15**) (18 mg, 0.03 mmol, 6% yield). Data : ^{1}H NMR (benzene-d_6): δ 1.99 (s, CH_3), δ 5.08 (s, Cp), δ 4.62 (s, Cp) δ 7.72 - 6.89 (m, C_6H_4). ^{13}C NMR (benzene-d_6): δ 97.06, 96.34 (Cp), δ 132.63, 130.28, 128.50 (C_6H_4). ^{31}P NMR: δ 187.60 (s). IR: ν (CO) at 2035vs, 1970s, 1949vs, 1924vs, 1917vs, 1826vs cm^{-1} (nujol). Anal. Calcd. for $C_{22}H_{17}Mo_2O_5PS_3$: C, 38.83; H, 2.52; Mo, 28.20; O, 11.76; P, 4.55; S, 14.14. Found: C, 38.76; H, 2.05; Mo, 27.97; O, 11.89; P, 3.87; S, 13.81%.

(iii) A dark pinkish eluate in toluene (30 mL) which when concentrated to dryness gave an uncharacterized dark red precipitate (47 mg). Data : ^{1}H NMR (benzene-*d*$_6$): δ 4.50, 4.26 (s, Cp), δ 5.73, 5.51, 5.35 (m, Cp), δ 7.64 - 6.96 (m, C_6H_4). ^{13}C NMR (benzene-d$_6$): δ 96.66, 96.21 (Cp), δ 132.63, 130.28, 128.50 (C_6H_4). IR: ν 1261vs, 1100s, 1016sh, 814sh, 807s, 727vs, 721sh, 701vs, 694vs, 676s cm^{-1} (nujol). Attempts to characterize its structure were unsuccessful.

A brown layer remained uneluted at the top rim of the column.

3.7.3 Reaction of $[CpMo(CO)_2]_2$ with 0.5 mole equivalent Davy's reagent at 110 °C

To a reddish brown solution of $[CpMo(CO)_2]_2$ (**4**) (500 mg, 1.15 mmoL) in toluene (30 mL) was added in 0.5 mole equivalent amount of Davy' reagent (251 mg, 0.575 mmoL). The solution was refluxed for 2 h under stirring. The resultant dark yellowish brown reaction mixture was filtered *via* a sintered-glass funnel to remove an uncharacterized insoluble dark brown residue (68 mg). The filtrate was absorbed onto Celite (~2.5 g) and evaporated to dryness under *vacuo*. It was loaded onto a silica gel column (10.5cm x 2cm) prepared in *n*-hexane. The following fractions were eluted :

(i) A light yellowish brown fraction in *n*-hexane-toluene (3:1) mixture (70 mL) which upon concentration to dryness gave orange red solids of $[CpMo(CO)_2S]_2$ (**19**) (68 mg, 0.14 mmoL, 12.2% yield). Data : ^{1}H NMR (benzene-*d*$_6$): δ 4.54 (s, Cp). ^{13}C NMR (benzene-*d*$_6$): δ 86.65 (Cp), δ 227.25 (CO). IR: ν(CO) at 1988s, 1947vs, 1902vs, 1865s cm^{-1} (nujol); other bands, 1260m, 1096m, 1059m, 1016s, 803s, 572w, 544vw, 530w, 496w, and 461w. Anal. Calcd. for $C_{14}H_{10}Mo_2O_4S_2$: C, 33.75; H, 2.02; Mo, 38.51; O, 12.84; S, 12.87. Found: C, 33.64; H, 2.05; Mo, 38.82; O, 12.96; S, 13.11%.

(ii) A yellowish orange fraction in *n*-hexane-toluene (2:1) mixture (35 mL) which upon concentration to dryness gave orange amorphous solids of $Cp_2Mo_2(CO)_2(\mu\text{-PS})(\mu\text{-}$

SC_6H_4Me) (**18**) (88 mg, 0.16 mmoL, 13.6% yield). Data : ^{1}H NMR (benzene-*d*$_6$): *δ* 1.98 (s, CH_3), *δ* 5.03 (s, Cp), *δ* 4.77 (s, Cp), *δ* 7.18 - 6.80 (m, C_6H_4). ^{13}C NMR (benzene-*d*$_6$): *δ* 21.10, (CH_3), *δ* 94.77, 88.83 (Cp), *δ* 136.64, 130.96, 130.92, 129.65, 128.90 (m, C_6H_4), *δ* 239.73, 233.81 (CO). ^{31}P NMR (benzene-*d*$_6$): *δ* -99.45. IR: ν(CO) at 1882.24vs, 1863.17vs, (PS) 804.28m cm^{-1} (nujol); other bands at 1159.40vw, 1105.50w, 1058.28m, and 1015.28m. Anal. Calcd. for $C_{19}H_{17}Mo_2O_2PS_2$: C, 40.44; H, 3.04; Mo, 34.00; O, 5.67; P, 5.49; S, 11.36. Found: C, 40.13; H, 3.25; Mo, 34.67; O, 5.24; P, 5.88; S, 11.92%.

(iii) A reddish brown fraction was eluted with *n*-hexane-toluene (1:2, 55 mL) which upon concentration to dryness gave fine brown residue of *trans-syn/trans-anti*-$[CpMo(CO)(SC_6H_4Me)]_2$ (**17**) mixture (117mg, 0.19mmoL, 16.5%yield) [39]. Data : ^{1}H NMR (benzene-*d*$_6$): *δ* 2.09, 2.07 (s, CH_3), *δ* 5.26, 5.05, 4.96 (s, Cp), *δ* 6.97 - 6.96 (m, C_6H_4), *δ* 7.35 - 7.33 (m, C_6H_4), *δ* 7.44 - 7.42 (m, C_6H_4) . ^{13}C NMR (benzene-*d*$_6$): *δ* 92.35, 92.31, 92.03 (Cp), *δ* 145.96, 136.62, 136.48, 131.63, 131.27, 129.67, 129.50, 129.41 (s, C_6H_4). IR: ν(CO) at 1911s, 1854vs, 1836vs cm^{-1} (nujol); other bands at 1178vw, 1156w, 1105m, 1062m, 1016m, 836vw, 816vw, 802m, 722vw, 499vw and 480vw. Anal. Calcd. for $C_{26}H_{24}Mo_2O_2S_2$: C, 50.01; H, 3.87; Mo, 30.73; O, 5.12; S, 10.27. Found: C, 49.88; H, 3.96; Mo, 31.02; O, 5.63; S, 10.83%.

(iv) A pinkish brown fraction in toluene (20 mL) which upon concentration to dryness gave fine deep pink solids of $Cp_2Mo_2(CO)_5(S_2P(SC_6H_4Me))$ (**15**) (40 mg, 0.06 mmol, 5.2% yield).

(v) A greenish brown fraction in toluene-ether (5:1, 30mL) which upon concentration to dryness gave fine dark brown crystalline solids of $Cp_3Mo_3(\mu\text{-}S)_2(\mu\text{-}S_2)(\mu_3\text{-}S)$ (**20**) (18mg, 0.03mmoL, 2.6%yield. Data : ^{1}H NMR (benzene-d$_6$): δ5.15 (s, Cp). ^{13}C NMR (benzene-d$_6$): *δ* 94.85, 92.96 (Cp). IR: ν at 1158m, 1112m, 1058m, 1002m, 835w, 805m, 722vw, 599vw and 547vw cm^{-1} (nujol). Anal. Calcd. for $C_{15}H_{15}Mo_3S_5$: C, 28.00; H, 2.35; Mo, 44.73; S, 24.92. Found: C, 28.45; H, 2.36; Mo, 44.98; S, 25.56%.

(vi) A dark brownish red in toluene-ether (4:1, 25mL) which upon concentration to dryness gave an uncharacterized dark brownish red precipitate (19 mg). Data : ^{1}H NMR (benzene-*d*$_6$): δ 2.03 (s, CH_3), δ 5.14, 4.61, 4.31 (s, Cp), δ 14.54 (br, Cp, $\nu_{½}$ = 57 Hz), δ 7.05 - 7.00 (m, C_6H_4), δ 7.72 - 7.70 (m, C_6H_4), δ 8.02 - 8.00 (m, C_6H_4). ^{13}C NMR (benzene-d$_6$): δ 96.57, 95.97, 94.62, 94.43 (Cp), δ 142.27, 138.65, 138.23, 132.42, 130.56, 129.67, 128.90, 127.78, 127.28, 126.03 (C_6H_4). Attempts to characterize its structure were unsuccessful.

A brown layer remained uneluted at the top rim of the column.

3.7.4 Reaction of $[CpMo(CO)_2]_2$ with 0.5 mole equivalent of Davy's reagent at 70 °C

To a reddish brown solution of $[CpMo(CO)_2]_2$ (**4**) (400 mg, 0.92 mmoL) in toluene (25 mL) was added in 0.5 mole equivalent of Davy' reagent (201mg, 0.46 mmoL). The solution was stirred at 70 °C for 18 h. The resultant dark yellowish brown reaction mixture was concentrated to *ca*. 3 mL and loaded onto a silica gel column (2 cm x 8 cm) prepared in *n*-hexane. Elution gave four fractions:

(i) A red fraction was eluted with *n*-hexane (30 mL) which upon concentration to dryness gave deep pink solids of unreacted $[CpMo(CO)_3]_2$ (**1**) (36 mg, 0.07mmol, 7.6% recovery).

(ii) A light yellowish brown fraction was eluted with *n*-hexane/toluene (3:1) mixture (5 mL) which upon concentrated to dryness gave orange red solids of $[CpMo(CO)_2S]_2$ (**19**) (8 mg, 0.02 mmoL, 2.2% yield).

(iii) A greenish brown fraction was eluted with *n*-hexane/toluene (2:1) mixture (15 mL) which upon concentration to dryness gave dark brown crystalline solids of **14** (54 mg, 0.10 mmol, 10.9% yield).

(iv) A yellowish orange fraction was eluted with *n*-hexane/toluene (2:1) mixture (35 mL) which upon concentration to dryness gave orange amorphous solids of $Cp_2Mo_2(CO)_2(\mu\text{-}PS)(\mu\text{-}SC_6H_4Me)$ (**18**) (27 mg, 0.05 mmoL, 5.4% yield).

(v) A yellowish brown fraction was eluted with *n*-hexane/toluene (2:1, 35 mL) which upon concentration to dryness gave fine brown solids of *trans-syn*-$[CpMo(CO)(SC_6H_4Me)]_2$ (**17a**) (39 mg, 0.06 mmoL, 6.5%yield) [39].

(iv) A pinkish brown fraction in *n*-hexane/toluene (1:1.5) (95 mL) which when concentrated to dryness gave fine deep pink solids of $Cp_2Mo_2(CO)_5(S_2P(SC_6H_4Me))$ (**15**) (48 mg, 0.07 mmol, 7.6% yield).

(vi) A purple fraction in *n*-hexane/toluene (1:3) (12 mL) which when concentrated to dryness yielded fine dark purple crystals of $[Cp_2Mo_2(\mu\text{-}S)(\mu\text{-}S_2)(SC_6H_4Me)]$ (**16**) (6 mg, 0.01 mmol, 1.1% yield).

(iv) An uncharacterized dark yellowish brown fraction was eluted with ether (45 mL) which when concentrated to dryness gave a dark brown oily residue (174 mg).

A dark brown residue remains uneluted as a rim on top of the column.

3.7.5 NMR Tube Reactions

(a) Thermolysis of $[CpMo(CO)_2(S_2P(SC_6H_4Me)_2)]$ (14)

A greenish brown solution of $[CpMo(CO)_2(S_2P(SC_6H_4Me)_2)]$ (20 mg, 0.036 mmol) in $C_6D_5CD_3$ (~0.5 mL) in a 5 mm NMR tube was thermolyzed at 110 °C and was monitored at regular intervals of 0.5 h *via* ^1H NMR. From the spectra, [Cp_2Mo_2(μ-S)(μ-S_2)(μ-SPhMe)] (**16**) (24.6% yield) was found after 7.5 h.

(b) Thermolysis of $Cp_2Mo_2(CO)_5(S_2P(SC_6H_4Me))$ (15)

A pinkish brown solution of $Cp_2Mo_2(CO)_5(S_2P(SC_6H_4Me))$ (7 mg, 0.015 mmol) in $C_6D_5CD_3$ (~0.5 mL) in a 5 mm NMR tube was thermolyzed at 110 °C and was monitored at regular intervals of 0.5 h *via* ^1H NMR for overnight. From the spectra, [Cp_2Mo_2(μ-S)(μ-S_2)(μ-SC_6H_4Me)] (**16**) (18.0% yield) was found after 24 h.

(c) Cothermolysis of [$CpMo(CO)_2(S_2P(SC_6H_4Me)_2)$] (14) with Davy's reagent at 110 °C

The complex [$CpMo(CO)_2(S_2P(SC_6H_4Me)_2)$] (20 mg, 0.036 mmol) together with Davy's reagent (16 mg, 0.036 mmol) was dissolved in $C_6D_5CD_3$ (~0.5 mL) in a 5 mm NMR tube. The reaction mixture was thermolyzed at 110 °C and the reaction was monitored at regular intervals of 0.5 h *via* ^1H NMR spectra. The final spectrum showed only the presence of [Cp_2Mo_2(μ-S)(μ-S_2)(μ-SC_6H_4Me)] (16.5% yield) after 5 h.

(d) Cothermolysis of [$CpMo(CO)_2(S_2P(SC_6H_4Me)_2)$] (14) with [$CpMo(CO)_2$]$_2$ at 110 °C

The complex [$CpMo(CO)_2(S_2P(SC_6H_4Me)_2)$] (**14**) (20 mg, 0.036 mmol) and [$CpMo(CO)_2$]$_2$ (16 mg, 0.036 mmol) were dissolved in $C_6D_5CD_3$ (~0.5 mL) in a 5 mm NMR tube. The reaction mixture was thermolyzed at 110 °C and was monitored *via* ^1H NMR at regular intervals. From the final spectrum, $Cp_2Mo_2(CO)_5(S_2P(SC_6H_4Me))$ (**15**) (1.35% yield), [$CpMo(CO)_2$(μ-S)]$_2$ (**19**) (0.84% yield), *trans-syn*[$CpMo(CO)(SC_6H_4Me)$]$_2$ (**17a**) (10.58% yield), *trans-anti*[$CpMo(CO)(SC_6H_4Me)$]$_2$ (**17b**) (5.76% yield), [$Cp_2Mo_2(CO)_2$(μ-PS)(μ-SC_6H_4Me)] (**18**) (9.78% yield), [Cp_2Mo_2(μ-S)(μ-S_2)(μ-SC_6H_4Me)] (**16**) (1.08% yield), Cp_3Mo_3(μ-S)$_2$(μ-S_2)(μ$_3$-S) (**20**) (1.32% yield), respectively, together with traces of unreacted [CpMo(CO)$_2$(S$_2$P(SC$_6$H$_4$Me)$_2$)] (**14**) (0.90% recovery) and [CpMo(CO)$_2$]$_2$ (**4**) (0.58% recovery) were found after 2.5 h.

(e) Thermolysis of [CpMo(CO)(SC$_6$H$_4$Me)]$_2$ (17) at 110 °C

The complex [CpMo(CO)(SC$_6$H$_4$Me)]$_2$ (8 mg, 0.013 mmol) were dissolved in C$_6$D$_6$ (~0.5 mL) in a 5 mm NMR tube. The solution was thermolyzed at 110 °C and was monitored by ^{1}H NMR at regular intervals of 1 h. After 11 h, only [Cp$_2$Mo$_2$(μ-S)(μ-S$_2$)(μ-SC$_6$H$_4$Me)] (**16**) (8.2% yield) was produced in this thermolysis study together with the unreacted [CpMo(CO)(SC$_6$H$_4$Me)]$_2$ (**17**) (33.6% recovery).

(f) Thermolysis of Cp$_2$Mo$_2$(CO)$_2$(μ-PS)(μ-SC$_6$H$_4$Me) (18) at 110 °C

The complex Cp$_2$Mo$_2$(CO)$_2$(μ-PS)(μ-SC$_6$H$_4$Me) (15 mg, 0.027 mmol) was dissolved in C$_6$D$_6$ (~0.5 mL) in a 5 mm NMR tube. The solution was thermolyzed at 110 °C and was monitored by ^{1}H NMR at regular intervals of 1 h. After prolonged thermolysis, only traces of [Cp$_2$Mo$_2$(μ-S)(μ-S$_2$)(μ-SC$_6$H$_4$Me)] (**16**) and [CpMo(CO)$_2$(μ-S)]$_2$ (**19**) together with unreacted Cp$_2$Mo$_2$(CO)$_2$(μ-PS)(μ-SC$_6$H$_4$Me) (**18**) were observed in the spectrum.

(g) Cothermolysis of [CpMo(CO)$_2$(μ-S)]$_2$ (19) with Davy's reagent

The complex [CpMo(CO)$_2$(μ-S)]$_2$ (10 mg, 0.02 mmol) and Davy's reagent (9 mg, 0.02 mmol) were dissolved in C$_6$D$_6$ (~0.5 mL) in a 5 mm NMR tube. The reaction mixture was thermolyzed at 110 °C and was monitored *via* ^{1}H NMR at regular intervals of 1 h. From the spectrum, [CpMo(CO)$_2$(μ-S)]$_2$ (**19**) (23.8% recovery) and [Cp$_2$Mo$_2$(μ-S)(μ-S$_2$)(μ-SC$_6$H$_4$Me)] (**16**) (43.7% yield) were found after 5 h.

(h) Thermolysis of [$Cp_2Mo_2(\mu\text{-}S)(\mu\text{-}S_2)(\mu\text{-}SC_6H_4Me)$] (16)

A solution of [$Cp_2Mo_2(\mu\text{-}S)(\mu\text{-}S_2)(\mu\text{-}SC_6H_4Me)$] (**16**) (3 mg, 0.006 mmol) in C_6D_6 (~0.5 mL) in a 5 mm NMR tube was thermolyzed at 110 °C and was monitored by ^1H NMR at regular intervals. After 3 h of thermolysis, complex **16** was totally decomposed.

3.8 Reaction of $Cp_2Cr_2(CO)_6$ with Woollins' reagent (WR)

3.8.1 Reactivity studies of $Cp_2Cr_2(CO)_6$ (1) with equimolar Woollins' reagent at ambient temperature

To a dirty green suspension of $Cp_2Cr_2(CO)_6$ (**1**) (200 mg, 0.497 mmol) in toluene (~ 15 mL) was added Woollins' reagent (264 mg, 0.497 mmol) and the mixture was stirred at ambient temperature. A dark orange brown suspension was obtained after *ca*. 5 min. The reaction mixture was stirred for another 0.5 h. The resultant dark orange brown solution was filtered through Celite and the filtrate was concentrated to *ca*.3-4 mL before loading onto a silica gel column (2 cm x 9 cm) prepared in *n*-hexane. Elution gave 3 fractions:

(i) A dark purplish orange fraction in *n*-hexane (65 mL) which when concentrated to dryness gave fine dark orange brown crystalline solids of [$CpCr(CO)_2]_2Se$ (**21**) (70 mg, 0.165 mmol, 33.2% yield) [46c-d], identified its ^1H NMR in benzene-d_6 [δ(Cp) 4.36] and TLC against an authentic sample [$R_f = 0.64$ in 6:3:1 *n*-hexane/ toluene/ ether as eluent] together with a trace amount of $CpCr(CO)_2(SeP(H)Ph)$ (**23**).

(ii) A dark orange brown fraction in toluene (48 mL) which when concentrated to dryness gave a dark brown oily precipitate (189 mg, 60%). Analyses *via* TLC showed it consisted of a mixture of [$CpCr(CO)_2]_2Se$ (**21**), *trans*-[$CpCr(CO)_2(SePPh)]_2$ (**22**) and $CpCr(CO)_2(SeP(H)Ph)$ (**23**) in ratio of 8 : 1 : 1. Despite repeated attempts, this mixture was not separated.

