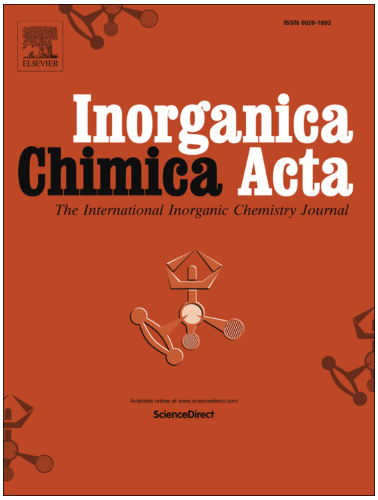

Research paper

Isolation and characterization of thiolato complexes of $[CpCr(SBz)]_2S$, isomeric trans $[CpMo(CO)(SBz)]_2$ and $[CpMo(SBz)_2]_2$ (Cp = (η^5-C_5H_5), Bz = $PhCH_2$-) from the reactivity of bibenzyl disulfide towards $[CpM(CO)_3]_2$ (M = Cr, Mo)

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Isolation and characterization of thiolato complexes of [CpCr(SBz)]$_2$S, isomeric trans [CpMo(CO)(SBz)]$_2$ and [CpMo(SBz)$_2$]$_2$ (Cp = (η^5-C$_5$H$_5$), Bz = PhCH$_2$-) from the reactivity of bibenzyl disulfide towards [CpM(CO)$_3$]$_2$ (M = Cr, Mo)

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Abstract

The reactions of [CpM(CO)$_3$]$_2$ (M = Cr (**1**), Mo (**3**)) with Bz$_2$S$_2$ have been investigated. **1** underwent a facile reaction at ambient temperature which led to the isolation of [CpCr(CO)$_2$]S (**5**), [CpCr(CO)$_2$(SBz)]$_2$ (**6**) and [CpCr(SBz)]$_2$S (**7**) in 28.8, 42.6 and 11.8% yield, respectively. A similar reaction at 110 °C with its congener, [CpCr(CO)$_2$]$_2$ (Cr≡Cr) (**2**) yielded only thermolytic products of **5** (40.3%) and Cp$_4$Cr$_4$S$_4$ (**8**) (10.6%). With the Mo analogue **3**, only the decarbonylated [CpMo(CO)$_2$]$_2$ (Mo≡Mo) (**4**) reacts at 70 °C to give an isomeric pair of trans *syn* and *anti* [CpMo(CO)(SBz)]$_2$ (**9a** & **9b**), [CpMo(SBz)(S)]$_2$ (**10**) and [CpMo(CO)(SBz)]$_2$S (**11**) in 43.3, 34.1, 5.5 and 3.1% yield, respectively. A totally decarbonylated new complex of [CpMo(SBz)$_2$]$_2$ (**12**) was obtained in 33.2% yield from the co-thermolysis of Bz$_2$S$_2$ with **9a** at 110 °C. All products were fully characterized with NMR and IR spectroscopy and C, H analysis. The molecular structures of **7**, **9b** and **12** have been elucidated by single crystal X-ray diffraction. Plausible mechanistic pathways leading to the formation of **7**, **9** and **12** were discussed.

Keywords: Bibenzyl disulfide; trans *syn* and *anti* isomers; Thermolytic studies; Desulfurization; Monoclinic.

1. Introduction

Dinuclear transition-metal [CpM(CO)$_3$]$_2$ complexes comprising of bridging thiolate ligands are a well-established class of compounds. The chemistry of these transition-metal carbonyl complexes which include synthesis, reactivity, novel structures and electrochemistry remains an area of continuous interest [1a-g]**.** Potential applications offered by transition-metal thiolates are diverse such as desulfurization of petroleum feedstock, active catalysts in various C-C and C-heteroatom bond-forming reactions, to biological models for the sulfur-rich metal centre of the metalloenzymes involved in the nitrogen cycle [1b-c, 1f]. Previously our group had reported the reaction of $[CpM(CO)_3]_2$ [M=Cr, Mo] with Bz-S-S-S-Bz reaction [2a-b]. However, we noticed that the common $[CpM(CO)(SR)]_2$ and $[CpM(SR)_2]_2$ type products were not isolated in the above mentioned reactions. Comparatively, it is worthwhile to continue the investigation for the reactivity of these Cr and Mo dimers toward the analogous Bz-S-S-Bz ligand in order to fully comprehend the reactivity nature of these benzyl thiolate ligands.

2. Experimental Section

2.1 General procedures

All synthetic manipulations were carried out using standard Schlenk techniques under an inert atmosphere of argon or in a Vacuum Atmosphere Dribox. ^{1}H and ^{13}C NMR spectra were measured on a JEOL Lambda 400 MHz and JEOL ECA 400 MHz spectrometer, and their chemical shifts referenced to residual C_6H_6 in C_6D_6. IR spectra in Nujol mulls were measured in the range of 4000–400 cm^{-1} by means of a Perkin-Elmer 2000 FTIR instrument. C, H analyses were performed by the in-house microanalytical laboratory using a Perkin–Elmer 2400 Series II CHNS System, except for Cr which was determined as CrO_4^{2-} [3]. Solvents were distilled from sodium/ benzophenone prior to use. Silica gel (Merck Kieselgel 60, 230-400 mesh) and Celite (Fluka AG) was activated at 140 °C overnight before chromatographic use. Bibenzyl disulfide was purchased from Sigma. $[CpM(CO)_3]_2$ [M = Cr(**1**) or Mo(**3**)] was synthesized as described by Manning [4] from chromium hexacarbonyl (99% purity from Merck) for **1** and molybdenum hexacarbonyl for **3** (Fluka AG). $[CpM(CO)_2]_2$ [M = Cr (**2**) or Mo (**4**)] were synthesized from their respective hexacarbonyl dimer **1** and **2** by thermolysis at 110 °C and 120 °C, respectively for overnight in toluene.

*2.2 Reactivity studies of $[CpCr(CO)_3]_2$ (**1**) with an equimolar of Bz_2S_2*

(a) At room temperature

A deep green suspension of **1** (200 mg, 0.498 mmol) and Bz_2S_2 (122 mg, 0.498 mmol) in toluene (~20mL) was allowed to stir at room temperature for 13.5 h until color had changed to dirty brown. The resultant reaction mixture was filtered through a disc of Celite

(1 x 1.5 cm), absorbed onto silica gel (3-4 g) before loading onto a silica gel column (1.5 x 10 cm) prepared in *n*-hexane. Two products were isolated in the following fractions:

(i) A yellowish brown eluate in *n*-hexane/toluene (2:1, 35 mL) which when concentrated to dryness yielded fine deep green crystalline solids of $[CpCr(CO)_2]_2S$ (**5**) (54 mg, 0.143 mmol, 28.8% yield), identified by its ^{1}H NMR δ(Cp) 4.36 in benzene-d_6 [5] and TLC against an authentic sample [R_f = 0.60 with n-hexane:toluene:ether (2:1:⅓) as eluent].

(ii) A dark brown eluate in toluene (15 mL) which when concentrated to dryness yielded fine dark brown crystalline solids of $[CpCr(CO)_2(SBz)]_2$ (**6**) (104 mg, 0.212 mmol, 42.6% yield), identified by its ^{1}H NMR δ(Cp) 4.16 in benzene-d_6 [2a] and TLC against an authentic sample [R_f = 0.72 with n-hexane:toluene:ether (2:1:1) as eluent].

