ABSTRACT

The reactivity of $[CpM(CO)_3]_2$ (M=Cr(**1**), Mo(**3**)) together with their congener, $[CpM(CO)_2]_2$ (M=Cr(**2**), Mo(**4**)) towards aryl disulfide ligands have been studied. The organic ligands include: (i) dicyclohexyl disulfide (ii) thienyl disulfide. Reactions that involve **1** occurred under mild condition *via* the highly reactive radical $CpCr(CO)_3$•. However, the reaction conditions with **2** and **4** are at elevated temperature.

All the products have been characterized spectroscopically and structually *via* IR, ^1H, ^{13}C and ^{31}P NMR, LCMS, elemental analyses, single crystal x-ray diffraction and cyclic voltammetry. Works are summarized below.

(i) The reaction of **1** with dicyclohexyl disulfide at 60 ºC for 60 h has led to the isolation of primary product $[CpCr(CO)_2]_2S$ (**5**) followed by a total decarbonylation of $[CpCr(SC_6H_{11})]_2S$ (**6**). After prolonged thermolysis, **6** was fully converted to a cubane-like cluster $Cp_4Cr_4S_4$ (**7**). Reaction of **4** with Dicyclohexyl Disulfide at elevated temperature had led to the isolation of a pair of isomeric products *trans-syn* and *trans-anti* $[CpMo(CO)(SC_6H_{11})]_2$(**8**) , $[Cp_2Mo_2(CO)(O)(SC_6H_{11})_2]$ (**9**) and $[Cp_3Mo_3(CO)_4(\mu_3\text{-}O)(SC_6H_{11})]$ (**10**) as main products. Thermolytic studies followed by ^1H NMR indicated that **8** underwent stepwise decarbonylation and oxidation to afford **9** and **10**.

(ii) The facile reaction of $[CpCr(CO)_3]_2$ (**1**) with Thienyl Disulfide at ambient temperature had led to the isolation of $CpCr(CO)_3H$ (**11**) as the primary products and $[CpCr(CO)_2]_2S$ (**5**) respectively. The reaction involves the 17e radicals $CpCr(CO)_3$· from the facile thermal dissociation of the Cr-Cr bond. At elevated temperature, $[CpCr(CO)_2]_2S$ (**5**) and $[CpCr(S_2C_4H_3)]_2S$ (**12**) were isolated as produts. Thermal degradation had led to a total decarbonylation of $[CpCr(S_2C_4H_3)]_2S$ (**12**). Prolong thermolysis of **12** was completely converted to $Cp_4Cr_4S_4$, as final thermolytic product. The reaction of **4** with one equimolar of Thienyl Disulfide at ambient and elevated temperature had led to a pair of isomeric products, *trans-syn*

$[CpMo(CO)(C_4H_3S_2)]_2$ (**13a**) , *trans-anti* $[CpMo(CO)(C_4H_3S_2)]_2$ (**13b**) dan $[CpMo(O)(C_4H_3S_2)]_2O$ (**14**).

ABSTRAK

Kereaktifan dari $[CpM(CO)_3]_2$ (M=Cr(**1**), Mo(**3**)) bersama dengan kongener mereka $[CpM(CO)_2]_2$ (M=Cr(**2**), Mo(**4**)) telah diselidik terhadap aril sulfida seperti (i): dicyclohexyl dilsulfide (ii) thienyl disulfide. Tindak balas yang menglibatkan **1** terjadi pada suhu bilik melalui monomer radikal, $CpCr(CO)_3$• yang sangat reaktif. Tetapi, bagi tindak balas yang menglibatkan **2** dan **4** telah dilakukan pada suhu bilik yang lebih tinggi.

Semua produk telah dikenalpasti dengan menggunakan IR, ^{1}H, ^{13}C dan ^{31}P NMR, LCMS, analisa elemental, Kristal tunggal x-ray diraksi dan voltammetri berkitar. Hasil penyelikan telah dihuraikan seperti yang berikut :

(i) Tindak balas **1** dengan dicyclohexyl disulfide pada suhu 60 ºC selama 60 jam telah menghasilkan produk utama iaitu $[CpCr(CO)_2]_2$ S (**5**) diikuti dengan produk $[CpCr(SC_6H_{11})]_2S$ (**6**) yang kehilangan semua karbon dioksida. Selepas pemanasan **6** telah ditukar menjadi $Cp_4Cr_4S_4$ (**7**) sebagai hasil kehilangan karbon dioksida yang lengkap. Tindak balas yang menglibatkan **4** pada suhu yang lebih tinggi dengan dicyclohexyl disulfide telah memberi hasil isomerik *trans-syn* dan *trans-anti* $[CpMo(CO)(SC_6H_{11})]_2$ (**8**), $[Cp_2Mo_2(CO)(O)(SC_6H_{11})_2]$ (**9**) dan $[Cp_3Mo_3(CO)_4(\mu_3\text{-}O)(SC_6H_{11})]$ (**10**) sebagai hasil utama. Kajian thermolitic diikuti dengan ^{1}H NMR membuktikan **8** mengalami proses kehilangan karbon dioksida dan pengoksidaan untuk hasil **9** dan **10**.

(ii) Tindak balas yang mudah iaitu antara $[CpCr(CO)_3]_2$ (**1**) dengan Thienyl Disulfide pada suhu bilik telah menghasilkan $CpCr(CO)_3H$ (**11**) dan $[CpCr(CO)_2]_2S$ (**5**) sebagai hasil produk utama. Tindak balas ini menglibatkan radikal monomer $CpCr(CO)_3$· daripada terma belahan ikatan antara Cr-Cr. Pada suhu tinggi, produk $[CpCr(CO)_2]_2S$ (**5**) and $[CpCr(S_2C_4H_3)]_2S$ (**12**) telah dihasilkan. Proses degradasi telah memberi $[CpCr(S_2C_4H_3)]_2S$ (**12**) sebagai hasil kehilangan karbon dioksida yang lengkap.

Reaksi thermolitic yang sepenuhnya telah menukar **12** to $Cp_4Cr_4S_4$ sebagai produk thermolytic. Tindak balas antara **4** dengan setara molar Thienyl Disulfide pada suhu bilik dan suhu tinggi menghasilkan produk isomerik iaitu *trans-syn* $[CpMo(CO)(C_4H_3S_2)]_2$ (**13a**) , *trans-anti* $[CpMo(CO)(C_4H_3S_2)]_2$, dan $[CpMo(O)(C_4H_3S_2)]_2O$ (**14**).

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LIST OF ABBREVIATIONS

e^-	Electron
σ	Sigma
π	Pi
δ	PPM
Cp	Cyclopentadienyl
C_6D_6	Deuterated benzene-d_6
Eqn	Equation
ESI	Electrospray ionization
h	Hour
I.R.	Infrared spectroscopy
LCMS	Liquid chromatography mass spectrometry
THF	Tetrahydrofuran
TLC	Thin layer chromatography