(iii) An uncharacterized green fraction was eluted with THF (60 mL) which when concentrated to dryness gave a green residue (162 mg).

A deep bluish green ring remained unmoved on top of the column.

3.8.2 Reaction of excess $Cp_2Cr_2(CO)_6$ (1) with Woollins' Reagent at ambient temperature

To a dirty green suspension of $Cp_2Cr_2(CO)_6$ (**1**) (101 mg, 0.251 mmol) in toluene (~10 mL) was added in 0.125 equivalent amount of Woollins' reagent (16 mg, 0.031 mmol). The color of the reaction mixture changed to orange brown instantaneously. The reaction mixture was stirred at ambient temperature for 1 h. The resultant dark orange brown reaction mixture was filtered through a sintered-glass funnel. The filtrate was concentrated to *ca*. 3 mL and loaded onto a silica gel column prepared in *n*-hexane (1.5 cm x 11.5 cm). Three fractions were eluted during chromatography:

i) A dark orange brown fraction was eluted with *n*-hexane (10 mL) which upon evaporation to dryness gave a black crystalline solid **21** (62 mg, 0.146 mmol, 58.2% yield).

ii) A dirty green fraction was eluted with *n*-hexane/toluene mixture (4 : 1) (18 mL) which upon evaporation to dryness gave green crystalline solids of unreacted $Cp_2Cr_2(CO)_6$ (**1**) (17 mg, 0.042 mmol, 16.7% recovery).

iii) A greyish brown fraction was eluted with toluene (36 mL) which upon evaporation to dryness gave the dark brown crystalline solids of *trans*-$[CpCr(CO)_2(SePPh)]_2$ (**22**) (45 mg, 0.062 mmol, 24.7% yield). Data : ^{1}H NMR (benzene-d_6): δ 4.01 (s, Cp); δ 7.72 - 7.02 (m, C_6H_5). ^{13}CNMR (benzene-d_6): δ 90.4 (Cp), δ 138.65, 138.23, 130.56, 129.65, 128.89 and 126.02 (C_6H_5), δ 254.22, 249.79 (CO). IR: ν(CO) at 1962vs, 1951vs, 1899vs cm^{-1}; other peaks at 1086m, 1063m, 1016m, 860vw, 844vw, 828w, 803w, 741w, 690w, 664vw cm^{-1} (nujol). *Anal*. Calcd. for $C_{26}H_{20}Cr_2O_4P_2Se_2$: C, 43.21; H, 2.77; Cr, 14.40; O, 8.86; P, 8.59; Se, 22.16. Found: C, 43.37; H, 2.89; Cr, 14.67; O, 8.45; P, 8.62; Se, 22.45.

A deep bluish green ring remained unmoved on top of the column.

3.8.3 Reaction of $Cp_2Cr_2(CO)_4$ (2) with equimolar Woollins' reagent at 60 °C

To a dirty green suspension of $Cp_2Cr_2(CO)_4$ (**2**) (300 mg, 0.867 mmol) in toluene (~ 15 mL) was added Woollins' reagent (461 mg, 0.867 mmol) and stirred at 60 °C for 3 h. The resultant dark brownish green reaction mixture was concentrated to *ca.* 10 mL and filtered through a sintered-glass funnel to remove an uncharacterized deep green residue (361 mg). The filtrate was concentrated to *ca*. 3 mL and then absorbed onto silica gel (~1 g). The dark brownish green slurry was evacuated to dryness under *vacuo* and chromatographed onto a silica gel column (1.5 cm x 9 cm) prepared in *n*-hexane. Elution under slight pressure gave four fractions:

(i) A grayish brown eluant in *n*-hexane-toluene (1:2) (45 mL) which when concentrated to dryness gave dark brown crystalline solids of **22** (18 mg, 0.022 mmol, 3% yield).

(ii) A dark pinkish purple eluant in *n*-hexane-toluene (1:1, 15 mL) and which when concentrated to dryness, gave dark pinkish purple crystalline solids of $CpCr(CO)_2(SeP(H)Ph)$ (**23**) (55 mg, 0.152 mmol, 18% yield). Data : ^{1}H NMR (benzene-*d*$_6$): δ 4.26 (s, Cp); δ 5.72 (s, P-H); δ 7.37 - 6.68 (m, C_6H_5); ^{13}C NMR (benzene-*d*$_6$): δ 89.53 (Cp), δ 132.71, 132.59, 131.37, 129.67, 129.62 and 129.50 (C_6H_5), δ 254.22, 249.79 (CO). ^{31}P NMR (benzene-*d*$_6$: proton coupled): δ 48.26, 45.84 (d, J = 387.6 Hz); (benzene-*d*$_6$: proton decoupled): δ 47.27, 46.68. IR: ν (CO) at 1954vs, 1942vs, 1871vs, 1853sh, and 1847sh cm^{-1} and other peaks at 1159m, 1110m, 1093m, 1067m, 1055m, 1014m, 921m, 912m, 846m, 823m, 748m, 727w, 706vw, 690m, 685m, 639m, 590m, 550m cm^{-1} (nujol).

Anal. Calcd. for $C_{13}H_{10}CrO_2PSe$: C, 43.09; H, 2.76; Cr, 14.36; O, 8.84; P, 8.56; Se, 22.10. Found: C, 43.37; H, 2.58; Cr, 14.39; O, 8.68; P, 8.47; Se, 22.54.

(iii) A dark green eluant in ether (9 mL) which when concentrated to dryness gave dark brownish green crystalline solids of $Cp_2Cr_2(Se_2P(O)Ph)_2$ (**24**) (14 mg, 0.018 mmol, 2% yield). Data : ^{1}H NMR (toluene-d_8): δ 5.04 (s, Cp); δ 7.08 - 6.82 (m, C_6H_5). ^{13}C NMR (benzene-d_6): δ 126.02 (Cp), δ 138.63, 138.20, 132.46, 130.56 and 129.67 (C_6H_5); ^{31}P NMR (benzene-d_6): δ -123.34. IR: ν at 1157w, 1106m, 1084m, 1058m, 1026m, 998m, 815m, 741w, 728sh, 686w cm^{-1} (nujol). *Anal.* Calcd. for $C_{20}H_{20}Cr_2O_2P_2Se_4$: C, 29.93; H, 2.49; Cr, 12.97; O, 3.99; P, 7.73; Se, 39.90. Found: C, 29.62; H, 2.54; Cr, 12.88; O, 3.96; P, 7.45; Se, 39.46.

(iv) A green eluant in THF (25 mL) which when concentrated to dryness gave an uncharacterized deep green crystalline precipitate (361 mg).

3.8.4 NMR tube reactions

(a) Thermolysis of $CpCr(CO)_2(SeP(H)Ph)$ (23)

A purple solution of **23** (20 mg, 0.055 mmol) in toluene-d_8 (~0.5 mL) in a 5mm capped NMR tube was thermolyzed at 110 °C and was monitored *via* ^{1}H NMR spectra at regular intervals for 14 h. The resultant dark brown solution consists of *trans*-$[CpCr(CO)_2(SePPh)]_2$ (**22**) (38%) and $Cp_2Cr_2(Se_2P(O)Ph)_2$ (**24**) (11%) together with some uncharacterized dark brown precipitates. The final product composition of this study is tabulated in Table 27.

(b) Thermolysis of *trans*-$[CpCr(CO)_2(SePPh)]_2$ (22)

A grayish brown solution of **22** (13 mg, 0.018 mmol) in toluene-d_8 (~0.5 mL) in a 5 mm capped NMR tube was thermolyzed at 110 °C and was monitored *via* ^{1}H NMR at regular intervals for 14 h. The resultant dark green solution consists of $CpCr(CO)_2(SePPh)$ (**23A**) (10%) and $Cp_2Cr_2(Se_2P(O)Ph)_2$ (**24**) (70%) together with some uncharacterized dark brown precipitates. The results of these studies are tabulated in Table 28.

(c) Thermolysis of $Cp_2Cr_2(Se_2P(O)Ph)_2$ (24)

A solution of $Cp_2Cr_2(Se_2P(O)Ph)_2$ (**24**) (22 mg, 0.013 mmol) in toluene-d_8 (~0.5 mL) in a 5 mm capped NMR tube was thermolyzed at 110 °C and was monitored *via* ^1H NMR at regular intervals. After 14 h, the resultant dark green solution consists of some uncharacterized dark brown precipitates.

(d) Cothermolysis of $CpCr(CO)_2(SeP(H)Ph)$ (23) and Woollins' reagent

A purple mixture of $CpCr(CO)_2(SeP(H)Ph)$ (**23**) (20 mg, 0.055 mmol) with an equimolar amount of WR (29 mg, 0.055 mmol) in toluene-d_8 (~0.5 mL) in a 5 mm capped NMR tube was maintained at 110 °C. Its ^1H NMR spectra were examined at intervals of 0.5 h, 2 h, 4 h, 5 h and 14 h. The resultant dark brown solution consists of **23** (19%), **22** (6%) and **24** (31%) together with some uncharacterized dark brown precipitates. The results of the reaction are presented in Table 29.

3.9 Reaction of $Cp_2Mo_2(CO)_4$ with Woollins' reagent

3.9.1 Reactivity studies of $Cp_2Mo_2(CO)_4$ with equimolar Woollins' reagent at 110 °C

A reddish brown solution of $Cp_2Mo_2(CO)_4$ (**4**) (300 mg, 0.612 mmol) and Woolins' reagent (326 mg, 0.612 mmol) in toluene (~25 mL) was refluxed with stirring for 4 h. The resultant dark purplish brown reaction mixture was filtered through a sintered-glass funnel to remove an uncharacterized brown residue (279 mg). The filtrate was concentrated to *ca.*

3-4 mL and loaded onto a silica gel column (1.5 cm x 12 cm) prepared in *n*-hexane. The following fractions were eluted:

(i) An orange pink fraction was eluted with *n*-hexane-toluene (2:1.5, 35 mL) which when concentrated to dryness gave unreacted fine orange red solids of $Cp_2Mo_2(CO)_4$ (**4**) (28 mg, 0.064 mmol, 10.5% recovery).

(ii) An orange brown fraction was eluted with *n*-hexane-toluene (1:1.5, 40 mL) which when concentrated to dryness gave dark reddish brown crystalline solids of $[Cp_2Mo_2\{(\mu\text{-}Se)_2(PPh(Se))\}\{(\mu\text{-}Se)(PPh)_3\}]$ (**25**) (114 mg, 0.107 mmol, 17.5% yield). Data : ^{1}H NMR (benzene-*d$_6$*): δ 5.60, 5.34, 4.72, 4.39 (s, Cp), δ 7.95 - 6.78 (m, C_6H_5). ^{13}C NMR (benzene-*d$_6$*): δ 90.37, 89.54, 89.43, 88.47 (Cp), δ 132.43, 130.57, 129.67, 128.90 and 126.04 (C_6H_5). ^{31}P NMR (benzene-*d$_6$*): δ 167.59, 160.79, 159.52, 158.91. Anal. Calcd. for $C_{34}H_{30}Mo_2P_4Se_4$: C, 38.01; H, 2.81; Mo, 18.24; P, 11.54; Se, 29.79. Found: C, 37.92; H, 2.75; Mo, 18.20; P, 11.83; Se, 29.56.

(iii) An orange brown fraction was eluted with *n*-hexane-toluene (1:1.5, 52 mL) which when concentrated to dryness gave an uncharacterized brown amorphous solid (42 mg). Data : ^{1}H NMR (benzene-*d$_6$*): δ 5.37, 5.26 (s, Cp), δ 7.13 - 7.01 (m, C_6H_5). ^{13}C NMR (benzene-*d$_6$*): δ 94.89, 94.77 (Cp), δ 129.67, 128.90, 126.03 (C_6H_5). IR: ν at 1276w, 1261vw, 1177vw, 1157vw, 1106w, 1091w, 1056w, 1024w, 1005w, 940vw, 918vw, 876vw, 841vw, 806w, 740w, 728w, 699w, 688w, 638vw cm^{-1} (nujol).

(iv) A blue fraction was eluted with *n*-hexane-toluene (1:1.75, 12 mL) which when concentrated to dryness gave dark greenish blue oily solids of $Cp_4Mo_4(CO)_3Se_4$ (**26**) (19 mg, 0.019 mmol, 3.1% yield). Data : ^{1}H NMR (benzene-*d$_6$*): δ 5.63, 5.52, 5.49, 5.43, 4.71, 4.57, 4.567, 4.56, 4.55, 4.53, 4.49, 4.48 (m, Cp); ^{13}C NMR (benzene-*d$_6$*): δ 92.59, 92.43, 92.07, 92.01, 91.73, 91.64, 91.09, 91.01, 90.77, 90.73, 89.86, 89.76 (Cp), δ 230.02, 196.02 (CO). IR: ν (CO) at 1933vs, 1870s cm^{-1} and other peaks at 804m, 738w, 722w, 551vw, 533w, 510vw cm^{-1} (nujol). Anal. Calcd. for $C_{23}H_{20}Mo_4O_3Se_4$: C, 26.15; H, 1.91; Mo, 37.11; O, 4.54; Se, 30.29. Found: C, 25.98; H, 1.93; Mo, 37.05; O, 4.56; Se, 30.35.

(v) A pink fraction was eluted with *n*-hexane-toluene (1:2, 54 mL) which when concentrated to dryness gave pink crystalline solids of $Cp_3Mo_3(CO)_4[Se_3(PPh)_2]$ (**27a**) (14 mg, 0.013 mmol, 2.1% yield). Data : ^{1}H NMR (benzene-*d₆*): δ 4.82, 4.78, 4.57 (s, Cp), δ 7.13 - 7.01, 8.95 - 8.91 (m, C_6H_5). ^{13}C NMR (benzene-*d₆*): δ 94.04, 91.15, 90.55 (Cp), δ 138.23, 129.67, 128.90, 126.03 (C_6H_5). ^{31}P NMR (benzene-*d₆*): δ 120.49, 118.55. IR: ν(CO) at 1973s, 1921vs, 1844s cm^{-1}; other peaks at 1156m, 1095m, 1021m, 820w, 794w, 748vw, 738vw, 724w, 697vw, 554vw, 511vw, 489w, 474w, 465w, 448w, 422w, 407vw cm^{-1} (nujol). Anal. Calcd. for $C_{31}H_{25}Mo_3O_4P_2Se_3$: C, 33.26; H, 2.25; Mo, 26.26; O, 5.72; P, 11.07; Se, 21.44. Found: C, 33.52; H, 2.29; Mo, 26.25; O, 5.70; P, 11.10; Se, 21.58.

(vi) A purplish pink fraction was eluted with toluene (25 mL) which when concentrated to dryness gave dark purplish pink crystalline solids of the polymorphic product of $Cp_3Mo_3(CO)_4[Se_3(PPh)_2]$ (**27b**)(19 mg, 0.017 mmol, 2.8% yield). Data : ^{1}H NMR (benzene-*d₆*): δ 4.85, 4.77, 4.58 (s, Cp), δ 7.14 - 7.01 (m, C_6H_5). ^{13}C NMR (benzene-*d₆*): δ 94.27, 90.72, 90.16 (Cp), δ 133.45, 129.67, 128.90, 126.03 (C_6H_5). ^{31}P NMR (benzene-*d₆*): δ 120.71, 118.73. IR: ν(CO) at 1960m, 1925s, 1846m, 1156m, 1105m, 1050m, 1020m, 875w, 817w, 743vw, 728vw, 693vw, 669vw, 550vw, 525vw, 517vw, 472vw, 466vw, 457vw, 442vw cm^{-1} (nujol). Anal. Calcd. for $C_{31}H_{25}Mo_3O_4P_2Se_3$: C, 33.26; H, 2.25; Mo, 26.26; O, 5.72; P, 11.07; Se, 21.44. Found: C, 33.37; H, 2.31; Mo, 26.28; O, 5.68; P, 11.13; Se, 21.50.

A dark brown ring remained unmoved on top of the column.

3.9.2 Reactivity studies of $Cp_2Mo_2(CO)_4$ with equimolar Woollins' reagent at 70 °C

$Cp_2Mo_2(CO)_4$ was generated *in situ* by refluxing the $Cp_2Mo_2(CO)_6$ (200 mg, 0.408 mmol) in toluene (~20 mL) at 120 °C for 20 h under stirring. After the solution has cooled down to room temperature, Woollins' reagent (230 mg, 0.408 mmol) was added to it. The reaction mixture was stirred at 70 °C for 2 h. The resultant brownish purple mixture was filtered through a sintered-glass funnel. The filtrate was concentrated to dryness and then redissolved in THF (~ 2 mL) followed by absorbed onto silica gel (~0.5 g). The dark brownish purple slurry was evacuated to dryness under *vacuo* and chromatographed onto a silica gel column (1.5 cm x 10 cm) prepared in *n*-hexane. The following fractions were eluted:

(i) A pinkish red fraction was eluted with *n*-hexane-toluene (2.5:1, 32 mL) which when concentrated to dryness, the unreacted $Cp_2Mo_2(CO)_6$ (**3**) (23 mg, 0.0469 mmol, 11.5% recovery) was recovered.

(ii) A brownish orange fraction was eluted with *n*-hexane-toluene (2:1, 20 mL) which when concentrated to dryness, the unreacted $Cp_2Mo_2(CO)_4$ (**4**) (10 mg, 0.023mmol, 5.6% recovery) was recovered.

(iii) A brownish orange fraction was eluted with *n*-hexane-toluene (1:1.5, 32 mL) which when concentrated to dryness, gave an uncharacterized Cp containing red precipitate (49 mg). Data : ^{1}H NMR (benzene-d_6): δ 4.27(s, Cp), δ 7.06 - 6.97, 7.13 - 7.11 (m, C_6H_5). ^{13}CNMR (benzene-d_6): δ92.46, 91.94, 91.42, 90.77 (Cp), δ138.22, 128.63, 128.15 (C_6H_5). ^{31}P NMR (benzene-d_6): δ237.41, 236.90, 176.34, 174.47, 63.86, 63.35.

(iv) An orange pink fraction was eluted with toluene (13 mL) which when concentrated to dryness gave $Cp_3Mo_3(CO)_4[Se_3(PPh)_2]$ (**27a**) (9 mg, 0.008 mmol, 2.0% yield).

(v) A purple fraction was eluted with ether (13 mL) which when concentrated to dryness gave the polymorphic product of $Cp_3Mo_3(CO)_4[Se_3(PPh)_2]$ (**27b**) (22 mg, 0.020 mmol, 4.9% yield).

A dark brown rim remained unmoved on top of the column.

3.9.3 NMR Tube Reaction

(a) Variable temperature NMR measurements of $Cp_4Mo_4(CO)_3Se_4$ (26)

The ^1H NMR spectrum of an approximately 2mM solution of $Cp_4Mo_4(CO)_3Se_4$ in toluene-d_8 in a capped 5 mm NMR tube under argon was recorded at room temperature, 30, 40, 50, 60, 70, 80 and 90 ºC, respectively. The temperature-dependent variation of the ^1H NMR spectral changes is presented in Figure 30.

3.10 Reaction of $Cp_2Cr_2(CO)_6$ with $P(C_6H_4SMe\text{-}p)_3$

3.10.1 Reaction of $Cp_2Cr_2(CO)_6$ with one mole equivalent of $P(C_6H_4SMe\text{-}p)_3$ at 70 °C

To a dirty green suspension of $Cp_2Cr_2(CO)_6$ (**1**) (200 mg, 0.497 mmol) in toluene (~20 mL) was added $P(C_6H_4SMe\text{-}p)_3$ (199 mg, 0.497 mmol). The reaction mixture was stirred at 70 °C for 12 h. The resultant deep dirty green reaction mixture was concentrated to *ca.* 4 mL left and chromatographed onto a silica gel column (8.0 cm x 2.0 cm) prepared in *n*-hexane. The following fractions were eluted:

(i) A deep green fraction was eluted with *n*-hexane (15 mL) and followed by *n*-hexane-toluene (2:1, 25 mL) which when concentrated to dryness gave dark green crystalline solids of $Cp_2Cr_2(CO)_4$ (**2**) (134 mg, 0.387 mmol, 77.9% yield).