(iii) A purple eluate in ether (10 mL) which when concentrated to dryness yielded purple crystalline solids of $[CpCr(SBz)]_2S$ (**7**) (30 mg, 0.058 mmol, 11.8% yield). ^{1}H NMR (benzene-d_6): δ 13.89 (br, Cp, $\upsilon_{½}$ = 57 Hz), δ 7.42-6.88 (m, C_6H_5), δ 3.35 (s, CH_2). ^{13}C NMR (benzene-d_6): δ 66.25 (CH_2), δ 101.04 (Cp), δ 129.20, 128.88, 128.63, 128.39, 128.28, 128.14 (S-CH_2-C_6H_5). IR: υ at 1063 vw, 1015 vw, 840 w, 732 w 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 band remained uneluted on top of the column.

(b) At 110 ˚C

A similar reaction was repeated at 110 °C for 1 h. Two products were isolated using a silica gel column (1.5 x 12 cm) prepared in *n*-hexane.

(i) A yellowish brown fraction in *n*-hexane-toluene (6:1) (50 mL) which when concentrated to dryness yielded deep green crystalline solids of **5** (101 mg, 0.267 mmol, 53.7% yield).

(ii) A dark brown fraction in toluene (15 mL) which when concentrated to dryness yielded fine dark brown solids of $Cp_4Cr_4S_4$ (**8**) (46 mg, 0.076 mmol, 15.4% yield), identified by its ^{1}H NMR δ(Cp) 4.90 in benzene-d_6 [5] and TLC against an authentic sample (R_f= 0.52 with n-hexane:toluene:ether (3:2:2) as eluent).

(iii) A dark brown fraction in ether-THF (1:1) (30 mL) which when concentrated to dryness yielded a dark brown residue (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. ^{1}H NMR analysis of the mixture showed δ 4.94 (s, Cp) and δ 5.13 (s, Cp) in benzene-d_6, respectively.

*2.3 Reactivity studies of $[CpCr(CO)_2]_2$ (**2**) with equimolar Bz_2S_2 at 110 ˚C*

To a deep green suspension of **2** (150 mg, 0.433 mmol) in toluene (~10 mL) was added 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. Filtration on Celite removed a small amount of dark insoluble solids. The ensuing chromatographic work up as in reaction above, gave the following fractions:

(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). ^{1}H NMR analysis of the mixture showed δ 4.94 (s, Cp) and δ 5.13 (s, Cp) in benzene-d_6, respectively.

*2.4 Reaction of $[CpMo(CO)_2]_2$ (**4**) with Bz_2S_2*

(a) At 70 °C

To a reddish brown solution of $[CpMo(CO)_2]_2$ (**4**) (200 mg, 0.460 mmol) in toluene (~20 mL) was added an equimolar of Bz_2S_2 (114 mg, 0.460 mmol) was stirred at 70 °C for 7.5 h. The resultant dark brown reaction mixture was treated with similar procedure as in 2.2 (a) using a silica gel column (9 x 1.5 cm) prepared in *n*-hexane. Four fractions were eluted:

(i) A yellowish brown fraction in a 4:1 *n*-hexane/toluene mixture (20 mL) which upon concentrated to dryness gave fine dark brown crystalline solids of *trans-syn* $[CpMo(CO)(SBz)]_2$ (**9a**) (124 mg, 0.199 mmol, 43.3% yield). ^{1}H NMR (benzene-d_6): δ7.50-7.08 (m, C_6H_5); δ4.69, 5.05 (s, Cp), δ3.61, 3.64 (d, CH_2), 3.93, 3.96 (d, CH_2). ^{13}C NMR (benzene-d_6): δ52.36 (CH_2); δ91.18, 91.58 (Cp), δ127.31, 129.00, 129.79, 141.86 (S-CH_2-

C_6H_5); δ246.50, 250.85 (CO). I.R.: *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. Found : C, 49.3; H, 3.5%.

(ii) A yellowish green fraction in a 1:1 *n*-hexane/toluene mixture (40 mL) which upon concentration to dryness gave fine green crystalline solids of *trans-anti* [CpMo(CO)(SBz)]$_2$ (**9b**) (98 mg, 0.158 mmol, 34.1% yield). ^{1}H NMR (benzene-d_6): δ7.72-7.01 (m, C_6H_5); δ 4.87 (s, Cp); δ3.31, 3.34 (d, CH_2), 3.93, 3.90 (d, CH_2). ^{13}C NMR (benzene-d_6): δ55.04 (CH_2); δ 91.18 (Cp), δ127.26, 128.95, 129.71, 130.56 (S-CH_2-C_6H_5); δ249.41 (CO). I.R.: *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. Found : C, 49.6; H, 3.7%.

(iii) A brownish pink fraction in toluene (40mL) which upon concentration to dryness gave fine pink crystalline solids of [CpMo(SBz)S]$_2$ (**10**) (16 mg, 0.025 mmol, 5.5% yield) identified by its ^{1}H NMR δ5.84 (Cp) in benzene-d_6 [2b] and TLC against an authentic sample [R_f = 0.20 with n-hexane:toluene:ether (2:1:⅓) as eluent].

(iv) A reddish brown fraction in ether (8mL) which upon concentration to dryness gave reddish brown solids of [CpMo(CO)(SBz)]$_2$S (**11**) (9 mg, 0.014 mmol, 3.1% yield) identified by its ^{1}H NMR δ(Cp) 4.83 in benzene-d_6 [2b] and TLC against an authentic sample [R_f = 0.13 with n-hexane:toluene:ether (2:1:⅓) as eluent].

(b) At 110 °C

A similar reaction as in 2.3 (a) but repeated at 110 °C for 2 h. The resultant dark yellowish brown reaction mixture was treated in a similar manner using a silica gel column (1.5 x 7 cm) prepared in *n*-hexane. The following fractions were eluted:

(i) A dark yellowish brown fraction in 4:1 *n*-hexane/toluene mixture (20 mL) which upon concentration to dryness gave dark brown crystalline of *trans-syn* [CpMo(CO)(SBz)]$_2$ (**9a**) (125 mg, 0.200 mmol, 43.6%).

(ii) A yellowish green fraction in 1:1 *n*-hexane/toluene mixture (40 mL) which upon concentration to dryness give green crystalline solids of *trans-anti*[CpMo(CO)(SBz)]$_2$ (**9b**) (119 mg, 0.191 mmol, 41.4%).

(iii) A brownish pink fraction was eluted with toluene (40 mL) which upon concentration to dryness gave pink solids of [CpMo(SBz)S]$_2$ (**10**) (15 mg, 0.024 mmol, 5.2%).

(iv) A reddish brown fraction in ether (8mL) which upon concentration to dryness gave reddish brown solids of [CpMo(CO)(SBz)]$_2$S (**11**) (16 mg, 0.024 mmol, 5.3%).