(ii) A greenish yellow fraction was eluted with toluene (79 mL) which when concentrated to dryness gave a yellowish brown oily precipitate of $[CpCr(CO)_2\{P(C_6H_4SMe\text{-}p)_3\}_2][CpCr(CO)_3]$ (**28**) (97 mg, 0.083 mmol, 16.7% yield).

Data : ^{1}H NMR (benzene-d_6): δ 4.33 (s, Cp), δ 9.94 (br, Cp, $\nu_{1/2}$ = 72 Hz), δ 1.88 (CH_3), δ 7.40 - 6.94 (m, C_6H_4). ^{13}C NMR (benzene-d_6): δ 21.77, 15.68, 15.11 (CH_3), δ 91.69 (Cp), δ 140.99, 138.22, 134.91, 134.71, 130.57, 129.67, 128.90, 126.79, 126.73, 126.04 (C_6H_4). ^{31}P NMR (benzene-d_6): δ -8.74. IR: ν(CO) at 1961s, 1887vs, 1863vs, 1769vs cm^{-1} and other peaks at 1658vs, 1598s, 1578vs, 1543s, 1277vs, 1260vs, 1194s, 1079vs, 807vs, 763w, 746s, 719s, 703s, 571m, 545m, 501w cm^{-1}(nujol). Anal. Calcd. for $C_{57}H_{52}Cr_2O_5P_2S_6$: C, 58.32; H, 4.46; Cr, 8.86; O, 6.81; P, 5.28; S, 16.35. Found: C, 58.56; H, 4.54; Cr, 8.67; O, 7.02; P, 5.53; S, 17.03.

A blue rim remained on top of the column.

3.10.2 Reaction of $Cp_2Cr_2(CO)_4$ with one mole equivalent of $P(C_6H_4SMe\text{-}p)_3$ at 110 °C

To a deep green suspension of $[CpCr(CO)_2]_2$ (**2**) (100 mg, 0.289 mmol) in toluene (~10 mL) was added $P(C_6H_4SMe\text{-}p)_3$ (116 mg, 0.289 mmol). The reaction mixture was stirred at 110 °C for 19.5 h. The resultant deep brownish green reaction mixture was concentrated to *ca.* 2 mL left and chromatographed onto a silica gel column (7.0 cm x 1.5 cm) prepared in *n*-hexane. The following fractions were eluted:

(i) A yellowish green fraction was eluted with *n*-hexane (3 mL) which when concentrated to dryness gave green solids of unreacted $[CpCr(CO)_2]_2$ (21 mg, 0.061 mmol, 21.1% recovery).

(ii) A yellowish green fraction was eluted with ether (18 mL) which when concentrated to dryness gave yellowish green solids of $[CpCr(CO)_2\{P(C_6H_4SMe\text{-}p)_3\}_2][CpCr(CO)_3]$ (**28**) (138 mg, 0.117 mmol, 40.5% yield).

A blue rim remained on top of the column.

3.11 Reactions of $Cp_2Mo_2(CO)_6$ with $P(C_6H_4SMe\text{-}p)_3$

3.11.1 Reaction of $Cp_2Mo_2(CO)_6$ with one mole equivalent of $P(C_6H_4SMe\text{-}p)_3$ at 70 °C

To a red solution of $Cp_2Mo_2(CO)_6$ (100 mg, 0.204 mmol) in toluene (~15 mL) was added $P(C_6H_4SMe\text{-}p)_3$ (82 mg, 0.204 mmol). The reaction mixture was stirred at 70 °C for 74 h. The resultant dark pink reaction mixture was filtered *via* a sintered-glass funnel and the filtrate was concentrated to *ca.* 3-4 mL and loaded onto a silica gel column (1.5 x 12 cm) prepared in *n*-hexane. The following fractions were eluted out:

(i) A red fraction was eluted with *n*-hexane-toluene (4:1, 67 mL) which when concentrated to dryness gave magenta crystalline solids of $Cp_2Mo_2(CO)_6$ (**3**) (49 mg, 0.100 mmol, 49.0% recovery).

(ii) A deep pink fraction was eluted with toluene (48 mL) which when concentrated to dryness gave deep pink crystalline solids of $Cp_2Mo_2(CO)_5\{P(C_6H_4SMe\text{-}p)_3\}$ (**29**) (33 mg, 0. 038 mmol, 18.6% yield). Data : ^{1}H NMR (benzene-d_6): δ1.82 (s, CH_3), δ4.92, 4.85 (s, Cp), δ7.65 - 6.90 (m, C_6H_4). ^{13}C NMR (benzene-d_6): δ1.75 (CH_3), δ93.34, 91.84 (Cp), δ 133.15, 133.05, 129.67, 128.90, 125.71 (C_6H_4). ^{31}P NMR (benzene-d_6): δ72.83**.** IR:ν(CO) at 1965s, 1896s, 1871vs, 1812s cm^{-1}; other peaks at 1152sh, 1094s, 1073s, 878vw, 808m, 746vw, 721vw, 668vw, 537w, 466w cm^{-1} (nujol). Anal. Calcd. for $C_{36}H_{31}Mo_2O_5PS_3$: C, 50.12; H, 3.62; Mo, 22.24; O, 9.27; P, 3.59; S, 11.15. Found: C, 50.76; H, 3.25; Mo, 22.45; O, 9.64; P, 3.48; S, 11.71.

A brown rim was uneluted on top of the column.

3.11.2 Reaction of $Cp_2Mo_2(CO)_4$ with one mole equivalent of $P(C_6H_4SMe\text{-}p)_3$ at 110 °C

To a reddish brown solution of $Cp_2Mo_2(CO)_4$ (200 mg, 0.46 mmol) in toluene (~25 mL) was added $P(C_6H_4SMe\text{-}p)_3$ (185 mg, 0.46 mmol). The reaction mixture was stirred at

110 °C for 6.5 h. The resultant dark brownish pink reaction mixture was filtered through a sintered-glass funnel to remove the pink residue (100 mg). The filtrate was concentrated to dryness and redissolved in THF (~10 mL) and absorbed onto silica gel (2.0 g). The dark brownish pink slurry was evacuated until dryness and was chromatographed onto a silica gel column (15 cm x 1.5 cm) prepared in *n*-hexane. The following fractions were eluted out:

(i) A red fraction was eluted with *n*-hexane-toluene (4:1, 23 mL) which when concentrated to dryness gave magenta crystalline solids of $Cp_2Mo_2(CO)_6$ (**3**) (8 mg, 0.016 mmol, 3.5% recovery).

(ii) A reddish brown fraction was eluted with *n*-hexane-toluene (1:1, 4 mL) which when concentrated to dryness gave brown crystalline solids of $Cp_2Mo_2(CO)_4$ (**4**) (28 mg, 0.064 mmol, 13.9% recovery).

(iii) A deep pink fraction was eluted with toluene (73 mL) which when concentrated to dryness gave deep pink crystalline precipitate (222 mg). Analysis with TLC showed a mixture of two products. After several chromatography attempts, $Cp_2Mo_2(CO)_5\{P(C_6H_4SMe\text{-}p)_3\}$ (**29**) (148 mg, 0.172 mmol, 37.4% yield) was isolated as deep pink crystalline solids. The other product of $Cp_2Mo_2(CO)(\mu\text{-}CO)_2\{P(C_6H_4SMe\text{-}p)_3\}$ (**30**) (74 mg, 0.092 mmol, 20% yield) was isolated as brownish pink crystalline solids. For $Cp_2Mo_2(CO)(\mu\text{-}CO)_2\{P(C_6H_4SMe\text{-}p)_3\}$ (**30**), Data : ^1H NMR (benzene-d_6): δ 1.89 (s, CH_3), δ 4.67, 4.57 (s, Cp), δ 7.79 - 6.97 (m, C_6H_4). ^{13}C NMR (benzene-d_6): δ 15.92 (CH_3), δ 93.09, 92.46 (Cp), δ 134.81, 134.70, 129.67, 128.91, 125.45, 125.35 (C_6H_4). ^{31}P NMR (benzene-d_6): δ 25.09. IR: ν(CO) at 1866s, 1786s, 1763vs cm^{-1}; other peaks at 836vw, 811m, 798m, 745m, 576vw, 552m, 540m, 494vw, 467w cm^{-1} (nujol). Anal. Calcd. for

$C_{34}H_{31}Mo_2O_3PS_3$: C, 50.62; H, 3.87; Mo, 23.79; O, 5.95; P, 3.84; S, 11.93. Found: C, 50.57; H, 4.05; Mo, 23.96; O, 6.02; P, 3.88; S, 12.06.

(iv) A brown fraction was eluted with THF (5 mL) which when concentrated to dryness gave a mixture of brown crystalline solids $Cp_4Mo_4(CO)_4(\mu_3\text{-}O)(\mu_2\text{-}O)_2(O)$ (**31**) (10 mg, 0.012 mmol, 2.6% yield). Data : ^1H NMR (benzene-d_6): δ 5.70, 4.98, 4.87, 4.72 (s, Cp). Anal. Calcd. for $C_{24}H_{10}Mo_4O_8$: C, 35.58; H, 1.24; Mo, 47.37; O, 15.80. Found: C, 35.64; H, 1.86; Mo, 47.30; O, 15.65.

A brown rim was uneluted on top of the column.

3.12 Reaction of $Cp_2Cr_2(CO)_6$ with $PPh_2(C_6H_4SMe\text{-}o)$

3.12.1 Reaction of $Cp_2Cr_2(CO)_6$ with 2.5 mole equivalent of $PPh_2(C_6H_4SMe\text{-}o)$ at 60 °C

To a deep green suspension of $Cp_2Cr_2(CO)_6$ (100 mg , 0.249 mmol) in toluene (~10 mL) was added $PPh_2(C_6H_4SMe\text{-}o)$ (192mg , 0.623 mmol). The reaction mixture was stirred at 60 ºC for 20 h. The resultant dark brownish pink reaction mixture was filtered through a sintered-glass funnel to remove some dark brown residue (38 mg). The filtrate was concentrated to *ca.* 2 mL and chromatographed onto a silica gel column prepared in *n*-hexane (8.5 cm x 1.5 cm). Three fractions were eluted out:

(i) A light yellowish green fraction using *n*-hexane-toluene (1:2, 5mL) which when concentrated to dryness gave oily white precipitate of the excess ligand, $PPh_2(C_6H_4SMe\text{-}o)$ (53 mg, unreacted).

(ii) A red fraction using *n*-hexane-toluene (1:2, 12.5mL) which when concentrated to dryness gave fine red crystalline solids of $CpCr(CO)_2(C_6H_4S)PPh_2$ (**32**) (154 mg, 0.330mmol, 66.3% yield). Data: ^1H NMR (benzene-d_6): δ 4.26 (s, Cp), δ 7.63 - 6.68 (m, Ph). ^{13}C NMR (benzene-d_6): δ 92.8 (Cp), δ 158.74, 158.38, 137.37, 133.62, 133.51, 132.20, 132.12, 130.40, 129.69, 122.18, 122.12 (Ph), δ 257.91, 253.33 (CO). ^{31}P NMR (benzene-d_6): δ 108.46. IR: ν(CO) at 1938vs, 1878vs, 1843sh cm^{-1}; other peaks at 1376m, 1245w, 1161w, 1099m, 1093m, 1069m, 1043m, 828w, 732w, 719w, 703m, 693m, 639w, 590w, 563m, 528m, 509w, 470m, 386m cm^{-1} (nujol). Anal. Calcd. for $C_{25}H_{19}CrO_2PS$: C, 64.37; H, 4.11; Cr, 11.15; O, 6.86; P, 6.64; S, 6.87. Found: C, 64.29; H, 4.07; Cr, 11.12; O, 6.33; P, 6.82; S, 7.12.

(iii) A dark brown fraction using THF (~11 mL) which when concentrated to dryness gave an uncharacterized brownish green oily residue (24mg).

A blue rim remained uneluted on top of the column.

3.12.2 NMR tube reaction

(a) Reaction of $Cp_2Cr_2(CO)_4$ with 2.5 mole equivalent of $PPh_2(C_6H_4SMe\text{-}o)$ at 60 °C

C_6D_6 (~ 0.5 mL) was added into a weighed deep green solid $Cp_2Cr_2(CO)_4$ (10 mg, 0.02 mmol) and 2.5 mole equivalent of $PPh_2(C_6H_4SMe\text{-}o)$ (9 mg, 0.02 mmol) in a 5 mm septum capped NMR tube. The reaction mixture was thermolyzed at 60 °C and was monitored at regular interval *via* its ^1H NMR spectra. From the spectra, $CpCr(CO)_2(C_6H_4S)PPh_2$ (**32**) (42.4% yield) was found after 15 h.

3.13 Reaction of $Cp_2Cr_2(CO)_6$ with $PPh(C_6H_4SMe\text{-}o)_2$

3.13.1 Reaction of $Cp_2Cr_2(CO)_6$ with one mole equivalent of $PPh(C_6H_4SMe\text{-}o)_2$ at 110 °C

To a deep green suspension of $Cp_2Cr_2(CO)_6$ (200 mg , 0.497 mmol) in toluene (~20 mL) was added $PPh(C_6H_4SMe\text{-}o)_2$ (176mg , 0.497 mmol). The reaction mixture was stirred at 110 ºC for 5 h. The resultant reddish brown reaction mixture was concentrated to *ca.* 2mL left and chromatographed onto a silica gel column (1.5 cm x 11.5 cm) prepared in *n*-hexane. Elution gave three fractions:

(i) A lemon green eluant in *n*-hexane (45 mL) which when concentrated to dryness gave dark green crystalline solids of $[CpCr(CO)_2]_2$ (142 mg, 0.410 mmol, 82.5% yield)

(ii) A pale pink eluent in *n*-hexane-toluene (2:1, 27 mL) which when concentrated to dryness gave fine dark pink crystalline solids of $[Cp_2Cr_2(CO)\{(\mu\text{-}C_6H_4S)_2PPh\}]$ (**33**) (12 mg, 0.021 mmol, 4.3% yield). Data : ^{1}H NMR (benzene-*d*6): δ 4.51, 4.36 (s, Cp), δ 7.71 - 6.45 (m, Ph). ^{13}C NMR (benzene-d_6): δ 94.0, 92.7 (Cp), δ 145.33, 145.05, 138.63, 135.28, 135.07, 134.27, 132.43, 130.56, 129.81, 129.30, 127.78, 126.02 (Ph), δ 196.02 (CO). ^{31}P NMR (benzene-d_6): δ 153.50. IR: ν(CO) at 1836vs cm^{-1}; other peaks at 1316w, 1270sh, 1160w, 1096m, 1069vw, 1043m, 1029sh, 998w, 966w, 946w, 807w, 746vs, 732sh, 719w and 697m cm^{-1} (nujol). Anal. Calcd. for $C_{29}H_{23}Cr_2OPS_2$: C, 59.38; H, 3.95; Cr, 17.73; O, 2.73; P, 5.28; S, 10.93. Found: C, 59.77; H, 4.03; Cr, 17.89; O, 2.62; P, 5.55; S, 11.24.

(iii) A brown eluant in ether (18 mL) which when concentrated to dryness gave fine brownish pink crystalline solids of $CpCr\{(\mu\text{-}C_6H_4S)_2PPh\}$ (**34**) (18 mg, 0.041 mmol, 8.2% yield). Data : ^{1}H NMR (benzene-*d*6): δ 11.37 (br, $\nu_{½}$ = 96 Hz Cp), δ 7.71 - 7.03 (m, Ph). ^{13}C NMR (benzene-d_6): Not detected (Cp), δ 138.21, 132.43, 130.56, 129.67, 128.90, 126.03 (Ph). Anal. Calcd. for $C_{23}H_{18}CrPS_2$: C, 62.59; H, 4.11; Cr, 11.78; P, 7.02; S, 14.50. Found: C, 61.84; H, 4.23; Cr, 11.82; P, 6.96; S, 14.94.

3.13.2 Reaction of $Cp_2Cr_2(CO)_4$ with one mole equivalent of $PPh(C_6H_4SMe\text{-}o)_2$ at 110 °C

To a deep green suspension of $Cp_2Cr_2(CO)_4$ (50 mg , 0.144 mmol) in toluene (~20 mL) was added $PPh(C_6H_4SMe\text{-}o)_2$ (51 mg , 0.144mmol) and the reaction mixture was stirred at 110 ºC for 3 h. The resultant reddish brown reaction mixture was concentrated to *ca.* 2mL left and chromatographed onto a silica gel column (1 cm × 9 cm) prepared in *n*-hexane. Elution gave two fractions:

(i) A deep green eluant in *n*-hexane (30 mL) which when concentrated to dryness gave dark green crystalline solids of $[CpCr(CO)_2]_2$ (22 mg, 0.064 mmol, 44.4% recovery).

(ii) An orange red eluant in *n*-hexane-toluene (1:1, 20mL) which when concentrated to dryness gave orange red crystalline solids of $[Cp_2Cr_2(CO)\{(\mu\text{-}C_6H_4S)_2PPh\}]$ (**33**) (36 mg, 0.061 mmol, 42.4% yield)

(iii) A pale brown eluant in ether (5mL) which when concentrated to dryness gave fine dark pink crystalline solids of $CpCr\{(\mu\text{-}C_6H_4S)_2PPh\}$ (**34**) (3 mg, 0.007 mmol, 4.9% yield).

3.13.3 NMR Tube Reaction

(a) Reaction of $[CpCr(CO)_3]_2$ (1) with one mole equivalent of $PPh(C_6H_4SMe\text{-}o)_2$

A dirty green suspension of $[CpCr(CO)_3]_2$ (**1**) (20 mg, 0.050 mmol) and $PPh(C_6H_4SMe\text{-}o)_2$ (18 mg, 0.050 mmol) in C_6D_6 (~0.5 mL) inside a 5mm NMR tube closed with a septun cap. The temperature was maintained at 110 °C and was monitored *via* its ^1H NMR spectra at regular intervals. From the spectra, the dimer **1** was converted initially to $[CpCr(CO)_2]_2$ (**2**) during first few 7.5 h. Subsequently, dimer **2** reacted with the ligand to give complexes $[Cp_2Cr_2(CO)\{(\mu\text{-}C_6H_4S)_2PPh\}]$ (**33**) and $CpCr\{(\mu\text{-}C_6H_4S)_2PPh\}$ (**34**). After 25 h almost all dimer **2** was completely reacted with the ligand. The time-dependent ^1H NMR spectra of this study is illustrated in Figure 38.

3.14 Reaction of $Cp_2Cr_2(CO)_6$ with $P(C_6H_4SMe\text{-}o)_3$

3.14.1 Reaction of $Cp_2Cr_2(CO)_6$ with one mole equivalent of $P(C_6H_4SMe\text{-}o)_3$ at 110 °C

To a deep green suspension of $Cp_2Cr_2(CO)_6$ (200 mg, 0.497 mmol) in toluene (~20 mL) was added $P(C_6H_4SMe\text{-}o)_3$ (200 mg, 0.497 mmol). The reaction mixture was stirred at 110 ºC for 5 h. The resultant reddish brown reaction mixture was concentrated to *ca*. 2 mL left and chromatographed onto a silica gel column (1.5 cm x 11.5 cm) prepared in *n*-hexane. Elution gave two fractions:

(i) A deep green fraction was eluted with *n*-hexane (12 mL) which when concentrated to dryness gave fine dark green crystalline solids of $[CpCr(CO)_2]_2$ (100 mg, 0.289 mmol, 58% recovery).