2.5 *Co-thermolysis reaction of trans-syn[CpMo(CO)(SBz)]$_2$ (**9a**) with an equimolar of Bz$_2$S$_2$ at 110 °C for 2 h*

To a yellowish brown suspension of *trans-syn* [CpMo(CO)(SBz)]$_2$ (**9a**) (69 mg, 0.111 mmol) in toluene (~10 mL) was added in an equimolar of Bz$_2$S$_2$ (27 mg, 0.111 mmol). The reaction mixture was refluxed under stirring for 2 h. The resultant dark yellowish brown reaction mixture was filtered, concentrated (*ca*. 2 mL) and chromatographed on a silica gel column (1.5 x 8 cm) in *n*-hexane. Four fractions were isolated:

(i) A yellowish brown fraction eluted with 3:1 *n*-hexane/toluene mixture (8 mL) which upon concentrated to dryness gave an oily orange solids of [CpMo(SBz)$_2$]$_2$ (**12**) (30 mg, 0.037 mmol, 33.2% yield). ^{1}H NMR (benzene-d_6): δ 4.92 (s, C$_5$H$_5$), δ 3.42 (s, CH$_2$), δ 7.09-7.15, 7.18-7.24 (m, C$_6$H$_5$). ^{13}C NMR (benzene-d_6): δ 90.24 (C$_5$H$_5$), δ 52.36 (CH$_2$), δ 127.45, 127.88, 129.00, 129.71, 130.09, 130.33, 138.27 and 139.07 (S-CH$_2$-C$_6$H$_5$). I.R.: *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$_2$S$_4$: C, 55.7; H, 4.6. Found : C, 55.4; H, 4.7 %.

(ii) A yellowish brown fraction eluted with 1:1.5 *n*-hexane/toluene mixture (18 mL) which upon concentrated to dryness gave a yellowish brown residue (32 mg). Analysis by ^{1}H NMR confirmed a mixture of *trans-syn* and *trans-anti* isomers of [CpMo(CO)(SBz)]$_2$ (**9a** and **9b**) in approximately 33 and 15% recovery, respectively.

(iii) A brownish pink fraction 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).

2.6 *NMR Tube Reactions. The following reactions were studied in septum-capped 5 mm tubes under argon via ^{1}H NMR spectral analysis. Product yields were obtained by integration of Cp resonances in ^{1}H NMR spectrum of product mixture.*

2.6.1 *Reaction of [CpCr(CO)$_2$]$_2$ (**2**) with equimolar Bz$_2$S$_2$ at 60 ºC*

A deep green solution of [CpCr(CO)$_2$]$_2$ (**2**) (20.0 mg, 0.058 mmol) with Bz$_2$S$_2$ (14 mg, 0.058 mmol) in benzene-*d*$_6$ (~0.5 mL) using 5 mm NMR tube was cothermolyzed at 60 °C and its ^{1}H NMR spectrum recorded at intervals. The final spectrum showed the presence and approximate yields of [CpCr(CO)$_2$]$_2$S (**5**), [CpCr(SBz)]$_2$S (**7**), Cp$_4$Cr$_4$S$_4$ (**8**) in 28, 4 and 19%, respectively, together with unreacted **2** (9.7% recovery) after 6 h.

2.6.2 *Reaction of [CpCr(CO)$_2$]$_2$S (**5**) with equimolar Bz$_2$S$_2$ at 60 ºC*

A dirty brown solution of [CpCr(CO)$_2$]$_2$S (**5**) (20 mg, 0.053 mmol) with Bz$_2$S$_2$ (13 mg, 0.053 mmol) in benzene-*d*$_6$ (~0.5 mL) was cothermolyzed at 110 °C. The reaction was monitored by recording its ^{1}H NMR spectrum at hourly intervals. The final spectrum showed only the presence of Cp$_4$Cr$_4$S$_4$ (**8**) (7% yield) together with unreacted [CpCr(CO)$_2$]$_2$S (**5**) (67% recovery) after 5 h.

2.6.3 *Thermolysis of trans-anti [CpMo(CO)(SBz)]$_2$ (**9b**)*

A yellowish green solution of *trans-anti* [CpMo(CO)(SBz)]$_2$ (**9b**) (20.0 mg, 0.030 mmol) in benzene-*d*$_6$ (~0.5mL), was thermolyzed at 110 °C and was monitored by ^{1}H NMR hourly. After 8 h, *trans-syn* [CpMo(CO)(SBz)]$_2$ (**9a**) (37%), *trans-anti* [CpMo(CO)(SBz)]$_2$ (**9b**) (54%), [CpMo(SBz)S]$_2$ (**10**) (1%) and [CpMo(SBz)$_2$]$_2$ (**12**) (1%) were recorded in the ^{1}H NMR spectrum. The final spectrum recorded after 14 h shows the presence of **9a** (4%), **9b** (55% recovery), **10** (4%), [CpMo(CO)(SBz)]$_2$S (**11**) (1%) and [CpMo(SBz)$_2$]$_2$ (**12**) (1%).

2.7 *Crystals structure determination*

Diffraction quality single crystals of [CpCr(SBz)]$_2$S (**7**) was obtained as dark purple plate grown in THF layered with ether after one week at ambient temperature; trans *anti* [CpMo(CO)(SBz)]$_2$ (**9b**) was obtained as green polyhedral from a solution of toluene/*n*-hexane after three days at ambient temperature; [CpMo(SBz)$_2$]$_2$ (**12**) were obtained as bright yellowish orange solids with irregular shape from a solution of toluene/*n*-hexane after one week at ambient temperature. X-ray data for **7** was collected on a Bruker SMART diffractometer while **9b** and **12** 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 [6] and for absorption effects with the SHELXTL suite of programs [7].

Details of crystal parameters, data collection, and structures refinement are given in Table 1. Bonding parameters are given in Table 3-5 and table of observed and calculated structure factors, hydrogen and non hydrogen atomic coordinates and thermal parameters and anisotropic thermal parameters are available from the authors.

Table 1. Crystal data and structure refinement for **7**, **9b** and **12**.

Complexes	**7**	**9b**	**12**
Empirical formula	C24 H24 Cr2 S3	C26 H24 Mo2 O2 S2	C38 H38 Mo2 S4
Formula weight	512.61	624.45	814.80
Temperature(K)	223(2)	100(2)	123(2)
Wavelength(Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	C 2/c	P21/c	P-1
Unit cell dimensions			
a(Å)	10.0033(10)	10.7994(3)	8.67740(10)
b(Å)	12.2554 (12)	13.8427 (5)	9.59540 (10)
c(Å)	18.9255(18)	8.3960(3)	12.1821(2)
α(°)	90	90	106.6410(10)
β(°)	100.605(2)	110.621(2)	97.7990(10)
δ(°)	90	90	116.2150(10)
Volume(Å^3)	2280.5(4)	1174.73(7)	830.323(19)
Z	4	2	1
Density (Mg/m^3)	1.493	1.765	1.630
Absorption coefficient(mm^{-1})	1.236	1.267	1.034
F(000)	1056	624	414
Crystal size(mm)	0.38 x 0.18 x 0.04	0.08 x 0.07 x 0.06	0.35 x 0.25 x 0.03
Theta range for data collection	2.19 to 27.50°.	2.50 to 27.50°	1.83 to 27.49°
Index ranges	-12<=h<=12 -8<=k<=15 -24<=l<=24	-14<=h<=14 -17<=k<=17 -10<=l<=10	-11<=h<=11 -12<=k<=11 -10<=l<=15
Reflections collected	7600	14047	3769
Independent reflections	2613 [R(int) = 0.0512]	2691 [R(int) = 0.0904]	3769 [R(int) = 0.0000]
Max. and min. transmission	0.9522 and 0.6509	0.9278 and 0.9054	0.9696 and 0.7135
Data / restraints / parameters	2613 / 146 / 213	2691 / 0 / 146	3769 / 128 / 219
Goodness-of-fit on F^2	1.092	1.015	1.295
Final R indices [I>2sigma(I)]	R1 = 0.0697, wR2 = 0.1717	R1 = 0.0467, wR2 = 0.1074	R1 = 0.0294, wR2 = 0.0876
R indices (all data)	R1 = 0.1014, wR2 = 0.1890	R1 = 0.0744, wR2 = 0.1238	R1 = 0.0304, wR2 = 0.0881
Largest diff. peak and hole	0.879 and -0.845 e.Å^{-3}	1.001 and -1.202 e.A^{-3}	3.167 and -3.493 e.A^{-3}

3. Results and discussion

3.1 Isolation of [CpCr(SBz)]$_2$S (7)

[CpCr(CO)$_3$]$_2$ (**1**) reacted with equimolar Bz$_2$S$_2$ under rigorous stirring at ambient temperature for 13.5 h to give [CpCr(CO)$_2$]$_2$S (**5**), [CpCr(CO)$_2$(SBz)]$_2$ (**6**) and [CpCr(SBz)]$_2$S (**7**) in 28.8, 42.6 and 11.8 % yield, respectively. A similar reaction at 110 °C for 1 h, gave [CpCr(CO)$_2$]$_2$S (**5**) and the final thermolytic product Cp$_4$Cr$_4$S$_4$ (**8**) in 53.7 and 15.4% yield, respectively. With its triply-bonded cogener, [CpCr(CO)$_2$]$_2$ (**2**) reacted under similar condition gave [CpCr(CO)$_2$]$_2$S (**5**) and Cp$_4$Cr$_4$S$_4$ (**8**) in 40.3 and 10.6 % yield, respectively, together with an uncharacterizable dark brown residue.

3.2 Mechanistic pathways: Formation of [CpCr(SBz)]$_2$S (7)

The products isolated from the reaction of [CpCr(CO)$_n$]$_2$ (n = 2 or 3) with one equivalent of Bz$_2$S$_2$ are comparatively similar to our previous reactivity studies with Bz$_2$S$_3$ [2a]. It is noteworthy that the only significant difference is the variation in products amount. Conversely, both Bz$_2$S$_2$ and Bz$_2$S$_3$ ligands exhibited different reactivity towards the chromium dimer. Reaction of **1** with Bz$_2$S$_3$ was completed after 2 h at ambient temperature whereas the disulfide ligand requires 13.5 h under similar condition. Apparently, this observation agrees with the higher dissociation energy of the disulfide ligand (+69 kcal/mole) as compared to the trisulfide ligand (+46 kcal/mole) reported by Tobolsky *et al* [8] using Me-S$_n$-Me (n = 2, 3 or 4) as reference models (Table 2) and it explains why the bond scission between the -S-S- linkage is less facile than that of the -S-S-S- linkage [9a-b]. Similar hypothesis was also raised by Gee [10] where it was suggested that fragments containing more than one sulfur atom may be stabilized by resonance interaction of the free electron with the sulfur chain. Using this concept, the preferable fragmentation patterns could be as following Eq (1-4):-

$\mathrm{Me\text{-}S\text{-}S\text{-}Me \longrightarrow 2\ Me\text{-}S\cdot}$ .... Eqn. (1)

$\mathrm{Me\text{-}S\text{-}S\text{-}S\text{-}Me \longrightarrow Me\text{-}S\cdot + Me\text{-}S\text{-}S\cdot}$ .... Eqn. (2)

$\mathrm{Me\text{-}S\text{-}S\text{-}S\text{-}S\text{-}Me \longrightarrow 2\ Me\text{-}S\text{-}S\cdot}$ .... Eqn. (3)

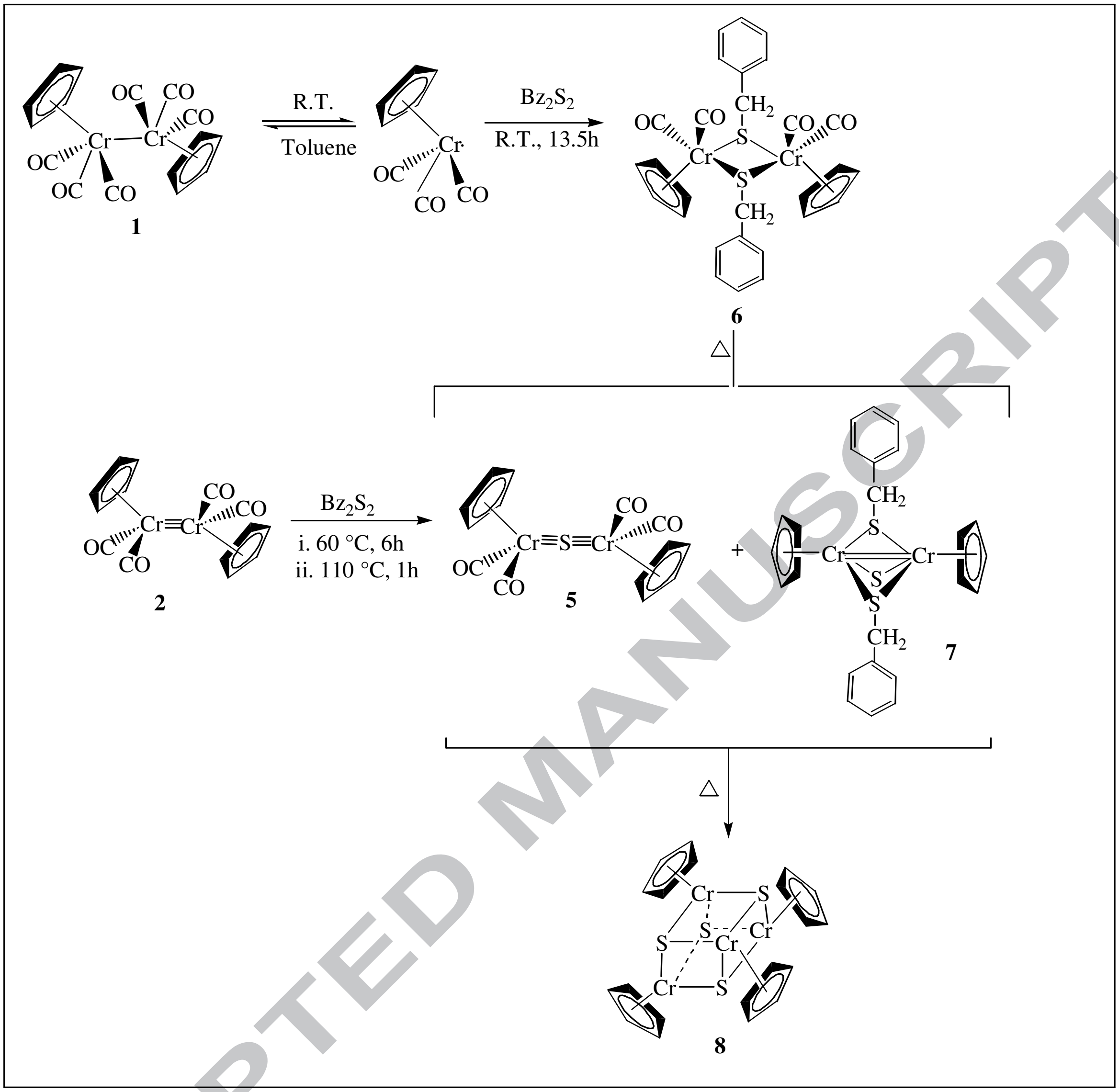
$\mathrm{Me\text{-}S\text{-}S\cdot \longleftrightarrow Me - S \overset{\cdots}{-} S}$ .... Eqn. (4)

If the $\mathrm{Me - S \overset{\cdots}{-} S}$ fragments are indeed more stable than the Me-S· fragments, then the predicted ease of cleavage of the polysulfide linkage is in the order of disulfide < trisulfide < tetrasulfide ~ S$_8$ ~ polymeric sulfur.