(ii) An orange pink fraction was eluted with toluene (15 mL) which when concentrated to dryness gave dark red crystalline solids of $[Cp_2Cr_2(CO)\{(\mu\text{-}C_6H_4S)_2(C_6H_4SMe\text{-}o)P\}]$ (**35**) (40 mg, 0.063 mmol, 12.7% yield). Data : ^{1}H NMR (benzene-d_6): δ 1.97 (s, CH_3), δ 4.74, 4.38 (s, Cp), δ 7.73 - 6.48 (m, C_6H_4). ^{13}C NMR (benzene-d_6): δ 17.29 (CH_3), δ 94.24, 93.77 (Cp), δ 146.69, 146.23, 145.60, 145.31, 144.10, 144.02, 138.61, 138.21, 137.52, 137.40, 134.46, 132.42, 132.08, 131.40, 130.55, 127.90, 127.86, 127.25, 127.19, 126.11, 126.02, 125.05, 124.67 (C_6H_4), δ 262.72 (CO). ^{31}P NMR (benzene-d_6): δ 153.80. IR: ν(CO) at 1833s cm^{-1} and other peaks at 1317m, 1276sh, 1253m, 1161m, 1100s, 1058sh, 1042vs, 1034sh, 966w, 948w, 918vw, 873vw, 807m, 748vs, 721m, 705m, 694w, 665.20vw, 638w cm^{-1} (nujol). Anal. Calcd. for $C_{30}H_{25}Cr_2OPS_3$: C, 56.95; H, 3.98; Cr, 16.44; O, 2.53; P, 4.90; S, 15.20. Found: C, 56.51; H, 4.14; Cr, 16.63; O, 2.76; P, 4.91; S, 15.75.

3.14.2 Reaction of $Cp_2Cr_2(CO)_4$ with one mole equivalent of $P(C_6H_4SMe\text{-}o)_3$ at 110 °C

To a deep green suspension of $Cp_2Cr_2(CO)_4$ (200 mg, 0.578 mmol) in toluene (~20 mL) was added $P(C_6H_4SMe\text{-}o)_3$ (200 mg, 0.578 mmol). The reaction mixture was stirred at 110 ºC for 5 h. The resultant reddish brown reaction mixture was concentrated to *ca.* 2mL and loaded onto a silica gel column (1.5 cm × 7.5 cm) prepared in *n*-hexane. Elution gave two fractions:

(i) A deep green fraction was eluted with *n*-hexane-toluene (2:1, 8 mL) which when concentrated to dryness gave unreacted fine dark green crystalline solids of $[CpCr(CO)_2]_2$ (73 mg, 0.210 mmol, 36.3% recovery).

(ii) An orange pink fraction was eluted with toluene (60 mL) which when concentrated to dryness gave dark red crystalline solid of $[Cp_2Cr_2(CO)\{(\mu\text{-}C_6H_4S)_2(C_6H_4SMe\text{-}o)P\}]$ (**35**) (148 mg, 0.234 mmol, 40.5% yield).

3.14.3 NMR tube reaction

(a) Reaction of $[CpCr(CO)_3]_2$ with $P(C_6H_4SMe\text{-}o)_3$ at 80 °C

A dirty green suspension of $[CpCr(CO)_3]_2$ (**1**) (13 mg, 0.038 mmol) and $P(C_6H_4SMe\text{-}o)_3$ (15 mg, 0.038 mmol) in C_6D_6 (~0.5 mL) in a 5 mm septum capped NMR tube was reacted at 80 °C. The reaction was monitored by ^1H NMR at intervals. During the first 6 h, the dimer **1** was converted to dimer **2**. After 14.5 h, **2** gradually reacted with the ligand to give traces of $[Cp_2Cr_2(CO)\{(\mu\text{-}C_6H_4S)_2(C_6H_4SMe\text{-}o)P\}]$ (**35**) (Figure 41).

3.15 Reactivity studies of $Cp_2Mo_2(CO)_4$ with $PPh_2(C_6H_4SMe$-*o*)

3.15.1 Reaction of $Cp_2Mo_2(CO)_4$ with one mole equivalent of $PPh_2(C_6H_4SMe$-*o*) at 110 °C

To a reddish brown solution of $Cp_2Mo_2(CO)_4$ (50 mg, 0.115 mmol) in toluene (~10 mL) was added $PPh_2(C_6H_4SMe$-*o*) (36 mg, 0.115 mmol). The reaction mixture was stirred at 110 °C for 21.5 h. The resultant yellowish brown reaction mixture was concentrated to *ca*. 1 mL and loaded onto a prepared silica gel column (9 cm x 1 cm) in *n*-hexane. 2 fractions were eluted out:

(i) A brownish red fraction was eluted with *n*-hexane (39 mL) which when concentrated to dryness gave the unreacted $Cp_2Mo_2(CO)_4$ (24 mg, 0.055 mmol, 47.7% recovery).

(ii) A yellowish orange fraction was eluted with toluene (18 mL) which when concentrated to dryness gave orange red cystals of $CpMo(CO)_2\{o\text{-}(C_6H_4S)PPh_2\}$ (**36**) (50 mg, 0.098 mmol, 42.5% yield). Data : ^1H NMR (benzene-d_6): δ4.59 (s, Cp), δ6.66 - 6.63, 6.78 - 6.75, 6.89 - 6.87, δ6.98 - 6.94, 7.02 - 7.01, 7.28 - 7.25, 7.61 - 7.56, 7.69 - 7.65, 7.80 - 7.78 (m, Ph). ^{13}C NMR (benzene-d_6): δ 95.21 (Cp), δ 133.22, 133.10, 132.14, 132.06, 131.04, 131.01, 130.83, 130.71, 130.33, 130.31, 130.15, 129.25, 129.14, 129.07, 128.97, 122.11, 122.05 (Ph). ^{31}P NMR (benzene-d_6): δ 90.88. IR : ν(CO) at 1944vs, 1873vs, 1841sh cm^{-1}; other peaks at 1159w, 1092m, 1044m, 1025m, 814m, 734w, 720w, 703m, 693m, 553m, 528m, 520m, 501w, 469w, 458w, 387w cm^{-1} (nujol). Anal. Calcd. for $C_{29}H_{23}Mo_2OPS_2$: C, 51.64; H, 3.44; Mo, 28.45; O, 2.37; P, 4.59; S, 9.51. Found: C, 51.62; H, 3.55; Mo, 28.36; O, 2.48; P, 4.62; S, 10.03.

3.16 Reactivity studies of $Cp_2Mo_2(CO)_4$ with $PPh(C_6H_4SMe\text{-}o)_2$

3.16.1 Reaction of $Cp_2Mo_2(CO)_4$ with one mole equivalent of $PPh(C_6H_4SMe\text{-}o)_2$ at 110 °C

To a reddish brown solution of $Cp_2Mo_2(CO)_4$ (200 mg, 0.461 mmol) in toluene (~20 mL) was added $PPh(C_6H_4SMe\text{-}o)_2$ (163 mg, 0.461 mmol). The reaction mixture was stirred at 110 °C for 14 h. The resultant orange brown reaction mixture was concentrated to *ca.* 10 mL and filtered through a sintered-glass funnel. The filtrate was concentrated to dryness and redissolved in THF (~10 mL) and absorbed onto celite (~3.0g). The orange brown slurry was evacuated to dryness under *vacuo* and loaded onto a florisil column (10 cm x 2.0 cm) prepared in *n*-hexane. The following fractions were eluted:

(i) A greenish yellow fraction was eluted with *n*-hexane-toluene (2:1, 70 mL) which when concentrated to dryness gave yellowish brown crystalline solids of $CpMo(CO)_3H$ (**37**) (81 mg, 0.329 mmol, 35.7% yield). Anal. Found : ^1H NMR (benzene-d_6): δ4.45 (s, Cp), δ 0.39 (Mo-H). ^{13}C NMR (benzene-d_6): δ92.77 (Cp), δ-21.64 (Mo-H) [119].

(ii) A dark yellowish red fraction was eluted with toluene-ether (10:1 57 mL) which when concentrated to dryness gave a deep orange precipitate (235 mg). Further analysis with TLC confirmed it to be a mixture of $Cp_2Mo_2(CO)\{(\mu\text{-}C_6H_4S)_2PPh\}$ (**38**), $CpMo(CO)\{(\mu\text{-}C_6H_4S)(C_6H_4SMe\text{-}o)PPh\}$ (**39**) and an uncharacterized orange product. $Cp_2Mo_2(CO)\{(\mu\text{-}C_6H_4S)_2PPh\}$ (**38**) and $CpMo(CO)\{(\mu\text{-}C_6H_4S)(C_6H_4SMe\text{-}o)PPh\}$ (**39**) were isolated after several separation attempts *via* column chromatography. $Cp_2Mo_2(CO)\{(\mu\text{-}C_6H_4S)_2PPh\}$ (**38**) (75.9 mg, 0.113 mmol, 24.5% yield); Data : ^1H NMR (benzene-d_6): δ 4.57, 4.55 (s, Cp), δ 7.85 - 7.01 (m, Ph). ^{13}C NMR (benzene-d_6): δ 92.93, 89.99 (Cp), δ 129.67, 128.90, 126.03 (Ph). ^{31}P NMR (benzene-d_6): δ 125.96. IR: ν(CO) at 1814vs cm^{-1}; other peaks at 1251w, 1091m, 793m, 768m, 741w, 729w, 696w, 537w, 531w, 501vw cm^{-1} (nujol). Anal. Calcd. for $C_{29}H_{23}Mo_2OPS_2$: C, 51.64; H, 3.44; Mo, 28.45; O, 2.37; P, 4.59; S, 9.51. Found: C, 52.06; H, 3.78; Mo, 28.40; O, 2.88; P, 4.53; S, 9.90. CpMo(CO){(μ-C_6H_4S)(C_6H_4SMe-*o*)PPh} (**39**) (63 mg, 0.119 mmol, 12.9% yield); Data : ^{1}H NMR (benzene-d_6): δ 2.36 (s, CH_3), δ 4.51 (s, Cp), δ 8.11 - 6.80 (m, Ph). ^{13}C NMR (benzene-d_6): δ 15.92 (CH_3), δ 92.05 (Cp), δ 132.43, 131.88, 131.63, 131.01, 130.90, 130.56, 130.38, 129.79, 129.67, 128.90, 127.83, 127.71, 126.03 (Ph), δ 247.13. ^{31}P NMR (benzene-d_6): δ 82.18. Anal. Calcd. for $C_{25}H_{21}MoOPS_2$: C, 56.82; H, 4.01; Mo, 18.15; O, 3.03; P, 5.86; S, 12.14. Found: C, 56.65; H, 3.97; Mo, 18.51; O, 3.43; P, 5.79; S, 12.44.

(iii) A yellowish orange fraction was eluted with THF (18 mL) which when concentrated to dryness gave brownish orange crystalline solids of CpMo(CO){(μ-C_6H_4S)(C_6H_4SMe-*o*)PPh} (**39**) (7 mg, 0.013 mmol, 1.4% yield).

3.16.2 NMR tube reaction

(a) Thermolysis of CpMo(CO){(μ-C_6H_4S)(C_6H_4SMe-*o*)PPh} (39)

A brownish orange solution of CpMo(CO){(μ-C_6H_4S)(C_6H_4SMe-*o*)PPh} (**39**) (9 mg, 0.017 mmol) in $C_6D_5CD_3$ (~0.5 mL) in a 5 mm septum capped NMR tube was thermolyzed at 110 °C. The reaction was monitored by ^{1}H NMR at regular intervals. **39** gradually slowly decomposed in the solution but no formation of any new product was observed even after prolonged thermolysis for 14 h.

3.17 Reaction of $Cp_2Mo_2(CO)_4$ with $P(C_6H_4SMe$-*o*$)_3$

3.17.1 Reaction of $Cp_2Mo_2(CO)_4$ with one mole equivalent of $P(C_6H_4SMe$-*o*$)_3$ at 110 °C

To a reddish brown solution of $Cp_2Mo_2(CO)_4$ (200 mg, 0.461 mmol) in toluene (~15 mL) was added $P(C_6H_4SMe$-*o*$)_3$ (163 mg, 0.461 mol). The reaction mixture was stirred at 110 °C for 24 h. The resultant dark reddish brown reaction mixture was filtered through a sintered-glass funnel to remove the small amount of insoluble dark brown residue. The filtrate was concentrated to dryness and redissolved in THF (~4 mL) and absorbed onto silica gel (~1.5 g). The dark reddish brown slurry was evacuated to dryness under *vacuo* and loaded onto a silica gel column (2.0 cm x 8.0 cm) prepared in *n*-hexane. The following fractions were eluted:

(i) A red fraction was eluted with *n*-hexane-toluene (3:1, 72 mL) which when concentrated to dryness gave magenta crystalline solids of unreacted $Cp_2Mo_2(CO)_4$ (**4**) (50 mg, 0.115 mmol, 28.2% recovery).

(ii) A golden brown fraction was eluted with *n*-hexane-toluene (1:1, 113 mL) which when concentrated to dryness gave dark brown crystalline solids of $[Cp_2Mo_2(CO)\{(\mu\text{-}C_6H_4S)_2(C_6H_4SCH_2)P\}]$ (**40**) (56 mg, 0.078 mmol, 19.1% yield). Data : ^1H NMR (benzene-d_6): δ 1.42 (s, CH_2), δ 4.57, 4.55 (s, Cp), δ 7.14 - 6.58, 7.52 - 7.48, 7.86 - 7.84 (m, C_6H_4). ^{13}C NMR (benzene-d_6): δ 15.92 (CH_2), δ 92.92, 89.97 (Cp), δ 138.23, 132.60, 132.49, 131.95, 129.65, 129.91, 128.89, 126.02 (C_6H_4). ^{31}P NMR (benzene-d_6): δ 127.29. IR: ν(CO) at 1815vs cm^{-1}; other peaks at 1158m, 1098s, 1051s, 876w, 794w, 769vw, 742vw, 728vw, 713vw, 695vw, 669vw, 537vw, 477vw, and 466vw cm^{-1} (nujol). Anal. Calcd. for $C_{30}H_{25}Mo_2OPS_3$: C, 50.01; H, 3.50; Mo, 26.63; O, 2.22; P, 4.30; S, 13.35. Found: C, 50.12; H, 3.45; Mo, 27.06; O, 2.54; P, 4.33; S, 14.12.

(iii) A reddish brown fraction was eluted with *n*-hexane-toluene (1:1.5, 46 mL) which when concentrated to dryness gave dark brown crystalline solids of $[Cp_2Mo_2(CO)\{(\mu\text{-}C_6H_4S)_2(C_6H_4SMe\text{-}o)P\}]$ (**41**) (76 mg, 0.122 mmol, 26.5% yield). Data : ^1H NMR (benzene-d_6): δ 1.97 (s, CH_3), δ 4.80, 4.57 (s, Cp), δ 7.13 - 6.53, 7.55 - 7.51, 7.63 - 7.60, 7.72 - 7.70, 7.85 - 7.83 (m, C_6H_4). ^{13}C NMR (benzene-d_6): δ 17.12 (CH_3), δ 93.07, 90.75 (Cp), δ 144.05, 143.97, 134.48, 132.36, 131.92, 130.57, 130.23, 129.85, 129.66, 127.04, 126.96, 126.12, 124.96, 124.53, 124.45 (C_6H_4), δ 238.27 (CO). ^{31}P NMR (benzene-d_6): δ

127.67. IR: ν(CO) at 1805vs cm^{-1} and other peaks at 1254m, 1162m, 1100m, 1042m, 966w, 948w, 795w, 748m, 543w and 483w cm^{-1} (nujol). Anal. Calcd. for $C_{30}H_{25}Mo_2OPS_3$: C, 50.01; H, 3.50; Mo, 26.63; O, 2.22; P, 4.30; S, 13.35. Found: C, 49.97; H, 3.37; Mo, 26.54; O, 2.37; P, 4.26; S, 13.86.

(iv) A yellowish brown fraction was eluted with toluene (40 mL) which when concentrated to dryness gave bright yellow crystalline solids of $Mo(CO)_3\{P(C_6H_4SMe\text{-}o)_3\}$ (**42**) (42 mg, 0.073mmol, 15.8% yield). Data : ^1H NMR (benzene-*d*$_6$): δ 2.45, 2.07, (s, CH_3), δ 7.60 - 6.70 (m, C_6H_4). ^{13}C NMR (benzene-*d*$_6$): δ 26.15, 21.76, 19.54 (CH_3), δ 130.85, 129.66, 128.89, 126.03 (C_6H_4), δ 223.07 (CO). ^{31}P NMR (benzene-*d*$_6$): δ 79.81. IR : ν(CO) at 1837vs, 1828sh, 1796sh cm^{-1} and other peaks at 1152w, 1061w, 1005w, 799w, 763w, 723vw, 698w, 560vw, 549vw, 535vw, 529vw, 490vw and 474vw cm^{-1} (nujol). Anal. Calcd. for $C_{24}H_{21}MoO_3PS_3$: C, 50.44; H, 2.12; Mo, 16.79; O, 8.40; P, 5.42; S, 16.83. Found: C, 50.46; H, 2.24; Mo, 16.81; O, 8.41; P, 5.63; S, 17.15.

(v) A brownish orange fraction was eluted with ether (25 mL) which when upon concentrated to dryness gave orange crystalline solids of $CpMo_2(CO)_3(\mu\text{-}S)\{(\mu\text{-}C_6H_4S)(C_6H_4SMe\text{-}o)P\}$ (**43**) (18 mg, 0.029mmol, 6.3% yield). Data : ^1H NMR (benzene-*d*$_6$): δ 2.42 (s, CH_3), δ 4.70 (s, Cp), δ 7.13 - 6.69, 7.59 - 7.54, 7.72 - 7.69, 8.10 - 8.05 (m, C_6H_4). ^{13}C NMR (benzene-*d*$_6$): δ 26.15 (CH_3), δ 92.38 (Cp), δ 138.22, 132.43, 130.56, 129.67, 128.90, 126.03 (C_6H_4). ^{31}P NMR (benzene-*d*$_6$): δ 114.88. IR: ν(CO) at 1953s, 1864s, 1829sh cm^{-1}; other peaks at 1317w, 1276m, 1258w, 1106m, 1075m, 1029m, 974w, 942w, 921w, 809w, 750m, 729sh, 702m, 667vw, 639vw, 548w, 481vw and 466vw cm^{-1} (nujol). Anal. Calcd. for $C_{27}H_{20}Mo_2O_3PS_4$: C, 43.61; H, 2.71; Mo, 25.81; O, 6.45; P, 4.17; S, 17.25. Found: C, 44.07; H, 2.70; Mo, 25.84; O, 6.76; P, 4.25; S, 17.63.

3.17.2 NMR tube reactions

(a) Thermolysis of [$Cp_2Mo_2(CO)\{(\mu\text{-}C_6H_4S)_2(C_6H_4SMe\text{-}o)P\}$] (41)

A dark reddish brown solution of [$Cp_2Mo_2(CO)\{(\mu\text{-}C_6H_4S)_2(C_6H_4SMe\text{-}o)P\}$] (**41**) (15 mg, 0.020 mmol) in $C_6D_5CD_3$ (~0.5 mL) in a 5 mm septum capped NMR tube was thermolyzed at 110 °C. The reaction was monitored by ^{1}H NMR at regular intervals. **41** gradually decomposed in the solution but no formation of any new product was observed even after prolonged thermolysis for 64 h.

(b) Thermolysis of $Mo(CO)_3\{o\text{-}P(PhSMe)_3\}$ (42)

A brownish yellow solution of $Mo(CO)_3\{P(C_6H_4SMe\text{-}o)_3\}$ (**42**) (10 mg, 0.017 mmol) in $C_6D_5CD_3$ (~0.5 mL) in a 5mm septum capped NMR tube was thermolyzed at 110 °C. The reaction was monitored by ^{1}H NMR at intervals. **42** gradually decomposed in the solution and given rise of a peak at δ 1.99 after 20 h.

3.18 Formation of specific transition metal carbonyl fragments adducts of [$CpM(SBz)]_2S_n$ (M = Cr, n =1 or Mo, n = 2)

3.18.1 Reaction of [$CpCr(SBz)]_2S$ with 2 mole equivalent of $Fe_2(CO)_9$

A mixture of [$CpCr(SBz)]_2S$ (**7**) (30 mg, 0.059 mmol) and $Fe_2(CO)_9$ (43mg, 0.118 mmol) in a 50 mL round bottom flask was flushed with CO for 5 minutes, THF (~10 mL) was injected in and the reaction mixture was stirred at ambient temperature under an atmosphere of CO. The color of the solution immediately changed from dark purple to brownish purple. 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 6.5 cm) prepared in *n*-hexane. Two fractions were eluted:

(i) A brownish purple fraction was eluted with *n*-hexane-toluene (2:1) (15 mL) which on concentration to *ca.* 2 mL and slow crystallization at -28 °C for 3 days yielded fine dark purplish brown crystals of $[Cp_2Cr_2(SBz)]S_2[Fe(CO)_3]$ (**44**) (11 mg, 0.0196 mmol, 33.2% yield). Data : ^{1}H NMR (benzene-d_6): δ 3.30 (s, CH_2), δ 4.91 (s, Cp), δ 7.72 - 7.01 (m, C_6H_5), ^{13}C NMR (benzene-d_6): δ 90.34 (Cp), δ 138.63, 132.41, 130.56, 129.65, 126.03 (C_6H_5), δ 196.02 (CO). Anal. Calcd. for $C_{20}H_{17}Cr_2FeO_3S_3$: C, 42.79; H, 3.05; Cr, 18.52; Fe, 9.95; O, 8.55; S, 17.14. Found: C, 43.16; H, 3.11; Cr, 18.55; Fe, 9.98; O, 8.69; S, 16.96.

(ii) A brownish green fraction was eluted with toluene (8 mL) which when concentrated to dryness yielded an uncharacterized dark brown precipitate (7 mg).

A dark greenish brown rim remained on top of the column.

3.18.2 Reaction of $[CpMo(SBz)(S)]_2$ with 2 mole equivalent of $Fe_2(CO)_9$ at room temperature

To a dark pink solution of $[CpMo(SBz)(S)]_2$ (70 mg, 0.1104 mmol) in THF (~15 mL) was added in 2 mole equivalent of $Fe_2(CO)_9$ (80 mg, 0.2208 mmol) and the reaction mixture was stirred at ambient temperature for 1.5 h. The resultant dark brownish pink reaction mixture was concentrated to dryness and the residue redissolved in toluene (*ca.* 2mL) and chromatographed onto a silica gel column (1.5 cm x 8 cm) prepared in *n*-hexane. Two fractions were eluted:

(i) A dark greenish brown fraction was eluted with *n*-hexane (10 mL) which on concentrated to dryness gave mixture of dark green crystalline solids of $[CpMo]_2S_4[Fe(CO)_3]_2$ (**45**) and dark red crystalline solids of $[CpMo]_2S_3[Fe(CO)_3]_2$ (**46**)**.** Products of $[CpMo]_2S_4[Fe(CO)_3]_2$ (**45**) and $[CpMo]_2S_3[Fe(CO)_3]_2$ (**46**) were isolated after several separation attempts *via* column chromatography. $[CpMo]_2S_4[Fe(CO)_3]_2$ (**45**) (16 mg, 0.0219 mmol, 19.8% yield), Data for $[CpMo]_2S_4[Fe(CO)_3]_2$: ^{1}H NMR (benzene-d_6) :

δ 5.73, 4.67 (s, Cp), ^{13}C NMR (benzene-d_6) : δ 95.23, 94.35 (s, Cp). IR: ν(CO) at 2070vw, 2043m, 2034s, 1996s, 1970vs, 1949s cm^{-1} (nujol); $[CpMo]_2S_3[Fe(CO)_3]_2$ (**46**) (8 mg, 0.0115 mmol, 10.4% yield). Anal. Calcd. for $C_{16}H_{10}Mo_2Fe_2O_6S_4$: C, 26.32; H, 1.38; Mo, 26.28; Fe, 15.30; O, 13.15; S, 17.57. Found: C, 26.38; H, 1.46; Mo, 26.21; Fe, 15.67; O, 13.06; S, 18.04.

(ii) A pink fraction was eluted with *n*-hexane-toluene (3:1) (35 mL) and which on concentrated to *ca.* 2 mL, layered with *n*-hexane and slow crystallization at -28 °C for 5 days yielded dark pink crystalline solid of $[CpMo(SBz)]_2S_2[Fe(CO)_2]$ (**47**) (15 mg, 0.0202 mmol, 18.3% yield). Data : ^{1}H NMR (benzene-d_6): δ 3.12, 3.98 (s, CH_2), δ 4.58 (s, Cp), δ 7.29 - 7.01 (m, C_6H_5), ^{13}CNMR (benzene-d_6): δ 92.76 (s, Cp), δ 141.12, 140.81, 130.20, 130.09, 129.22, 129.01, 128.92, 127.77, 127.42 (m, C_6H_5), δ 221.35 (s, CO). IR: ν (CO) at 1934vs, 1926sh, 1858vs, 1824sh cm^{-1}, other peaks at 1108w, 1067w, 1027w, 1008w, 838vw, 815m, 770m, 701m, 642m, 576w, 561w (nujol). Anal. Calcd. for $C_{26}H_{24}Mo_2FeO_2S_4$: C, 41.95; H, 3.25; Mo, 25.77; Fe, 7.50; O, 4.30; S, 17.23. Found: C, 41.88; H, 3.36; Mo, 25.75; Fe, 7.46; O, 4.86; S, 17.89.

A brown rim remained on top of the column.

3.19 Reaction of $[CpMo(CO)_2(S_2P(SC_6H_4Me)_2)]$ (14) with one mole equivalent of $[CpCr(CO)_3]_2$ (1) at 110 °C

To a greenish brown solution of $[CpMo(CO)_2(S_2P(SC_6H_4Me)_2)]$ (**14**) (125 mg, 0.224 mmol) in toluene (~15 mL) was added $[CpCr(CO)_3]_2$ (**1**) (100mg, 0.224 mmol). The reaction mixture was stirred at 110 °C for 1.5 h. The resultant dark purplish brown reaction mixture was concentrated to *ca.* 3 mL and loaded onto a silica gel column (2 cm x 10 cm) prepared in *n*-hexane. Elution gave 5 fractions.

(i) A pale yellow fraction was eluted with *n*-hexane (12.5 mL) which on concentrated to dryness yielded an uncharacterized oily yellow residue (16 mg).

(ii) A reddish brown fraction was eluted with *n*-hexane-toluene (2:1) (65 mL) which when concentrated to dryness yielded reddish brown crystalline solids of $[CpMo(CO)_2(\mu\text{-}S)]_2$ (**19**) (12 mg, 0.024 mmol, 10.8% yield). Data : ^1H NMR (benzene-d_6): δ 4.54 (s, Cp), ^{13}C NMR (benzene-d_6): δ 86.65 (s, Cp), δ 227.25 (s, CO). IR: ν(CO) at 1988s, 1947vs, 1902vs, 1865s cm^{-1} and other bands at 1260s, 803s 572w, 544vw, 530w, 496w, 461w cm^{-1} (nujol). Anal. Calcd. for $C_{14}H_{10}Mo_2O_4S_2$: C, 33.75; H, 2.02; Mo, 38.51; O, 12.84; S, 12.87. Found: C, 33.46; H, 2.34; Mo, 38.51; O, 12.88; S, 12.94.

(iii) A yellowish brown fraction was eluted with *n*-hexane/toluene mixture (1:1) (60 mL) which when concentrated to dryness yielded dark brown solids (18 mg). Analyses with ^1H NMR showed the presence of the *trans-syn/trans-anti* isomer of $[CpMo(CO)(SC_6H_4Me)]_2$ (**17**) (7.1% yield), traces of $Cp_4Cr_4S_4$ (**8**), and an uncharacterized peak at δ4.77.

(iv) A greenish brown fraction was eluted with toluene (45 mL) which when concentrated to dryness yielded uncharacterized dark grayish brown residue (41 mg). Data : ^1H NMR (benzene-d_6): δ 19.97 (br). ^{13}C NMR (benzene-d_6): δ 26.16, 15.93 (CH_3), δ 138.65, 138.23, 132.42, 130.56, 129.67, 126.03 (C_6H_4), δ 196.02 (CO).

(v) A purple fraction was eluted with ether (15 mL) which when concentrated to dryness yielded dark purple crystalline solids of $[CpCr(\mu\text{-}SC_6H_4Me)]_2S$ (**48**) (9 mg, 0.018 mmol, 7.9% yield). Data : ^1H NMR (benzene-d_6): δ 13.05 (br, Cp, $\nu_{1/2}$ = 47.8 Hz), δ2.46, 2.20 (s, CH_3). ^{13}C NMR (benzene-d_6): δ 100.98 (Cp), δ 26.16 ($-CH_3$). IR.: ν at 1302vw, 1261vw, 1155w, 1103m, 1081m, 1060m, 1017m, 1011m, 839w, 802m, 496w, 490w, 399w cm^{-1} (nujol) Anal. Calcd. for $C_{24}H_{24}Cr_2S_3$: C, 56.23; H, 4.72; Cr, 20.29; S, 18.77. Found: C, 56.62; H, 4.69; Cr, 20.26; S, 19.61.

3.20 Crystal structure determinations

3.20.1 Structure determination of $[CpCr(CO)_2(SBz)]_2$ (6)

Diffraction quality single crystals of **6** were obtained as dark red block from a solution in toluene layered with *n*-hexane after 3 days at –28 °C. Details of crystal parameters, data collection, and structure refinement were given in Table 76. The structure was solved by direct methods with SHELXL-97; the H-atoms were generated with C-H = 0.97 Å and allowed to ride on their respective atoms. Computer programs used for structure solution and refinement were from the SHELXL-97 [129].

3.20.2 Structure determination of $[CpCr(SBz)]_2S$ (7)

Diffraction quality single crystals of **7** obtained as dark purple plate from a solution in THF layered with ether after one week at ambient temperature. Details of crystal parameters, data collection, and structure refinement were given in Table 77. The structure was solved by SHELXS-97 and refinement were from SHELXL-97 [129].

Table 76. Crystal data and structure refinement for $[CpCr(CO)_2(SBz)]_2$ (**6**)

Complex	$[CpCr(CO)_2(SBz)]_2$ (**6**)
Empirical formula	C_{28} H_{24} Cr_2 O_4 S_2
Formula weight	592.59
Temperature (K)	293(2) K
Wavelength (Å)	0.71073 Å
Crystal system	Monoclinic
Space group	P 2(1)/c
Unit cell dimensions	
a (Å)	8.6155(17) Å
b (Å)	24.551(5)Å
c (Å)	12.975(3) Å
α (°)	90 °
β (°)	107.98(3) °
γ (°)	90 °
Volume ($Å^3$)	2610.5(9) $Å^3$
Z	4
Density (Mg m^{-3})	1.508 Mg/m^3
Absorption coefficient (mm^{-1})	1.025 mm^{-1}
F(000)	1216
Crystal size (mm)	0.38 x 0.20 x 0.16 mm
θ range for data collection	1.66 to 27.54 °
Limiting indices	-11<=h<=11,
	-28<=k<=31
	-15<=l<=16
Reflections collected/unique	18368 / 5994 [R(int) = 0.0304]
Data/restraints/parameters	5994 / 0 / 325
Goodness-of-fit on F^2	0.832
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0373
	wR2 = 0.1052
R indices (all data)	R1 = 0.0477
	wR2 = 0.1159
Largest different peak and hole ($eÅ^{-3}$)	0.583 and -0.205 $eÅ^{-3}$

Table 77. Crystal data and structure refinement for $[CpCr(SBz)]_2S$ (**7**)

Complex	$[CpCr(SBz)]_2S$ (**7**)
Empirical formula	C_{24} H_{24} Cr_2 S_3
Formula weight	512.61
Temperature (K)	223(2) K
Wavelength (Å)	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	
a (Å)	10.0033(10) Å
b (Å)	12.2554(12) Å
c (Å)	18.9255(18) Å
α (°)	90 °
β (°)	100.605(2) °
γ (°)	90 °
Volume ($Å^3$)	2280.5(4)$Å^3$
Z	4
Density ($Mg\ m^{-3}$)	1.493 Mg/m^3
Absorption coefficient (mm^{-1})	1.236 mm^{-1}
F(000)	1056
Crystal size (mm)	0.38 x 0.18 x 0.04 mm
θ range for data collection	2.19 to 27.50 °
Limiting indices	-12<=h<=12,
	-8<=k<=15
	-24<=l<=24
Reflections collected/unique	7600 / 2613 [R(int) = 0.0512]
Data/restraints/parameters	2613 / 146 / 213
Goodness-of-fit on F^2	1.092
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0631
	wR2 = 0.1609
R indices (all data)	R1 = 0.0938
	wR2 = 0.1761
Largest different peak and hole ($eÅ^{-3}$)	0.879 and -0.845$eÅ^{-3}$

3.20.3 Structure determination of $[CpMo(CO)_2(SBz)]_2$ (9), $[CpMo(SBz)(S)]_2$ (10a & b) and $[CpMo(CO)(SBz)]_2S$ (11)

Diffraction quality single crystals of **9** were obtained as dark red plate from a solution in toluene layered with *n*-hexane after 2 days at –28 °C. Details of crystal parameters, data collection, and structure refinement were given in Table 78. The structure was solved by direct methods with SHELXL-97; the H-atoms were placed at calculated postions in the riding model approximation [C-H aromatic 0.95 Å and C-H aliphatic 0.99Å; U(H) = 1.2U~eq~(C)]. Computer programs used for structure solution and refinement were from the SHELXL-97 [129].

$[CpMo(SBz)(S)]_2$ (**10**) can be obtained as two polymorphous species. Complex **10a** crystallizes in the space group Pcba of the orthorhombic system and **10b** in the space group P21/c of the monoclinic system. Diffraction quality single crystals of **10a** were obtained as dark pink plates from a solution in toluene layered with *n*-hexane after 2 days at –28 °C while **10b** obtained as fine dark pink block from a solution in toluene layered with ether after a week at ambient temperature. Details of crystal parameters, data collection, and structure refinement were given in Table 79. Both of the structures of **10a** and **10b** were solved by direct methods with SHELXTL and refinement were from the SHELXL-97 [129].

Diffraction quality single crystals of **11** were obtained as dark pinkish brown blocks from a solution in ether after one day at -28 °C. Details of crystal parameters, data collection, and structure refinement were given in Table 78. The structure was solved by SHELXS-97 and refinement were from SHELXL-97 [129].

Table 78. Crystal data and structure refinement for $[CpMo(CO)_2(SBz)]_2$ (**9**) and $[CpMo(CO)(SBz)]_2S$ (**11**)

Complex	$[CpMo(CO)_2(SBz)]_2$ (**9**)	$[CpMo(CO)(SBz)]_2S$ (**11**)
Empirical formula	$C_{28}H_{24}Mo_2O_4S_2$	$C_{26}H_{24}Mo_2O_2S_3$
Formula weight	632.55	632.55
Temperature (K)	163(2) K	223(2) K
Wavelength (Å)	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	P 2(1)/c	P-1
Unit cell dimensions		
a (Å)	8.6302(6) Å	11.325(1)
b (Å)	24.801(2) Å	16.104(1)
c (Å)	13.2751(9) Å	22.723(1)
α (°)	90 °	74.15(1)
β (°)	108.702(1) °	86.10(1)
γ (°)	90 °	69.52(1)
Volume ($Å^3$)	2691.3(3)$Å^3$	3732.9(4) $Å^3$
Z	4	6
Density ($Mg\ m^{-3}$)	1.679 Mg/m^3	1.752 Mg/m^3
Absorption coefficient (mm^{-1})	1.119 mm^{-1}	1.282 mm^{-1}
F(000)	1360	1968
Crystal size (mm)	0.33 x 0.14 x 0.04 mm	0.38 x 0.30 x 0.28 mm
θ range for data collection	1.64 to 26.47 °	0.93 to 27.50 °
Limiting indices	-10<=h<=10,	-14<=h<=14
	-31<=k<=31	-20<=k<=19
	-15<=l<=16	29<=l<=29
Reflections collected/unique	34532 / 5537 [R(int) = 0.0481]	36947 / 17028 [R(int) = 0.041]
Data/restraints/parameters	5537 / 0 / 325	17028 / 0 / 766
Goodness-of-fit on F^2	0.902	1.067
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0252	R1 = 0.0663
	wR2 = 0.0466	wR2 = 0.1957
R indices (all data)	R1 = 0.0444	R1 = 0.0996
	wR2 = 0.0499	wR2 = 0.2157
Largest different peak and hole ($eÅ^{-3}$)	0.39 and -0.34$eÅ^{-3}$	2.42 and -1.69 $eÅ^{-3}$

Table 79. Crystals data and structure refinement for [CpMo(SBz)(S)]$_2$ (**10a & b**)

Complex	[CpMo(SBz)(S)]$_2$ (**10a**)	[CpMo(SBz)(S)]$_2$ (**10b**)
Empirical formula	$C_{24} H_{24} Mo_2 S_4$	$C_{24} H_{24} Mo_2 S_4$
Formula weight	680.47	680.47
Temperature (K)	223(2) K	223(2) K
Wavelength (Å)	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Orthorhombic
Space group	P 2(1)/c	Pcba
Unit cell dimensions		
a (Å)	12.084(1) Å	8.052(1) A
b (Å)	7.834(1) Å	12.328(1) A
c (Å)	12.563(1) Å	23.838(1) A
α (°)	90 °	90 °
β (°)	98.542(1) °	90 °
γ (°)	90 °	90 °
Volume (Å^3)	1176.1(2) Å^3	2366.3(4) Å^3
Z	2	4
Density (Mg m^{-3})	1.786 Mg/m^3	1.776 Mg/m^3
Absorption coefficient (mm^{-1})	1.432 mm^{-1}	1.423 mm^{-1}
F(000)	632	1264
Crystal size (mm)	0.10 x 0.10 x 0.04 mm	0.14 x 0.10 x 0.09 mm
θ range for data collection	1.70 to 27.54 °	1.71 to 27.53
Limiting indices	-15<=h<=13	-9<=h<=10
	-10<=k<=10	-16<=k<=14
	-16<=l<=15	-24<=l<=30
Reflections collected/unique	8009 / 2693 [R(int) = 0.0360]	15518 / 2722 [R(int) = 0.0543]
Data/restraints/parameters	2693 / 0 / 136	2722 / 0 / 136
Goodness-of-fit on F^2	1.063	1.013
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0434	R1 = 0.0360
	wR2 = 0.1036	wR2 = 0.0753
R indices (all data)	R1 = 0.0559	R1 = 0.0533
	wR2 = 0.1102	wR2 = 0.0816
Largest different peak and hole (eÅ^{-3})	0.39 and -0.34eÅ^{-3}	0.506 and -0.364 eÅ^{-3}

3.20.4 Structure determination of *trans-anti*[CpMo(CO)(SBz)]$_2$ (12b) and [CpMo(SBz)$_2$]$_2$ (13)

Green polyhedral of *trans-anti*[CpMo(CO)(SBz)]$_2$ (**12b**) suitable for X-ray structural analysis were obtained from a solution toluene/*n*-hexane after *ca*. 3 days at ambient temperature. Bright yellowish orange solids with irregular shape of [CpMo(SBz)$_2$]$_2$ (**13**) were obtained from a solution of toluene/*n*-hexane after one week at ambient temperature.