Table 2. Dissociation Energies of polysulfide [8]

Compound	Dissociation energy (kcal/mole)
Me-S-S-Me	69
Me-S-S-S-Me	46
Me-S-S-S-S-Me	37
S_8 (ring) $\rightleftharpoons$ $\cdot S\text{-}S_6\text{-}S\cdot$	33
$\cdot S\cdot_{x+y} \rightleftharpoons \cdot S\cdot_x + \cdot S\cdot_y$	33

The facile nature of this reaction supports the hypothesis that the reaction pathway proceeds *via* the 17-electrons $CpCr(CO)_3\cdot$ monomeric species generated from **1**. The propensity of **1** to dissociate into these free radicals species in solution is well-documented [11]. Apparently, S-S bond cleavage by $CpCr(CO)_3\cdot$ radicals resulted in the formation of a pair of Bz-S· fragments. Comparison with a similar reaction with Bz_2S_3 from previous study [2a], a substantially lower yield of **5** (29%) with Bz_2S_2 as compared to 57% with Bz_2S_3 is consistent to a lesser availability of free sulfur atoms. It is significant that **7** was not detected in the NMR reaction of **5** with Bz_2S_2, which validates that its formation follows an independent pathway via both decarbonylation and sulfurization processes as shown in Scheme 1. Further thermal degradation of **6** afforded $[CpCr(CO)_2]_2S$ (**5**), $[CpCr(SBz)]_2S$ (**7**) and ultimately the cubane $Cp_4Cr_4S_4$ (**8**) as the final thermolytic product.



Scheme 1. Proposed synthetic pathways for the reaction of $[CpCr(CO)_3]_2$ (**1**) with Bz_2S_2 at R.T and $[CpCr(CO)_2]_2$ (**2**) with Bz_2S_2 at (i) 60 °C and (ii) 110 °C, respectively.

*3.3 Isolation of isomeric [CpMo(CO)(SBz)]$_2$ (**9a,b**) and [CpMo(SBz)$_2$]$_2$ (**12**).*

A reddish brown solution of $[CpMo(CO)_2]_2$ (**4**) in toluene reacts with an equimolar of Bz_2S_2 at 70 °C for 7.5 h to give a dark yellowish brown product from which was isolated *trans-syn* $[CpMo(CO)(SBz)]_2$ (**9a**), *trans-anti* $[CpMo(CO)(SBz)]_2$ (**9b**), $[CpMo(SBz)S]_2$ (**10**) and $[CpMo(CO)(SBz)]_2S$ (**11**) in 43.3, 34.1, 5.5, and 3.1% yield, respectively. Similar reaction performed at 110 °C for 2 h, gave **9a**, *trans-anti* $[CpMo(CO)(SBz)]_2$ (**9b**),

$[CpMo(SBz)S]_2$ (**10**) and $[CpMo(CO)(SBz)]_2S$ (**11**) in 43.6, 41.4, 5.2 and 5.3% yield, respectively.

*3.4 Mechanistic pathways: Formation of isomeric $[CpMo(CO)(SBz)]_2$ (**9a** & **9b**) and $[CpMo(SBz)_2]_2$ (**12**)*

The E-E linkage in the REER (E = S, Se, Te; R = Me, Et, Ph) [12a-e] are easily cleaved by nucleophilic, electrophilic or radical processes (Eqn. (5)).

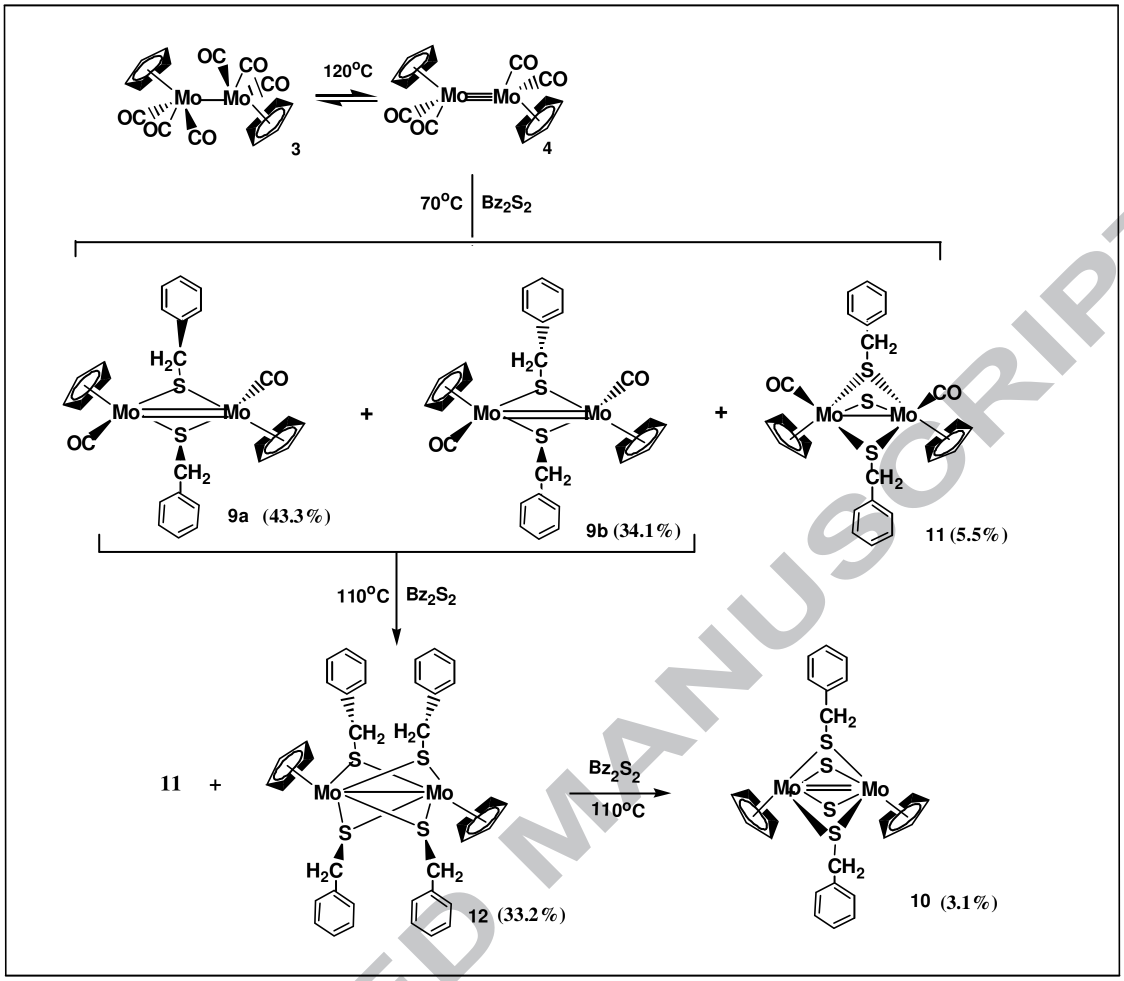
$$\text{R-E-E-R} \longrightarrow 2\ \text{R-E}\cdot \qquad \ldots\ \text{Eqn. (5)}$$

In the reaction of $[CpMo(CO)_2]_2$ (**4**) with Bz_2S_2, it is postulated that the BzS· moiety generated as in Eqn (5) underwent an electrophilic attack towards the M≡M bonds to form the thiolato-bridged isomers *trans-syn*/*trans-anti* $[CpMo(CO)(SBz)]_2$ (***9a*** *&* ***9b***). The *trans-syn* isomer converts to the more stable *trans-anti* isomer when it was slowly cooled to -28 °C for a couple of days. Both isomers showed markedly different physical properties. The *trans-syn* isomer is yellowish brown whereas the *trans-anti* isomer is yellowish green in color. This phenomenon was commonly shared by other similar *trans-syn*/*trans-anti* complexes of $[(RC_5H_4)M(CO)(\mu\text{-ER'})]_2$ [M = Mo or W; E = S, Se or Te; R = H, MeCO, MeO_2C, EtO_2C; R' = Me, Ph, Pr^i and Bu^t] [12f-g].

Thermolytic NMR tube reaction of **9b** in the presence of Bz_2S_2 has shown that the yields of $[CpMo(SBz)S]_2$ (**10**) and $[CpMo(CO)(SBz)]_2S$ (**11**) were higher as compared to the thermolysis of **9b** alone. This observation indicates the extra free sulfur moiety S· resulted from the desulfurization process of the Bz_2S_2 undergoes an electrophilic attack towards the Mo=Mo bond in **9b** to afford **11**. Consequently, decarbonylation and sulfurization of **11** in a concerted manner give **10**.

In a similar manner, formation of $[CpMo(SBz)_2]_2$ (**12**) from the co-thermolysis of **9a** or **9b** in the presence of Bz_2S_2 at 110 °C was initiated by decarbonylation coupled with oxidative insertion of a pair of benzylthiolate moieties across the doubly bonded Mo=Mo dimer.

The synthetic pathways for products **9a**, **9b**, **10**, **11** and **12** are shown in Scheme 2.



Scheme 2. Synthetic pathways of *trans-syn*/*trans-anti* $[CpMo(CO)(SBz)]_2$ (**9a** & **b**) $[CpMo(SBz)S]_2$ (**10**), $[CpMo(CO)(SBz)]_2S$ (**11**) and $[CpMo(SBz)_2]_2$ (**12**)

*3.5 Structural studies of **7**, **9b** and **12***

7 crystallized in monoclinic, space group C2/c. A perspective view of **7** is shown in Figure 1 and the bonding parameters are given in Table 3. The structure is very similar to the analogous $[CpCr(SPh)]_2S$ [13] and $Cp_2Cr_2(S)(SCMe_3)_2$ complexes [14] where the Cr atoms are in +3 oxidation state. The bond distance between Cr(1)-Cr(2) [2.692 (1) Å] is close to those in $[CpCr(SPh)]_2S$ [2.676 (1) Å] and $Cp_2Cr_2(S)(SCMe_3)_2$ [2.689 (8) Å] complexes but is much shorter than the singly bonded $[CpCr(CO)_3]_2$ [3.281 (1) Å] [15]. This indicates that the Cr-Cr bond in **7** is doubly-bonded with a 17 e^- configuration, which agrees with the proton paramagnetic chemical shift at δ 13.89 (br, Cp, $\nu_{½}$ = 57 Hz). Comparable to $[CpCr(SPh)]_2S$, each Cr atom in **7** is in an elongated tetrahedral coordination environment, with the Cp ligand occupying the apical position. The Cr-S (thiolato) bond distance of Cr1-S1 [2.346(2) Å] and Cr1-S1’ [2.327(2) Å] in **7** is longer than the Cr-S (sulfido) [2.240(3) Å] which is possibly due to the partial π-back donation at S(1) is enhanced by the aromatic ring of the benzyl moiety. The two Cp rings are approximately in an eclipsed configuration about the Cr(1)-Cr(2) bond.

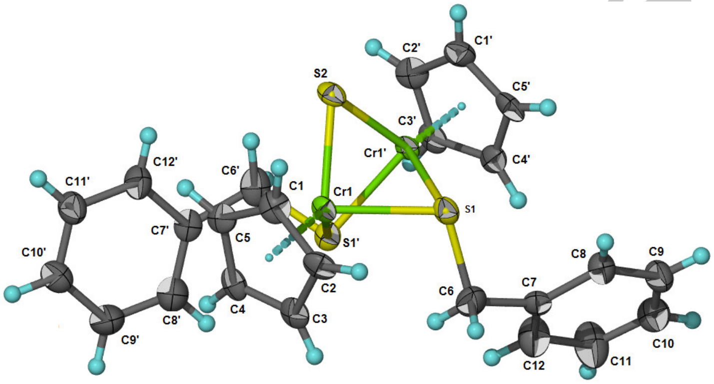


Figure 1. Molecular structure of **7**

Table 3. Selected bond lengths [Å] and angles [°] for **7**

Bond length			
Cr(1)-Cr(1’)	2.692(1)	Cr(1’)-S(1)	2.327(2)
Cr(1)-S(2)	2.240(3)	Cr(1’)-S(1’)	2.346(2)
Cr(1)-S(1)	2.346(2)	Cr(1’)-S(2)	2.257(2)
Cr(1)-S(1’)	2.327(2)	S(1)-C(6)	1.880(3)
Bond angles			
Cr(1’)-Cr(1)-S(1)	54.50(2)	Cr(1)-Cr(1’)-S(1)	55.17(2)
Cr(1’)-Cr(1)-S(2)	53.45(2)	Cr(1)-Cr(1’)-S(2)	53.17(1)
Cr(1’)-Cr(1)-S(1’)	55.21(1)	Cr(1)-Cr(1’)-S(1’)	55.70(2)
S(1)-Cr(1)-S(2)	107.66(1)	S(1)-Cr(1’)-S(2)	93.89(2)
S(1)-Cr(1)-S(1’)	89.84(3)	S(1)-Cr(1’)-S(1’)	90.66(2)
S(2)-Cr(1)-S(1’)	84.64(3)	S(2)-Cr(1’)-S(1’)	84.79(3)

Symmetry transformations used to generate equivalent atoms: 1’: -x+1,y,-z+1/2

9b crystallized in monoclinic, space group $P2_1/c$. The molecular structure of **9b** is shown in Figure 2 and its bond lengths and bond angles are tabulated in Table 4. **9b** consists of a *trans-anti* configuration whereby the two carbonyl moieties are in the *trans* positions while the two benzylthiolate moieties are in the *trans-anti* positions. Both the benzyl thiolate moieties bridge across the two CpMo(CO)- fragments and form a butterfly core complex. Consequently, **9b** comprises a similar framework with *trans-anti* $[(\eta^5\text{-}C_5H_4R)Mo(CO)(SPh)]_2$ (R = H or MeCO) [16]. The Mo-Mo bond distance 2.5917(8) Å indicates a double bond and is comparable to those in other dicarbonyl molybdenum complexes of *trans-anti* $[(\eta^5\text{-}MeCOC_5H_4)Mo(CO)(SPh)]_2$ (2.609(1) Å), *cis*$[CpMo(CO)(SBu^t)]_2$ (2.616(2) Å) [12e] and *trans-syn* [CpMo(CO)(*p*-PhCH$_3$)]$_2$ (2.6052(8) Å) and 2.5751(8) Å) [16]. The planar Mo_2S_2 ring of **9b** is also observed in other known analogues as mentioned above.