The crystals of *trans-anti*[CpMo(CO)(SBz)]$_2$ (**12b**) and [CpMo(SBz)$_2$]$_2$ (**13**) used for unit cell determination and data collection was coated with low temperature oil to prevent decomposition in air. Details of both the crystals parameters data collection and structure refinement are given in Table 80. The structure of both **12b** and **13** were solved by SHELXS-97 and refinement were from SHELXL-97 [129].

Table 80. Crystals data and structure refinement for *trans-anti*[CpMo(CO)(SBz)]$_2$ (**12b**) and [CpMo(SBz)$_2$]$_2$ (**13**).

Complex	*trans-anti*[CpMo(CO)(SBz)]$_2$ (**12b**)	[CpMo(SBz)$_2$]$_2$ (**13**)
Empirical formula	$C_{26}H_{24}Mo_2O_2S_2$	$C_{38}H_{38}Mo_2S_4$
Formula weight	624.45	814.80
Temperature (K)	100(2) K	123(2) K
Wavelength (Å)	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	P 2(1)/c	P-1
Unit cell dimensions		
a (Å)	10.7994(3) Å	8.67740(10) Å
b (Å)	13.8427(5) Å	9.59540(10) Å
c (Å)	8.3960(3) Å	12.1821(2) Å
α (°)	90 °	106.6410(10) °
β (°)	110.621(2) °	97.7990(10) °
γ (°)	90 °	116.2150(10) °
Volume (Å^3)	1174.73(7)Å ^{3}	830.323(19) Å ^{3}
Z	2	1
Density (Mg m^{-3})	1.765 Mg/m^3	1.630 Mg/m^3
Absorption coefficient (mm^{-1})	1.267 mm^{-1}	1.034 mm^{-1}
F(000)	624	414
Crystal size (mm)	0.08 x 0.07 x 0.06 mm	0.35 x 0.25 x 0.03 mm
θ range for data collection	2.50 to 27.50 °	1.83 to 27.49 °
Limiting indices	-14<=h<=14	-11<=h<=11
	-17<=k<=17	-12<=k<=11
	-10<=l<=10	-10<=l<=15
Reflections collected/unique	14047 / 2691 [R(int) = 0.0904]	3769 / 3769 [R(int) = 0.0000]
Data/restraints/parameters	2691 / 0 / 146	3769 / 128 / 219
Goodness-of-fit on F^2	1.015	1.295
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0467	R1 = 0.0932
	wR2 = 0.1074	wR2 = 0.2581
R indices (all data)	R1 = 0.0744	R1 = 0.0957
	wR2 = 0.1237	wR2 = 0.2591
Largest different peak and hole (eÅ^{-3})	1.001 and -1.202eÅ^{-3}	3.167 and -3.493 eÅ^{-3}

3.20.5 Structure determination of $CpMo(CO)_2\{S_2P(SC_6H_4Me)_2\}$ (14), $Cp_2Mo_2(CO)_5\{S_2P(SC_6H_4Me)\}$ (15) and $Cp_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SC_6H_4Me)$ (16)

Diffraction-quality single crystals were obtained from the solution at ambient temperature. **14** was obtained as dark brown crystals from *n*-hexane/toluene after 2 days whereas **15** as deep pink crystals in *n*-hexane/toluene after 1 week and **16** as dark purple crystals from a toluene-THF mixture after 12 days.

Diffractions measurements were carried out at 25 °C for **14** and -50 °C for **15** and **16** on a Bruker SMART diffractometer equipped MoK\α radiation. The data were corrected for absorption effects with SADABS [130]. Structures solution and refinement were carried out with the Bruker-SHELXTL programs [129]. The structure of **14** refined to *R* = 0.071 for the 4186 reflections, that of **15** to *R* = 0.084 for 3369 reflections and that of **16** to *R* = 0.046 for 4215 reflections. The toluene and tetrahydrofuran molecules are disordered with respect to each other over a center-of-inversion. The molecular structures of **14**, **15** and **16** are shown in Figures 40-42. The data collection and processing parameters are shown in Table 81 and selected bond lengths and bond angles are listed in Table 24.

Table 81. Data collection and processing parameters of $CpMo(CO)_2\{S_2P(SPhMe)_2\}$ (**14**), $Cp_2Mo_2(CO)_5\{S_2P(SPhMe)\}$ (**15**) and $Cp_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SPhMe)$ (**16**).

Complexes	$CpMo(CO)_2\{S_2P(SPhMe)_2\}$ (**14**)	$Cp_2Mo_2(CO)_5\{S_2P(SPhMe)\}$ (**15**)	$Cp_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SPhMe)$ (**16**)
Empirical formula	$C_{21}H_{19}MoO_2PS_4$	$C_{22}H_{17}Mo_2O_5PS_3$	$C_{19.75}H_{21}Mo_2O_{0.25}S_4$
Formula weight	558.51	680.39	582.49
Temperature (K)	295 (2)	293 (2)	223 (2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	orthorhombic	Monoclinic	monoclinic
Space group	*Pbca*	$P2_1/a$	$P2_1/n$
Unit cell dimensions			
a (Å)	15.8742(7)	11.9267(9)	8.0346 (4)
b (Å)	15.9439(7)	17.0042(13)	14.9560 (6)
c (Å)	18.7590(9)	12.4336(9)	17.3168 (8)
α (°)	90	90	90
β (°)	90	102.204(2)	95.797 (1)
γ (°)	90	90	90
Volume ($Å^3$)	4747.8(4)	2464.6(3)	2070.2 (2)
Z	8	4	4
Density ($Mg\ m^{-3}$)	1.563	1.834	1.869
Absorption coefficient (mm^{-1})	0.987	1.369	1.618
$F(000)$	2256	1344	1158
Crystal size (mm)	0.20 x 0.14 x 0.10	0.28 x 0.04 x 0.02	0.22 x 0.12 x 0.10
θ range for data collection	2.5 – 29.4	1.00 - 25.00	2.36 – 29.77
Limiting indices	$-18 \leq h \leq 20$,	$-14 \leq h \leq 14$,	$-9 \leq h \leq 10$,
	$-20 \leq k \leq 20$,	$-19 \leq k \leq 20$,	$-19 \leq k \leq 12$,
	$-24 \leq l \leq 15$	$-14 \leq l \leq 13$	$-22 \leq l \leq 22$
Reflections collected/unique	5445/4186	4342/3369	4738/4215
Data/restraints/parameters	31395/0/264	14037/0/299	14455/0/245
Goodness-of-fit on F^2	1.190	1.100	1.150
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.071$	$R_1 = 0.0842$	$R_1 = 0.0458$
	$wR_2 = 0.144$	$R_1 = 0.1073$	$wR_2 = 0.1097$
R indices (all data)	$R_1 = 0.094$	$R_1 = 0.1073$	$R_1 = 0.0535$
	$wR_2 = 0.153$	$wR_2 = 0.2105$	$wR_2 = 0.1147$
Largest different peak and hole ($eÅ^{-3}$)	1.064 and -0.551	3.167 and -1.065	1.013 and -0.657

3.20.6 Structure determination of $Cp_2Mo_2(CO)_2(\mu\text{-}PS)(\mu\text{-}SC_6H_4Me)$ (18) and $Cp_3Mo_3(\mu\text{-}S)_2(\mu\text{-}S_2)(\mu_3\text{-}S)$ (20)

Diffraction-quality single crystals were obtained from the solution at ambient temperature. **18** was obtained as dark orange crystals from *n*-hexane/toluene after 2 days whereas **20** as deep greenish brown crystals in *n*-hexane/toluene after 1 week.

Diffractions measurements were carried out at -173 °C for both **18** and **20** on a Bruker SMART diffractometer equipped MoK\α radiation. The data were corrected for absorption effects with SADABS [130]. Structures solution and refinement were carried out with the Bruker-SHELXTL programs [129]. The structure of **18** refined to R = 0.090 for the 4304 reflections, that of **20** to R = 0.038 for 4776 reflections. The processing parameters are tabulated in Table 82 and selected bond lengths and bond angles are listed in Table 25-26.

Table 82. Data collection and processing parameters of $Cp_2Mo_2(CO)_2(\mu\text{-}PS)(\mu\text{-}SC_6H_4Me)$ (**18**) and $Cp_3Mo_3(\mu\text{-}S)_2(\mu\text{-}S_2)(\mu_3\text{-}S)$ (**20**)

Complex	$Cp_2Mo_2(CO)_2(\mu\text{-}PS)(\mu\text{-}SC_6H_4Me)$ (**18**)	$Cp_3Mo_3(\mu\text{-}S)_2(\mu\text{-}S_2)(\mu_3\text{-}S)$ (**20**)
Empirical formula	$C_{19}H_{17}Mo_2O_2PS_2$	$C_{18.50}H_{19}Mo_3S_5$
Formula weight	564.30	689.46
Temperature (K)	100(2) K	100(2) K
Wavelength (Å)	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	P-1	P21/c
Unit cell dimensions		
a (Å)	7.851(10)	10.4750(2)
b (Å)	10.534(14)	18.9056(3)
c (Å)	12.728(15)	11.2550(2)
α (°)	81.37(4) °	90 °
β (°)	75.83(3) °	110.8850(10) °
γ (°)	71.56(3) °	90 °
Volume ($Å^3$)	965(2) $Å^3$	2082.45(6) $Å^3$
Z	2	4
Density (Mg m^{-3})	1.942 Mg/m^3	2.199 Mg/m^3
Absorption coefficient (mm^{-1})	1.610 mm^{-1}	2.283 mm^{-1}
F(000)	556	1344
Crystal size (mm)	0.10 x 0.07 x 0.03 mm	0.15 x 0.05 x 0.03 mm
θ range for data collection	2.04 to 30.16 °	2.08 to 27.50 °
Limiting indices	$-10 \leq h \leq 10$	$-13 \leq h \leq 13$
	$-14 \leq k \leq 14$	$-24 \leq k \leq 24$
	$-17 \leq l \leq 16$	$-14 \leq l \leq 14$
Reflections collected/unique	9002 / 5036 [R(int) = 0.0994]	19407 / 4776 [R(int) = 0.0388]
Data/restraints/parameters	5036 / 0 / 236	4776 / 42 / 260
Goodness-of-fit on F^2	10.975	1.029
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0953	R1 = 0.0381
	wR2 = 0.2205	wR2 = 0.0932
R indices (all data)	R1 = 0.1976	R1 = 0.0515
	wR2 = 0.2775	wR2 = 0.1002
Largest different peak and hole ($eÅ^{-3}$)	3.932 and -3.182$eÅ^{-3}$	3.099 and -1.020 $eÅ^{-3}$

3.20.7 Structure determination of *trans*-$[CpCr(CO)_2(SePPh)]_2$ (22), $CpCr(CO)_2$-{SeP(H)Ph} (23) and $[CpCr(Se_2P(O)Ph)]_2$ (24)

Diffraction-quality single crystals of complex **23** was obtained as dark purple crystals from n-hexane/ THF at room temperature after 2-3 days. Complex **22** was obtained as dark brown crystals and **24** as dark brownish green crystals in THF at -28 °C after one week and two weeks, respectively. The crystals are mounted on quartz fibers. X-ray data were collected on a Bruker SMART diffractometer, equipped with a CCD area detector, using Mo Kα radiation (λ = 0.71073Å). The data were corrected for Lorentz and polarization effects with SMART suite of programs [129] and for absorption effects with the SHELXTL suite of programs [130]. The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. The Cp and alkyl hydrogens were placed in calculated positions. The molecular structures of **22**, **23** and **24** are shown in Figures 51-53 and their selected bond lengths and bond angles are shown in Table 33-35, respectively. Details of crystal parameters, data collection, structure refinement and bonding parameters are shown in Table 83.

Table 83. Data collection and processing parameters of trans-[CpCr(CO)$_2$(SePPh)]$_2$ (**22**), CpCr(CO)$_2$(SeP(H)Ph) (**23**) and Cp$_2$Cr$_2$(Se$_2$P(O)Ph)$_2$ (**24**)

Complexes	*trans*-[CpCr(CO)$_2$(SePPh)]$_2$ (**22**)	CpCr(CO)$_2${SeP(H)Ph} (**23**)	[CpCr(Se$_2$P(O)Ph)]$_2$ (**24**)
Empirical formula	$C_{26}H_{20}Cr_2O_4P_2Se_2$	$C_{13}H_{10}CrO_2PSe$	$C_{22}H_{20}Cr_2O_2P_2Se_4$
Formula weight	720.28	360.14	399.08
Temperature (K)	223(2)	243(2)	223 (2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2(1)/c	$P2_1/n$	$P2_1/n$
Unit cell dimensions			
a (Å)	7.9095(8)	6.3855(6)	9.6596(6)
b (Å)	18.688(2)	18.3404(17)	8.0501(5)
c (Å)	9.2154(10)	11.3791(11)	17.2372(11)
α (°)	90	90	90
β (°)	104.246(2)	95.489(2)	103.2300(10)
γ (°)	90	90	90
Volume (Å^3)	1320.3(2)	1326.5(2)	1304.80(14)
Z	2	4	4
Density (Mg m^{-3})	1.812	1.803	2.032
Absorption coefficient (mm^{-1})	3.733	3.715	6.553
F(000)	708	708	764
Crystal size (mm)	0.16 x 0.10 x 0.10	0.12 x 0.06 x 0.03	0.64 x 0.18 x 0.14
θ range for data collection	2.18 to 25.00	2.11 to 27.50	2.17 – 27.50
Limiting indices	$-9 \leq h \leq 9$,	-7<=h<=8	$-11 \leq h \leq 12$,
	$-22 \leq k \leq 21$,	-22<=k<=23,	$-10 \leq k \leq 9$,
	$-10 \leq l \leq 10$	-14<=l<=14	$-22 \leq l \leq 20$
Reflections collected/unique	7378/2329 [R(int) = 0.0452]	9213/3048 [R(int) = 0.0531]	9000/3002 [R(int) = 0.0316]
Data/restraints/parameters	2329 / 0 / 163	3048 / 0 / 163	3002 / 0 / 145
Goodness-of-fit on F^2	1.165	1.159	1.026
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0561$	$R_1 = 0.0592$	$R_1 = 0.0321$
	$wR_2 = 0.1268$	$wR_2= 0.1152$	$wR_2 = 0.0791$
R indices (all data)	$R_1 = 0.0720$	R1 = 0.0785	$R_1 = 0.0395$
	$wR_2 = 0.1317$	$wR_2 = 0.2105$	$wR_2 = 0.0820$
Largest different peak and hole (eÅ^{-3})	1.828 and -0.533	0.676 and -0.472	0.658 and -0.372

3.20.8 Structure determination of $[Cp_2Mo_2\{(\mu\text{-}Se)_2(PPh(Se))\}\{(\mu\text{-}Se)(PPh)_3\}]$ (25), $Cp_4Mo_4(CO)_3Se_4$ (26) and $Cp_3Mo_3(CO)_4[Se_3(PPh)_2]$ (27)

Diffraction-quality single crystals of complex **25** was obtained as dark reddish brown crystals from *n*-hexane/ toluene after 2-3 days. Complex **26** was obtained as dark greenish blue crystals from n-hexane/ toluene and **27** as dark pink crystals in THF at -28 °C, after one and two weeks, respectively. The crystals are mounted on quartz fibers. X-ray data for **25** and **27** were collected on a Bruker SMART diffractometer while **26** were collected on a Bruker APEX-II diffractometer, respectively. Both diffractometer equipped with a CCD area detector, using Mo Kα radiation (λ = 0.71073Å). The data were corrected for Lorentz and polarization effects with SMART suite of programs [129] and for absorption effects with the SHELXTL suite of programs [130]. The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. The Cp and alkyl hydrogens were placed in calculated positions. The molecular structures of **25**, **26** and **27** are shown in Figures 63-65 and their selected bond lengths and bond angles are tabulated in Table 40-42, respectively. Details of crystal parameters, data collection, structure refinement and bonding parameters are tabulated in Table 84.

Table 84. Data collection and processing parameters of [$Cp_2Mo_2\{(\mu\text{-}Se)_2(PPh(Se))\}\{(\mu\text{-}Se)(PPh)_3\}$] (**25**), $Cp_4Mo_4(CO)_3Se_4$ (**26**) and $Cp_3Mo_3(CO)_4[Se_3(PPh)_2]$ (**27**)

Complexes	[$Cp_2Mo_2\{(\mu\text{-}Se)_2(PPh(Se))\}$ $\{(\mu\text{-}Se)(PPh)_3\}$] (**25**)	$Cp_4Mo_4(CO)_3Se_4$ (**26**)	$Cp_3Mo_3(CO)_4[Se_3(PPh)_2]$ (**27**)
Empirical formula	$C_{37.50}$ H_{34} Mo_2 P_4 Se_4	$C_{30}H_{28}Mo_4O_3Se_4$	$C_{35}H_{33}Mo_3O_5P_2Se_3$
Formula weight	1116.25	1136.12	1120.25
Temperature (K)	223(2)	100(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	Monoclinic	monoclinic
Space group	C2/c	$P2_1/c$	$P2_1/n$
Unit cell dimensions			
a (Å)	17.888(5)	20.2570(4)	10.488(2)
b (Å)	12.803(4)	7.8829(2)	31.636(7)
c (Å)	33.299(9)	20.8045(4)	10.937(2)
α (°)	90	90	90
β (°)	94.584(5)	113.3110(10)	92.907(5)
γ (°)	90	90	90
Volume (Å^3)	1320.3(2)	3050.96(11)	3624.2(14)
Z	8	4	4
Density (Mg m^{-3})	1.951	2.473	2.053
Absorption coefficient (mm^{-1})	4.686	6.411	4.165
F(000)	4312	2144	2164
Crystal size (mm)	0.28 x 0.28 x 0.22	0.80 x 0.20 x 0.10	0.40 x 0.06 x 0.02
θ range for data collection	1.96 to 24.96	1.97 to 30.58	1.29 to 27.50
Limiting indices	$-21 \leq h \leq 21$	$-28\leq h \leq 28$	-13<=h<=6
	$-12 \leq k \leq 15$,	$-11\leq k \leq 8$	-40<=k<=41
	$-39 \leq l \leq 37$	$-29\leq l \leq 29$	-14<=l<=14
Reflections collected/unique	18045/6615 [R(int) = 0.1013]	32798/8879 [R(int) = 0.0272]	25645/8299 [R(int) = 0.0524]
Data/restraints/parameters	6615 / 98 / 439	8879 / 0 / 371	8299 / 6 / 433
Goodness-of-fit on F^2	1.068	1.136	1.043
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0842$	$R_1 = 0.0306$	$R_1 = 0.0490$
	$wR_2 = 0.1965$	$wR_2= 0.0704$	$wR_2= 0.1022$
R indices (all data)	$R_1 = 0.1725$	$R_1 = 0.0383$	$R_1 = 0.0727$
	$wR_2 = 0.2275$	$wR_2 = 0.0727$	$wR_2 = 0.1101$
Largest different peak and hole (eÅ^{-3})	1.102 and -1.599	1.450 and -0.611	1.962 and -0.554

3.20.9 Structure determination of $Cp_2Mo_2(CO)_5\{P(C_6H_4SMe\text{-}p)_3\}$ (29), $Cp_2Mo_2(CO)(\mu\text{-}CO)_2\{P(C_6H_4SMe\text{-}p)_3\}$ (30) and $Cp_4Mo_4(CO)_4(\mu_3\text{-}O)(\mu_2\text{-}O)_2(O)$ (31)

Diffraction-quality single crystals of complex **29** was obtained as dark pink crystals from toluene/ether mixture after 2 weeks at -28ºC whereas complex **30** as dark brownish pink crystals in CH_2Cl_2/ether mixture after 1 day and **31** as dark brown crystals from a THF solution after 1 day at ambient temperature, respectively.