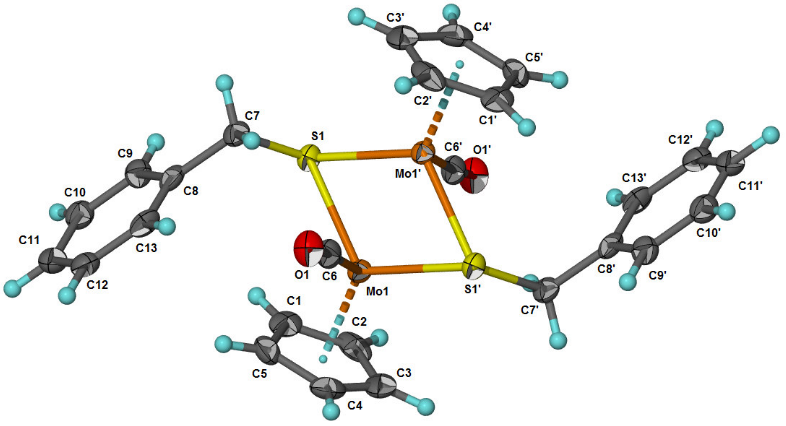


Figure 2. Molecular structure of **9b**

Table 4. Selected bond lengths [Å] and angles [°] for **9b**

Bond lengths

Mo(1)-C(6)	1.945(5)	Mo(1)-S(1’)	2.4106(12)
Mo(1)-C(4)	2.304(5)	Mo(1)-S(1)	2.4226(13)
Mo(1)-C(5)	2.321(5)	Mo(1)-Mo(1’)	2.5917(8)
Mo(1)-C(1)	2.336(5)	S(1)-C(7)	1.841(5)

Mo(1)-C(3)	2.344(5)	S(1)-Mo(1’)	2.4106(12)
Mo(1)-C(2)	2.365(5)	O(1)-C(6)	1.153(6)

Bond angles

C(6)-Mo(1)-S(1’)	80.99(15)	C(7)-S(1)-Mo(1’)	112.34(17)
C(6)-Mo(1)-S(1)	87.51(15)	C(7)-S(1)-Mo(1)	111.33(17)
S(1’)-Mo(1)-S(1)	115.14(3)	Mo(1’)-S(1)-Mo(1)	64.85(3)
C(6)-Mo(1)-Mo(1)#1	79.26(16)	O(1)-C(6)-Mo(1)	175.0(5)
S(1’)-Mo(1)-Mo(1’)	57.79(3)	C(8)-C(7)-S(1)	110.9(3)
S(1)-Mo(1)-Mo(1’)	57.35(3)		

Symmetry transformations used to generate equivalent atoms: 1’: -x+1,-y+1,-z+1

12 crystallized in triclinic, space group P-1. The molecular structure is illustrated in Figure 3 and its bond lengths and bond angles are tabulated in Table 5. **12** consists of four benzylthiolate moieties and two CpMo fragments. Each Mo atom is in a tetragonal-pyramidal coordination environment with both the cyclopentadienyl groups occupying the axial positions. The two Mo atoms are bridged by four benzylthiolate groups. The benzylthiolate moieties of ‘A’ and ‘C’ are in *trans-anti* arrangement to each other while the benzylthiolate moieties of ‘B’ and ‘D’ form another pair of *trans-anti* arrangement ligand in order to decrease the steric tension and stabilize the molecule. The Mo-Mo bond distance of 2.616 Å is comparable to other known Mo=Mo double bonded complexes [12e, 17].

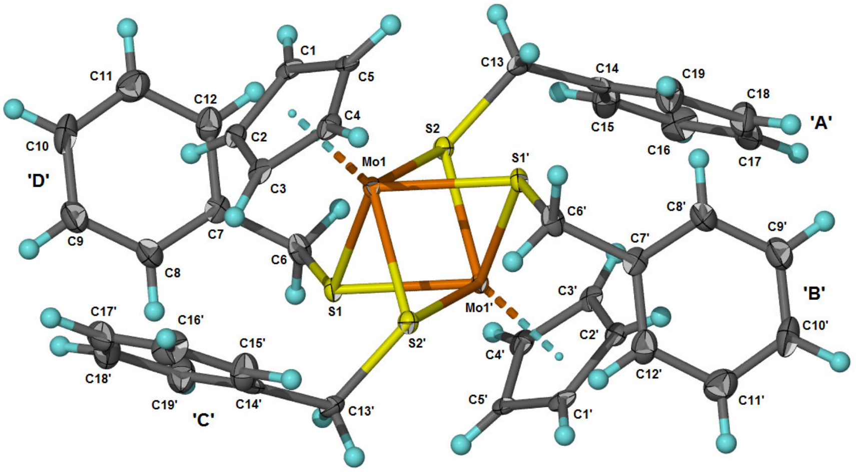


Figure 3. Molecular structure of **12**

Table 5. Selected bond lengths [Å] and angles [°] for **12**

Bond lengths

Mo(1)-S(1’)	2.446(8)	Mo(1’)-S(1’)	2.480(8)
Mo(1)-S(2’)	2.441(8)	Mo(1’)-S(2’)	2.501(8)
Mo(1)-S(1)	2.4514(13)	Mo(1’)-S(1)	2.451(11)
Mo(1)-S(2)	2.4577(13)	Mo(1’)-S(2)	2.458(11)
Mo(1)-Mo(1’)	2.616(13)	S(1’)-C(6’)	1.819(9)
S(1)-C(6)	1.841(5)	S(2')-C(13’)	1.803(9)
S(2)-C(13)	1.850(5)		

Bond angles

S(2')-Mo(1)-S(1’)	74.4(3)	C(6)-S(1’)-Mo(1)	117.6(4)
Mo(1)-S(1)-Mo(1’)	64.40(4)	C(6)-S(1’)-Mo(1’)	117.5(4)
Mo(1)-S(2)-Mo(1’)	64.08(4)	C(13)-S(2)-Mo(1’)	117.69(16)
Mo(1)-S(1’)-Mo(1’)	64.16(19)	C(13)-S(2)-Mo(1)	115.62(16)
Mo(1)-S(2’)-Mo(1’)	63.9(2)	C(13)-S(2’)-Mo(1)	119.2(4)
C(6)-(S1)-Mo(1’)	117.89(15)	C(13)-S(2’)-Mo(1’)	117.6(4)
C(6)-S(1)-Mo(1)	116.11(16)		

Symmetry transformations used to generate equivalent atoms: 1’ -x+1,-y+1,-z+1

4.0 Conclusions

Benzyl disulfide had shown less facile reactivity towards group 6 metal complexes as compared to its trisulfide congener. Indeed, the study shows the importance of the C-S bond strength in the formation of different framework of these metal thiolate complexes.

Acknowledgements

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Appendix A. Supplementary material

CCDC 867164, 867166 and 867167 contain the supplementary crystallographic data for **7**, **9b** and **12**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Highlights

- Bibenzyl disulfide showed different reactivity towards CpM(CO)$_3$ [M = Cr (**1**) or Mo (**3**)] as compare to bibenzyl trisulfide.
- Reaction of bibenzyl disulfide with Cp$_2$Cr$_2$(CO)$_6$ give a total decarbonylated metal sulfide complex.
- Reaction of bibenzyl disulfide with Cp$_2$Mo$_2$(CO)$_4$ give a pair of isomer complexes together with a tetra-μ$_2$-SBz Mo complex.
- All three molecular structures are structurally characterized.

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Graphical Abstract - graphical

Isolation and characterization of thiolato complexes of $[CpCr(SBz)]_2S$, isomeric trans $[CpMo(CO)(SBz)]_2$ and $[CpMo(SBz)_2]_2$ (Cp = (η^5-C_5H_5), Bz = $PhCH_2$-) from the reactivity of bibenzyl disulfide towards $[CpM(CO)_3]_2$ (M = Cr, Mo)

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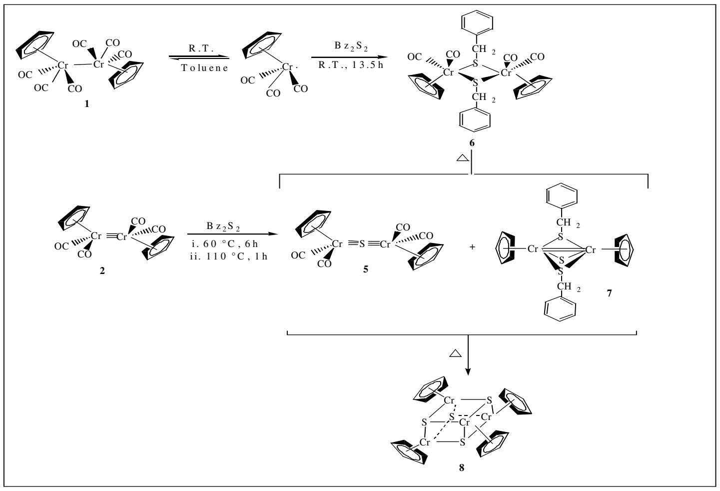
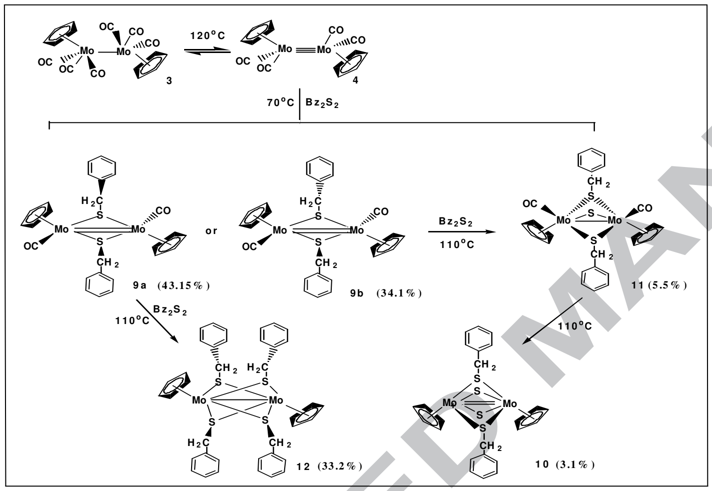
[c] *School of Pharmacy, University of Nottingham, Malaysia*

Reaction of $[CpM(CO)_n]_2$ [M=Cr (**1**), or Mo (**3**)] with an equivalent molar of Bz_2S_2 led to the isolation of two new isomers of trans *syn* and *anti* $[CpMo(CO)(SBz)]_2$ (**9a** & **9b**) together with six others known products. Cothermolysis of trans *syn* $[CpMo(CO)(SBz)]_2$ (**9a**) with an equivalent molar of Bz_2S_2 affords another new complex of $[CpMo(SBz)_2]_2$ (**12**).


R.T.
Toluene
Bz$_2$S$_2$
R.T., 13.5h
1
6
△
2
Bz$_2$S$_2$
i. 60 °C, 6h
ii. 110 °C, 1h
5
+
7
△
8


120°C
3
4
70°C
Bz$_2$S$_2$
or
Bz$_2$S$_2$
110°C
9a (43.15%)
9b (34.1%)
11 (5.5%)
Bz$_2$S$_2$
110°C
110°C
12 (33.2%)
10 (3.1%)

Graphical Abstract - synopsis

Isolation and characterization of thiolato complexes of $[CpCr(SBz)]_2S$, isomeric trans $[CpMo(CO)(SBz)]_2$ and $[CpMo(SBz)_2]_2$ (Cp = (η^5-C_5H_5), Bz = $PhCH_2$-) from the reactivity of bibenzyl disulfide towards $[CpM(CO)_3]_2$ (M = Cr, Mo)

Mei Lee Ooi[a,b], Chu Er Lim[a], Richard C. S. Wong[b*] and Seik Weng Ng[c]

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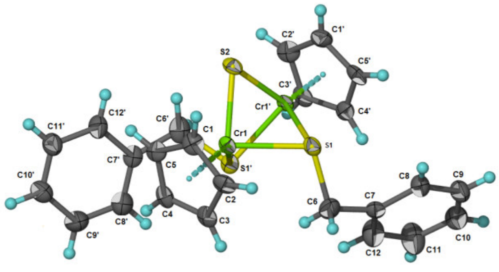
[b]*Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia*
[c]*Department of Chemistry, University of Nottingham, Malaysia*

Reaction of $[CpM(CO)_n]_2$ [M=Cr (**1**) or Mo (**3**)] with an equivalent molar of Bz_2S_2 led to the isolation of two new isomers of trans *syn* and *anti* $[CpMo(CO)(SBz)]_2$ (**9a** & **9b**) together with six others known products. Cothermolysis of trans *syn* $[CpMo(CO)(SBz)]_2$ (**9a**) with an equivalent molar of Bz_2S_2 affords another new complex of $[CpMo(SBz)_2]_2$ (**12**).



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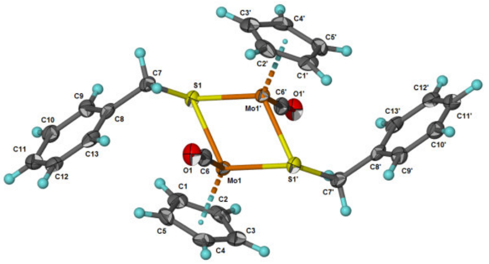
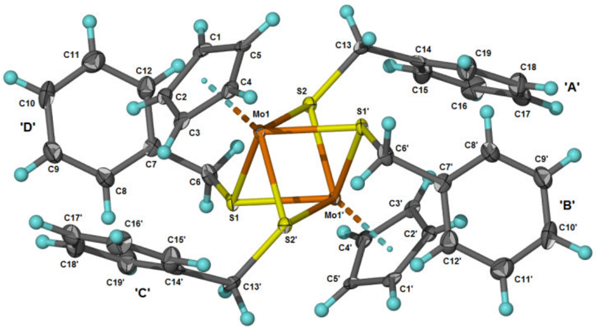


9b



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