Diffractions measurements were carried out at 23 °C for **29** and -173 °C for **30** and **31** on a Bruker APEX-II diffractometer equipped with a CCD area detector, using MoK\α radiation. The data were corrected for absorption effects with SADABS [130]. Structures solution and refinement were carried out with the Bruker-SHELXTL programs [129]. The structure of **29** refined to $R = 0.0575$ for the 5274 reflections, that of **30** to $R = 0.038$ for 4776 reflections and that of **31** to $R = 0.024$ for 5412 reflections. The molecular structures of **29**, **30** and **31** are shown in Figures 72-74. The data collection and processing parameters are shown in Table 85 and selected bond lengths and bond angles are listed in Table 46 - 48.

Table 85. Data collection and processing parameters of $Cp_2Mo_2(CO)_5\{P(C_6H_4SMe\text{-}p)_3\}$ (**29**), $Cp_2Mo_2(CO)(\mu\text{-}CO)_2\text{-}\{P(C_6H_4SMe\text{-}p)_3\}$ (**30**) and $Cp_4Mo_4(CO)_4(\mu_3\text{-}O)(\mu_2\text{-}O)_2(O)$ (**31**)

Complex	$Cp_2Mo_2(CO)_5\{P(C_6H_4SMe\text{-}p)_3\}$ (**29**)	$Cp_2Mo_2(CO)(\mu\text{-}CO)_2\text{-}\{P(C_6H_4SMe\text{-}p)_3\}$ (**30**)	$Cp_4Mo_4(CO)_4(\mu_3\text{-}O)(\mu_2\text{-}O)_2(O)$ (**31**)
Empirical formula	$C_{36}H_{31}Mo_2O_5PS_3$	$C_{18.50}\ H_{19}\ Mo_3\ S_5$	$C_{24}\ H_{20}\ Mo_4\ O_8$
Formula weight	862.64	689.46	820.16
Temperature (K)	296(2) K	100(2) K	100(2) K
Wavelength (Å)	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P21/c	P21/c
Unit cell dimensions			
a (Å)	8.201(2)	10.4750(2)	10.1093(2)
b (Å)	11.544(3)	18.9056(3)	12.4488(2)
c (Å)	18.221(5)	11.2550(2)	18.8895(3)
α (°)	83.791(4) °	90 °	90°
β (°)	80.911(3) °	110.8850(10) °	90.9460(10)°
γ (°)	88.705(3) °	90 °	90°
Volume ($Å^3$)	1693.8(8) $Å^3$	2082.45(6) $Å^3$	2376.89(7) $Å^3$
Z	2	4	4
Density (Mg m^{-3})	1.692 Mg/m^3	2.199 Mg/m^3	2.292 Mg/m^3
Absorption coefficient (mm^{-1})	1.016 mm^{-1}	2.283 mm^{-1}	2.112 mm^{-1}
F(000)	868	1344	1584
Crystal size (mm)	0.01 x 0.02 x 0.20 mm	0.15 x 0.05 x 0.03 mm	0.20 x 0.06 x 0.04 mm
θ range for data collection	1.14 to 25.00 °	2.08 to 27.50 °	1.96 to 27.50 °
Limiting indices	-5 ≤ h≤ 9	-13 ≤ h ≤ 13	-12 ≤ h ≤ 12
	-13 ≤ k ≤ 13	-24 ≤ k ≤ 24	-16 ≤ k ≤16
	-20 ≤ l ≤ 21	-14 ≤ l ≤ 14	-24 ≤ l ≤ 24
Reflections collected/unique	6791 / 5274 [R(int) = 0.1100]	19407 / 4776 [R(int) = 0.0388]	16436 / 5412 [R(int) = 0.0290]
Data/restraints/parameters	5274 / 0 / 427	4776 / 42 / 260	5412 / 0 / 325
Goodness-of-fit on F^2	0.900	1.029	1.036
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0575	R1 = 0.0381	R1 = 0.0237
	wR2 = 0.1374	wR2 = 0.0932	wR2 = 0.0548
R indices (all data)	R1 = 0.1079	R1 = 0.0515	R1 = 0.0297
	wR2 = 0.1262	wR2 = 0.1002	wR2 = 0.0572
Largest different peak and hole ($eÅ^{-3}$)	0.991 and -1.113$eÅ^{-3}$	3.099 and -1.020 $eÅ^{-3}$	0.868 and -0.547 $eÅ^{-3}$

3.20.10 Structure determination of $CpCr(CO)_2\{o\text{-}(C_6H_4S)PPh_2\}$ (32)

Diffraction-quality single crystals were obtained from the solution at ambient temperature. **32** was obtained as dark brown crystals from *n*-hexane-toluene/ether mixture after 2 days at -28ºC.

Diffractions measurements were carried out at 23 °C for **32** on a Bruker APEX-II diffractometer equipped with a CCD area detector, using MoK\α radiation. The data were corrected for absorption effects with SADABS [130]. Structures solution and refinement were carried out with the Bruker-SHELXTL programs [129]. The structure of **32** refined to R = 0.069 for the 4288 reflections. The molecular structure of **32** is shown in Figures 77. The data collection and processing parameters are tabulated in Table 86 and selected bond lengths and bond angles are listed in Table 50.

Table 86. Data collection and processing parameters of CpCr(CO)$_2${*o*-(C$_6$H$_4$S)PPh$_2$} (**32**)

Complex	CpCr(CO)$_2${*o*-(C$_6$H$_4$S)PPh$_2$} (**32**)
Empirical formula	$C_{25}H_{19}CrO_2PS$
Formula weight	466.43
Temperature (K)	103(2) K
Wavelength (Å)	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	
a (Å)	8.009(3)
b (Å)	15.182(5)
c (Å)	17.263(6)
α (°)	90
β (°)	93.069(7)
γ (°)	90
Volume (Å^3)	2095.9(12)
Z	4
Density (Mg m^{-3})	1.478
Absorption coefficient (mm^{-1})	0.742
F(000)	960
Crystal size (mm)	0.45 x 0.12 x 0.09
θ range for data collection	1.79 to 30.72
Limiting indices	-11<=h<=6
	-21<=k<=18
	-23<=l<=19
Reflections collected/unique	5956 / 4288 [R(int) = 0.1052]
Data/restraints/parameters	4288 / 0 / 271
Goodness-of-fit on F^2	0.856
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0694
	wR2 = 0.1589
R indices (all data)	R1 = 0.1793
	wR2 = 0.2173
Largest different peak and hole (eÅ^{-3})	0.606 and -0.746 eÅ^{-3}

3.20.11 Structure determination of [$Cp_2Cr_2(CO)\{(\mu\text{-}C_6H_4S)_2PPh\}$] (33) and $CpCr\{(\mu\text{-}C_6H_4S)_2PPh\}$ (34)

Diffraction-quality single crystals were obtained from the solution at -28 °C. **33** was obtained as dark pink crystals from THF/ether mixture after 2 weeks whereas **34** as dark pink crystals in ether/*n*-hexane mixture after 2 weeks.

Diffractions measurements were carried out at -50 °C for **33** and **34** on a Bruker SMART diffractometer equipped with a CCD area detector, using MoK\α radiation. The data were corrected for absorption effects with SADABS [130]. Structures solution and refinement were carried out with the Bruker-SHELXTL programs [129]. The structure of **33** refined to R = 0.0575 for the 5772 reflections, that of **34** to R = 0.0581 for 4669 reflections. The molecular structures of **33** and **34** are shown in Figures 81-82. The data collection and processing parameters are tabulated in Table 87 and selected bond lengths and bond angles are listed in Table 52-53.

Table 87. Data collection and processing parameters of [$Cp_2Cr_2(CO)\{(\mu-C_6H_4S)_2PPh\}$] (**33**) and $CpCr\{(\mu-C_6H_4S)_2PPh\}$ (**34**)

Complex	[$Cp_2Cr_2(CO)\{(\mu-C_6H_4S)_2PPh\}$] (**33**)	$CpCr\{(\mu-C_6H_4S)_2PPh\}$ (**34**)
Empirical formula	$C_{29}H_{23}Cr_2OPS_2$	$C_{23}H_{18}CrPS_2$
Formula weight	586.56	441.46
Temperature (K)	223(2) K	223(2) K
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/*n*	P2(1)/*c*
Unit cell dimensions		
a (Å)	10.4500(6)	11.7541(6)
b (Å)	16.5143(9)	9.2420(5)
c (Å)	14.8300(8)	18.9209(11)
α (°)	90	90
β (°)	100.574(2)	98.227(2)
γ (°)	90	90
Volume ($Å^3$)	2515.8(2)	2034.25(19)
Z	4	4
Density ($Mg\ m^{-3}$)	1.549	1.441
Absorption coefficient (mm^{-1})	1.115	0.851
F(000)	1200	908
Crystal size (mm)	0.22 x 0.10 x 0.09	0.30 x 0.14 x 0.10
θ range for data collection	1.86 to 27.50°.	1.75 to 27.50°
Limiting indices	-13<=h<=10	-12<=h<=15
	-20<=k<=21	-12<=k<=8
	-19<=l<=19	-24<=l<=24
Reflections collected/unique	17463/5772 [R(int) = 0.0750]	13860/4669 [R(int) = 0.0540]
Data/restraints/parameters	5772 / 0 / 316	4669 / 0 / 244
Goodness-of-fit on F^2	1.060	1.046
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0575	R1 = 0.0581
	wR2 = 0.1165	wR2 = 0.1217
R indices (all data)	R1 = 0.0842	R1 = 0.0912
	wR2 = 0.1265	wR2 = 0.1346
Largest different peak and hole ($eÅ^{-3}$)	0.532 and -0.359 $e.Å^{-3}$	0.476 and -0.313 $e.Å^{-3}$

3.20.12 Structure determination of [$Cp_2Cr_2(CO)\{(\mu\text{-}C_6H_4S)_2(C_6H_4SMe\text{-}o)P\}$] (35)

Diffraction-quality single crystal of **35** was obtained as reddish pink crystals from the solution of toluene/ether mixture after 5 days at ambient temperature.

Diffractions measurements were carried out at -50 °C for **35** on a Bruker SMART diffractometer equipped with a CCD area detector, using MoK\α radiation. The data were corrected for absorption effects with SADABS [130]. Structures solution and refinement were carried out with the Bruker-SHELXTL programs [129]. The structure of **35** refined to R = 0.0489 for the 6256 reflections. The molecular structure of **35** is shown in Figures 86. The data collection and processing parameters are tabulated in Table 88 and selected bond lengths and bond angles are listed in Table 55.

Table 88. Data collection and processing parameters of $[Cp_2Cr_2(CO)\{(\mu\text{-}C_6H_4S)_2\text{-}(C_6H_4SMe\text{-}o)P\}]$ (**35**)

Complex	$[Cp_2Cr_2(CO)\{(\mu\text{-}C_6H_4S)_2(C_6H_4SMe\text{-}o)P\}]$ (**35**)
Empirical formula	$C_{30}H_{25}Cr_2OPS_3$
Formula weight	632.65
Temperature (K)	223(2) K
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/*c*
Unit cell dimensions	
a (Å)	14.6497(7)
b (Å)	10.3342(5)
c (Å)	17.9881(9)
α (°)	90
β (°)	91.140(1)
γ (°)	90
Volume ($Å^3$)	2722.7(2)
Z	4
Density ($Mg\ m^{-3}$)	1.543
Absorption coefficient (mm^{-1})	1.111
F(000)	1296
Crystal size (mm)	0.40 x 0.12 x 0.10
θ range for data collection	2.26 to 27.50°
Limiting indices	-19<=h<=16
	-13<=k<=10
	-23<=l<=23
Reflections collected/unique	18870 / 6256 [R(int) = 0.0562]
Data/restraints/parameters	6256 / 0 / 335
Goodness-of-fit on F^2	1.050
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0489
	wR2 = 0.1115
R indices (all data)	R1 = 0.0682
	wR2 = 0.1209
Largest different peak and hole ($eÅ^{-3}$)	0.768 and -0.307 $eÅ^{-3}$

3.20.13 Structure determination of CpMo(CO)$_2${*o*-(C$_6$H$_4$S)PPh$_2$} (36)

Diffraction-quality single crystal of **36** was obtained as reddish orange crystals from the solution of CH_2Cl_2/ether mixture after 5 days at ambient temperature. Diffractions measurements were carried out at -103 °C for **36** on a Bruker APEX-II diffractometer equipped with a CCD area detector, using MoK\α radiation. The data were corrected for absorption effects with SADABS [130]. Structures solution and refinement were carried out with the Bruker-SHELXTL programs [129]. The structure of **36** refined to $R = 0.0261$ for the 5874 reflections. The molecular structure of **36** is shown in Figures 89. The data collection and processing parameters are tabulated in Table 89 and selected bond lengths and bond angles are listed in Table 57.

Table 89. Data collection and processing parameters of CpMo(CO)$_2${*o*-(C$_6$H$_4$S)PPh$_2$} (**36**)

Complex	CpMo(CO)$_2${*o*-(C$_6$H$_4$S)PPh$_2$} (**36**)
Empirical formula	$C_{25}H_{19}MoO_2PS$
Formula weight	510.37
Temperature (K)	170(2) K
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/*c*
Unit cell dimensions	
a (Å)	8.1665(16)
b (Å)	15.117(3)
c (Å)	17.320(4)
α (°)	90
β (°)	92.37(3)
γ (°)	90
Volume (Å^3)	2136.4(7)
Z	4
Density (Mg m^{-3})	1.587
Absorption coefficient (mm^{-1})	0.806
F(000)	1032
Crystal size (mm)	0.51 x 0.45 x 0.33
θ range for data collection	1.79 to 30.48°
Limiting indices	-7<=h<=11
	-20<=k<=20
	-24<=l<=24
Reflections collected/unique	13971 / 5874 [R(int) = 0.0377]
Data/restraints/parameters	5874 / 0 / 271
Goodness-of-fit on F^2	0.672
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0261
	wR2 = 0.0645
R indices (all data)	R1 = 0.0296
	wR2 = 0.0677
Largest different peak and hole (eÅ^{-3})	0.970 and -0.497 eÅ^{-3}

3.20.14 Structure determination of [$Cp_2Mo_2(CO)\{(\mu-C_6H_4S)_2PPh\}$] (38) and $CpMo(CO)\{(\mu-C_6H_4S)(\mu-C_6H_4SMe)PPh\}$ (39)

Diffraction-quality single crystals were obtained from the solution at ambient temperature. **38** was obtained as dark pink crystals from toluene/ether mixture after 2 weeks at -28 ºC whereas **39** as dark pink crystals in ether/THF mixture after 1 day.

Diffractions measurements were carried out at -50 °C for **38** and 23 ºC on a Bruker SMART diffractometer equipped with a CCD area detector, using MoK\α radiation. The data were corrected for absorption effects with SADABS [130]. Structures solution and refinement were carried out with the Bruker-SHELXTL programs [129]. The structure of **38** refined to $R = 0.0406$ for the 5973 reflections while structure of **39** refined to $R = 0.0481$ for the 7689 reflections. The molecular structures of **38** and **39** are shown in Figures 93-94. The data collection and processing parameters are tabulated in Table 90 and selected bond lengths and bond angles are listed in Table 60-61.

Table 90. Data collection and processing parameters of [$Cp_2Mo_2(CO)\{(\mu\text{-}C_6H_4S)_2PPh\}$] (**38**) and $CpMo(CO)\{(\mu\text{-}C_6H_4S)(\mu\text{-}C_6H_4SMe)PPh\}$ (**39**)

Complex	[$Cp_2Mo_2(CO)\{(\mu\text{-}C_6H_4S)_2PPh\}$] (**38**)	$CpMo(CO)\{(\mu\text{-}C_6H_4S)(\mu\text{-}C_6H_4S\ )PPh\}$ (**39**)
Empirical formula	$C_{29}H_{23}Mo_2OPS_2$	$C_{25}H_{21}MoOPS_2$
Formula weight	674.44	528.45
Temperature (K)	223(2) K	295(2) K
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/*n*	C*c*
Unit cell dimensions		
a (Å)	10.4853(5)	9.0175(4)
b (Å)	16.8079(9)	18.7879(8)
c (Å)	14.9897(8)	26.8274(12)
α (°)	90	90
β (°)	99.547(2)	94.2620(10)
γ (°)	90	90
Volume (Å^3)	2605.1(2)	4532.5(3)
Z	4	8
Density (Mg m^{-3})	1.720	1.549
Absorption coefficient (mm^{-1})	1.206	0.848
F(000)	1344	2144
Crystal size (mm)	0.34 x 0.12 x 0.06	0.44 x 0.12 x 0.10
θ range for data collection	1.83 to 27.50°	1.52 to 27.50°
Limiting indices	-6<=h<=13	-11<=h<=11
	-21<=k<=21	-20<=k<=24
	-19<=l<=19	-34<=l<=31
Reflections collected/unique	17526 / 5973 [R(int) = 0.0461]	15814/7689 [R(int) = 0.0419]
Data/restraints/parameters	5973 / 0 / 316	7689 / 2 / 543
Goodness-of-fit on F^2	1.013	1.015
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0406	R1 = 0.0481
	wR2 = 0.0826	wR2 = 0.0862
R indices (all data)	R1 = 0.0555	R1 = 0.0611
	wR2 = 0.0877	wR2 = 0.0912
Largest different peak and hole (eÅ^{-3})	0.671 and -0.373 eÅ^{-3}	0.698 and -0.342 e.Å^{-3}

3.20.15 Structure determination of [$Cp_2Mo_2(CO)\{(\mu-C_6H_4S)_2(C_6H_4SCH_2)P\}$] (40), [$Cp_2Mo_2(CO)\{(\mu-C_6H_4S)_2(C_6H_4SMe$-*o*)P}] (41), $Mo(CO)_3\{P(C_6H_4SMe$-*o*$)_3\}$ (42) and $CpMo_2(CO)_3(\mu-S)\{(\mu-C_6H_4S)(C_6H_4SMe$-*o*)P} (43)

Diffraction-quality single crystals were obtained from the solution at ambient temperature. **40** was obtained as dark brown crystals from *n*-hexane/toluene mixture after 1 weeks whereas **41** as dark brown crystals in CH_2Cl_2/*n*-hexane mixture after 2 day at ambient temperature. Both **42** and **43** were recrystallized from THF after couple of days as bright yellow crystals and reddish orange crystals, respectively.

Diffractions measurements were carried out at 22 ºC on a Bruker SMART diffractometer equipped with a CCD area detector, using MoK\α radiation for **40**, **42** and **43**. However, diffraction measurements for **41** was carried out at -50 °C. All data were corrected for absorption effects with SADABS [130]. Structures solution and refinement were carried out with the Bruker-SHELXTL programs [129]. The structure of **40** refined to $R = 0.0505$ for the 10432 reflections while structure of **41** refined to $R = 0.030$ for the 7338 reflections. For **42**, the structure was refined to 0.0549 for the 6411 reflections and for **43**, the structure was refined to 0.0453 for the 6956 reflections. The molecular structures of **40**, **41**, **42** and **43** are shown in Figures 103-106. The data collection and processing parameters are shown in Table 91-92 and selected bond lengths and bond angles are listed in Table 64-67.

Table 91. Data collection and processing parameters of [$Cp_2Mo_2(CO)\{(\mu\text{-}C_6H_4S)_2(C_6H_4SCH_2)P\}$] (**40**) and [$Cp_2Mo_2(CO)\{(\mu\text{-}C_6H_4S)_2(C_6H_4SMe\text{-}o)P\}$] (**41**)

Complex	[$Cp_2Mo_2(CO)\{(\mu\text{-}C_6H_4S)_2(C_6H_4SCH_2)P\}$] (**40**)	[$Cp_2Mo_2(CO)\{(\mu\text{-}C_6H_4S)_2(C_6H_4SMe\text{-}o)P\}$] (**41**)
Empirical formula	$C_{31.75}H_{27}Mo_2OPS_3$	$C_{34}H_{33}Mo_2O_2PS_3$
Formula weight	743.56	792.63
Temperature (K)	295(2) K	223(2) K
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2(1)/c
Unit cell dimensions		
a (Å)	10.2968(4)	10.6386(4)
b (Å)	14.3104(6)	10.3647(4)
c (Å)	20.8641(8)	29.3071(12)
α (°)	104.2600(10)	90
β (°)	94.6340(10)	99.1100(10)
γ (°)	90.9120(10)	90
Volume ($Å^3$)	2967.8(2)	3190.8(2)
Z	4	4
Density (Mg m^{-3})	1.664	1.650
Absorption coefficient (mm^{-1})	1.135	1.063
F(000)	1490	1600
Crystal size (mm)	0.34 x 0.26 x 0.04	0.40 x 0.22 x 0.10
θ range for data collection	1.47 to 25.00°	1.41 to 27.50°
Limiting indices	-12<=h<=12	-13<=h<=13
	-17<=k<=17	-13<=k<=13
	-24<=l<=24	-38<=l<=38
Reflections collected/unique	29062/10432 [R(int) = 0.0479]	40405/7338 [R(int) = 0.0318]
Data/restraints/parameters	10432 / 36 / 718	7338 / 0 / 380
Goodness-of-fit on F^2	1.054	1.106
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0505	R1 = 0.0300
	wR2 = 0.1156	wR2 = 0.0721
R indices (all data)	R1 = 0.0721	R1 = 0.0336
	wR2 = 0.1254	wR2 = 0.0774
Largest different peak and hole ($eÅ^{-3}$)	1.048 and -0.654 e.$Å^{-3}$	0.653 and -0.425 e.$Å^{-3}$

Table 92. Data collection and processing parameters of $Mo(CO)_3\{C_6H_4SMe\text{-}o\}$ (**42**) and $CpMo_2(CO)_3(\mu\text{-}S)\{(\mu\text{-}C_6H_4S)(C_6H_4SMe\text{-}o)P\}$(**43**)

Complex	$Mo(CO)_3\{P(C_6H_4SMe\text{-}o)_3\}$ (**42**)	$CpMo_2(CO)_3(\mu\text{-}S)\{(\mu\text{-}C_6H_4SMe\text{-}o)(C_6H_4SMe\text{-}o)P\}$(**43**)
Empirical formula	$C_{27.50}H_{25}MoO_3PS_3$	$C_{30.50}H_{24}Mo_2O_3PS_4$
Formula weight	626.57	789.0
Temperature (K)	295(2) K	295(2) K
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P-1
Unit cell dimensions		
a (Å)	34.932(4)	9.6494(5)
b (Å)	8.5938(8)	10.6228(5)
c (Å)	19.892(2)	16.0366(8)
α (°)	90	85.4830(10)
β (°)	110.738(2)	86.5930(10)
γ (°)	90	67.0640(10)
Volume (Å^3)	5584.8(10)	1508.41(13)
Z	8	2
Density (Mg m^{-3})	1.490	1.738
Absorption coefficient (mm^{-1})	0.779	1.193
F(000)	2552	788
Crystal size (mm)	0.60 x 0.26 x 0.16	0.28 x 0.20 x 0.14
θ range for data collection	1.25 to 27.49°	2.09 to 27.70°
Limiting indices	-45<=h<=45	-12<=h<=12
	-10<=k<=11	-13<=k<=13
	-25<=l<=25	-20<=l<=20
Reflections collected/unique	18711/6411 [R(int) = 0.0436]	19198/6956 [R(int) = 0.0562]
Data/restraints/parameters	6411 / 38 / 325	6956 / 49 / 386
Goodness-of-fit on F^2	1.075	0.945
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0549	R1 = 0.0453
	wR2 = 0.1277	wR2 = 0.0909
R indices (all data)	R1 = 0.0760	R1 = 0.0766
	wR2 = 0.1361	wR2 = 0.1109
Largest different peak and hole (eÅ^{-3})	0.863 and -0.793 e.Å^{-3}	0.807 and -0.616 e.Å^{-3}

3.20.16 Structure determination of $[Cp_2Cr_2(SBz)]S_2[Fe(CO)_3]$ (44)

Diffraction-quality single crystal of **44** was obtained as dark purplish brown crystals from the solution of *n*-hexane/toluene mixture after 3 days at -28 °C. Diffractions measurements were carried out at -120 °C for **44** on a Bruker FRAMBO diffractometer equipped with a multiwire proportional detector, using MoK\α radiation. Structure solution and refinement were carried out with the Bruker-SHELXTL programs [129]. The structure of **44** refined to $R = 0.0874$ for the 4966 reflections. The molecular structure of **44** is shown in Figures 109. The data collection and processing parameters are tabulated in Table 93 and selected bond lengths and bond angles are listed in Table 70.

Table 93. Data collection and processing parameters of $[Cp_2Cr_2(SBz)]S_2[Fe(CO)_3]$ (**44**)

Complex	$[Cp_2Cr_2(SBz)]S_2[Fe(CO)_3]$ (**44**)
Empirical formula	$C_{20}H_{17}Cr_2FeO_3S_3$
Formula weight	561.37
Temperature (K)	426(2) K
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	
a (Å)	9.4877(12)
b (Å)	22.869(3)
c (Å)	10.0080(12)
α (°)	90
β (°)	90.949(3)
γ (°)	90
Volume (Å^3)	2171.2(5)
Z	4
Density (Mg m^{-3})	1.717
Absorption coefficient (mm^{-1})	1.950
F(000)	1132
Crystal size (mm)	0.14 x 0.10 x 0.05
θ range for data collection	2.15 to 27.50°
Limiting indices	-12<=h<=12
	-16<=k<=29
	-13<=l<=12
Reflections collected/unique	14913 / 4966 [R(int) = 0.1183]
Data/restraints/parameters	4966 / 0 / 262
Goodness-of-fit on F^2	1.033
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0874
	wR2 = 0.1480
R indices (all data)	R1 = 0.1577
	wR2 = 0.1732
Largest different peak and hole (eÅ^{-3})	0.768 and -0.549 eÅ^{-3}

3.20.17 Structure determination of $[CpMo]_2S_4[Fe(CO)_3]_2$ (45), $[CpMo]_2S_3[Fe(CO)_3]_2$ (46) and $[CpMo(SBz)]_2S_2[Fe(CO)_2]$ (47)

Diffraction-quality single crystals were obtained from the solution at ambient temperature. **45** was obtained as dark green crystals from *n*-hexane/toluene mixture after 1 weeks whereas **46** as dark red crystals in *n*-hexane/toluene mixture after 1 weeks at ambient temperature. Both **42** and **43** were recrystallized from THF after couple of days as bright yellow crystals and reddish orange crystals, respectively.

Diffractions measurements were carried out at -50 ºC on a Bruker SMART diffractometer equipped with a CCD area detector, using MoK\α radiation for **45** and **46**. However, diffractions measurement for **47** was carried out at 22 °C. All data were corrected for absorption effects with SADABS [130]. Structures solution and refinement were carried out with the Bruker-SHELXTL programs [129]. The structure of **45** refined to R = 0.0385 for the 4931 reflections, structure of **46** refined to R = 0.0215 for the 966 reflections and for **47**, the structure was refined to 0.0467 for the 12525 reflections. The molecular structures of **45**, **46** and **47** are shown in Figures 110-112. The data collection and processing parameters are tabulated in Table 94 and selected bond lengths and bond angles are listed in Table 71-73.

Table 94. Data collection and processing parameters of $[CpMo]_2S_4[Fe(CO)_3]_2$ (**45**), $[CpMo]_2S_3[Fe(CO)_3]_2$ (**46**) and $[CpMo(SBz)]_2S_2[Fe(CO)_2]$ (**47**)

Complex	$[CpMo]_2S_4[Fe(CO)_3]_2$ (**45**)	$[CpMo]_2S_3[Fe(CO)_3]_2$ (**46**)	$[CpMo(SBz)]_2S_2[Fe(CO)_2]$ (**47**)
Empirical formula	$C_{16}H_{10}Fe_2Mo_2O_6S_4$	$C_{16}H_{10}Fe_2Mo_2O_6S_3$	$C_{26}H_{24}FeMo_2O_2S_4$
Formula weight	730.06	698.00	744.42
Temperature (K)	223(2) K	223(2) K	295(2) K
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	P21/c	Cmcm	P-1
Unit cell dimensions			
a (Å)	6.5710(6)	10.3716(4)	11.8762(4)
b (Å)	16.5832(14)	12.4622(5)	13.2903(5)
c (Å)	19.7312(18)	15.3270(7)	17.4358(6)
α (°)	90	90	99.682(1)
β (°)	92.396(2)	90	90.638(1)
γ (°)	90	90	90.579(1)
Volume (Å^3)	2148.2(3)	1981.06(14)	2712.5(2)
Z	4	4	4
Density (Mg m^{-3})	2.257	2.340	1.823
Absorption coefficient (mm^{-1})	2.885	3.021	1.769
F(000)	1416	1352	1480
Crystal size (mm)	0.43 x 0.08 x 0.04	0.26 x 0.20 x 0.06	0.70 x 0.20 x 0.16
θ range for data collection	2.07 to 27.49°	2.55 to 24.99°	1.18 to 27.62°
Limiting indices	-7<=h<=8	-12<= h<=12	-15<=h<=15
	-19<=k<=21	-14<=k<=14	-17<=k<=17
	-24<=l<=25	-18<=l<=18	-22<=l<=22
Reflections collected/unique	15221/4931 [R(int) = 0.0448]	10485 /966 [R(int) = 0.0329]	35372/12525 [R(int) = 0.0343]
Data/restraints/parameters	4931 / 0 / 271	966 / 0 / 77	12525 / 0 / 696
Goodness-of-fit on F^2	0.990	1.006	1.019
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0385	R1 = 0.0215	R1 = 0.0467
	wR2 = 0.0811	wR2 = 0.0576	wR2 = 0.1179
R indices (all data)	R1 = 0.0535	R1 = 0.0226	R1 = 0.0595
	wR2 = 0.0876	wR2 = 0.0589	wR2 = 0.1272
Largest different peak and hole (eÅ^{-3})	0.944 and -0.446 eÅ^{-3}	0.599 and -0.328 eÅ^{-3}	1.333 and -0.495eÅ^{-3}

3.20.18 Structure determination of [CpMo(CO)$_2$(μ-S)]$_2$ (19) and [CpCr(μ-SC$_6$H$_4$Me)]$_2$S (47)

Diffraction-quality single crystals were obtained from the solution at ambient temperature. **19** was obtained as reddish brown crystals from *n*-hexane/toluene mixture after 2 days at ambient temperature whereas **47** as dark purple crystals in *n*-hexane/toluene mixture after 1 week at -28 °C.

Diffractions measurements were carried out at -173 °C for **19** on a Bruker APEX-II diffractometer and -50 ºC on a Bruker SMART diffractometer. Both diffractometer equipped with a CCD area detector, using MoK\α radiation. The datas were corrected for absorption effects with SADABS [130]. Structures solution and refinement were carried out with the Bruker-SHELXTL programs [129]. The structure of **19** refined to R = 0.0245 for the 3634 reflections while structure of **47** refined to R = 0.0841 for the 3979 reflections. The molecular structures of **19** and **47** are shown in Figures 114-115. The data collection and processing parameters are tabulated in Table 95 and selected bond lengths and bond angles are listed in Table 74-75.

Table 95. Data collection and processing parameters of $[CpMo(CO)_2(\mu\text{-}S)]_2$ (**19**) and $[CpCr(\mu\text{-}SC_6H_4Me)]_2S$ (**47**)

Complex	$[CpMo(CO)_2(\mu\text{-}S)]_2$ (**19**)	$[CpCr(\mu\text{-}SC_6H_4Me)]_2S$ (**47**)
Empirical formula	$C_{14}H_{10}Mo_2O_4S_2$	$C_{24}H_{24}Cr_2S_3$
Formula weight	498.22	512.61
Temperature (K)	100(2) K	273(2) K
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	Pbca
Unit cell dimensions		
a (Å)	13.4736(2)	14.8704(14)
b (Å)	7.42600(10)	15.7755(14)
c (Å)	15.8841(2)	19.2517(17)
α (°)	90	90
β (°)	96.4990(10)	90
γ (°)	90	90
Volume (Å^3)	1579.07(4)	4516.2(7)
Z	4	8
Density (Mg m^{-3})	2.096	1.508
Absorption coefficient (mm^{-1})	1.865	1.248
F(000)	968	2112
Crystal size (mm)	0.44 x 0.15 x 0.03	0.30 x 0.10 x 0.02
θ range for data collection	2.10 to 27.49°	2.12 to 24.99°
Limiting indices	-17<=h<=14	-17<=h<=17
	-8<=k<=9	-14<=k<=18
	-20<=l<=20	-22<=l<=22
Reflections collected/unique	12827 / 3634 [R(int) = 0.0348]	24873 / 3979 [R(int) = 0.1069]
Data/restraints/parameters	3634 / 0 / 199	3979 / 0 / 264
Goodness-of-fit on F^2	1.049	1.061
Final R indices ($I > 2\sigma(I)$)	R1 = 0.0245	R1 = 0.0565
	wR2 = 0.0601	wR2 = 0.1117
R indices (all data)	R1 = 0.0298	R1 = 0.0841
	wR2 = 0.0645	wR2 = 0.1214
Largest different peak and hole (eÅ^{-3})	0.432 and -0.686 eÅ^{-3}	0.434 and -0.340 eÅ^{-3}

3.21 R.F. values of complexes

Table 96. R.F. values on silica gel 60F$_{254}$ plate

Complex	Color	R.f. Value
1. $[CpCr(CO)_3]_2$ (**1**)	Dirty green	0.71
2. $[CpCr(CO)_2]_2$ (**2**)	Deep green	0.72
3. $[CpMo(CO)_3]_2$ (**3**)	Magenta	0.72
4. $[CpMo(CO)_2]_2$ (**4**)	Reddish brown	0.67
5. $[CpCr(CO)_2]_2S$ (**5**)	Dirty brown	0.60
6. $[CpCr(CO)_2(SBz)]_2$ (**6**)	Reddish brown	0.72^b
7. $[CpCr(SBz)]_2S$ (**7**)	Purple	0.04/0.15^b
8. $[CpMo(CO)_2(SBz)]_2$ (**9**)	Dark brown	0.48
9. $[CpMo(SBz)(S)]_2$ (**10a**)	Pink	0.30
10. $[CpMo(SBz)(S)]_2$ (**10b**)	Brownish pink	0.20
11. $[CpMo(CO)(SBz)]_2S$ (**11**)	Pinkish brown	0.13
12. *trans-syn*$[CpMo(CO)(SBz)]_2$ (**12a**)	Yellowish brown	0.52
13. *trans-anti*$[CpMo(CO)(SBz)]_2$ (**12b**)	Yellowish green	0.42
14. $[CpMo(SBz)_2]_2$ (**13**)	Orange	0.52
15. $[CpMo(CO)_2(S_2P(SC_6H_4Me)_2)]$ (**14**)	Greenish brown	0.67
16. $Cp_2Mo_2(CO)_5(S_2P(SC_6H_4Me))$ (**15**)	Pinkish purple	0.58
17. $[Cp_2Mo_2(\mu\text{-}S)(\mu\text{-}S_2)(\mu\text{-}C_6H_4Me)]$ (**16**)	Purple	0.24
18. $[CpMo(CO)(C_6H_4SMe)]_2$ (**17**)	Yellowish brown	0.58
19. $Cp_2Mo_2(CO)_2(\mu\text{-}PS)(\mu\text{-}SC_6H_4Me)$ (**18**)	Orange brown	0.60
20. $[CpMo(CO)_2S]_2$ (**19**)	Yellowish brown	0.63
21. $Cp_3Mo_3(\mu\text{-}S)_2(\mu\text{-}S_2)(\mu_3\text{-}S)$ (**20**)	Brownish green	0.14
22. $Cp_2Cr_2(CO)_4Se$ (**21**)	Orange	0.64
23. *trans*-$[CpCr(CO)_2(SePPh)]_2$ (**22**)	Greyish brown	0.51
24. $CpCr(CO)_2(SeP(H)Ph)$ (**23**)	Purple	0.40
25. $[CpCr(Se_2P(O)Ph)]_2$ (**24**)	Brownish green	0.06
26.$[Cp_2Mo_2\{(\mu\text{-}Se)_2(PPh(Se))\{(\mu\text{-}Se)(PPh)_3\}]$ (**25**)	Brown	0.40
27. $Cp_4Mo_4(CO)_3Se_4$ (**26**)	Blue	0.35

28. $Cp_3Mo_3(CO)_4[Se_3(PPh)_2]$ (**27a**)	Pink	0.12
29. $Cp_3Mo_3(CO)_4[Se_3(PPh)_2]$ (**27b**)	Purplish pink	0.18
30. $[Cp_2Cr_2(CO)_5\{P(C_6H_4SMe\text{-}p)_3\}_2]$ (**28**)	Bright yellowish green	0.48
31. $Cp_2Mo_2(CO)_5\{P(C_6H_4SMe\text{-}p)_3\}$ (**29**)	Pink	0.43
32.$Cp_2Mo_2(CO)(\mu\text{-}CO)_2\{P(C_6H_4SMe\text{-}p)_3\}$(**30**)	Brownish pink	0.18
33. $CpCr(CO)_2(C_6H_4S)PPh_2$ (**32**)	Pink	0.30
34. $[Cp_2Cr_2(CO)\{(\mu\text{-}C_6H_4S)_2PPh\}]$ (**33**)	Pink	0.60
35. $CpCr\{(\mu\text{-}C_6H_4S)_2PPh\}$ (**34**)	Brown	0.18
36. $[Cp_2Cr_2(CO)\{(\mu\text{-}C_6H_4S)_2(C_6H_4SMe\text{-}o)P\}]$ (**35**)	Pink	0.51
37. $CpMo(CO)_2\{o\text{-}(C_6H_4S)PPh_2\}$ (**36**)	Orange yellow	0.42
38. $CpMo(CO)_3H$ (**37**)	Yellow	0.70
39. $[Cp_2Mo_2(CO)\{(\mu\text{-}C_6H_4S)_2PPh\}]$ (**38**)	Brown	0.42
40.$CpMo(CO)\{(\mu\text{-}C_6H_4S)(\mu\text{-}SMePh)PPh\}$ (**39**)	Orange	0.22
41.$[Cp_2Mo_2(CO)\{(\mu\text{-}C_6H_4S)_2(C_6H_4SCH_2)P\}]$ (**40**)	Brown	0.48
42. $[Cp_2Mo_2(CO)\{(\mu\text{-}C_6H_4S)_2(C_6H_4SMe\text{-}o)P\}]$ (**41**)	Dark reddish brown	0.40
43. $Mo(CO)_3\{P(C_6H_4SMe\text{-}o)_3\}$ (**42**)	Yellow	0.13
44.$CpMo_2(CO)_3(\mu\text{-}S)\{(\mu\text{-}C_6H_4S)(C_6H_4SMe\text{-}o)P\}$(**43**)	Yellowish orange	0.07
45. $[Cp_2Cr_2(SBz)]S_2[Fe(CO)_3]$ (**44**)	Brownish purple	0.12
46. $[CpCr(SC_6H_4Me)]_2S$ (**48**)	Purple	0.04

Eluent for all complexes with *n*-hexane : toluene : ether (2 : 1 : ⅓), unless stated otherwise;
[b]- Eluent with *n*-hexane : toluene : ether (2 : 1 : 1).