

ABSTRACT

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

All the products have been characterized spectroscopically and structurally *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 $\mathbf{1}$ with dicyclohexyl disulfide at $60\text{ }^\circ\text{C}$ for 60 h has led to the isolation of primary product $[\text{CpCr}(\text{CO})_2]_2\text{S}$ ($\mathbf{5}$) followed by a total decarbonylation of $[\text{CpCr}(\text{SC}_6\text{H}_{11})]_2\text{S}$ ($\mathbf{6}$). After prolonged thermolysis, $\mathbf{6}$ was fully converted to a cubane-like cluster $\text{Cp}_4\text{Cr}_4\text{S}_4$ ($\mathbf{7}$). Reaction of $\mathbf{4}$ with Dicyclohexyl Disulfide at elevated temperature had led to the isolation of a pair of isomeric products *trans-syn* and *trans-anti* $[\text{CpMo}(\text{CO})(\text{SC}_6\text{H}_{11})]_2$ ($\mathbf{8}$), $[\text{Cp}_2\text{Mo}_2(\text{CO})(\text{O})(\text{SC}_6\text{H}_{11})_2]$ ($\mathbf{9}$) and $[\text{Cp}_3\text{Mo}_3(\text{CO})_4(\mu_3\text{-O})(\text{SC}_6\text{H}_{11})]$ ($\mathbf{10}$) as main products. Thermolytic studies followed by ^1H NMR indicated that $\mathbf{8}$ underwent stepwise decarbonylation and oxidation to afford $\mathbf{9}$ and $\mathbf{10}$.

(ii) The facile reaction of $[\text{CpCr}(\text{CO})_3]_2$ ($\mathbf{1}$) with Thienyl Disulfide at ambient temperature had led to the isolation of $\text{CpCr}(\text{CO})_3\text{H}$ ($\mathbf{11}$) as the primary products and $[\text{CpCr}(\text{CO})_2]_2\text{S}$ ($\mathbf{5}$) respectively. The reaction involves the 17e radicals $\text{CpCr}(\text{CO})_3\cdot$ from the facile thermal dissociation of the Cr-Cr bond. At elevated temperature, $[\text{CpCr}(\text{CO})_2]_2\text{S}$ ($\mathbf{5}$) and $[\text{CpCr}(\text{S}_2\text{C}_4\text{H}_3)]_2\text{S}$ ($\mathbf{12}$) were isolated as products. Thermal degradation had led to a total decarbonylation of $[\text{CpCr}(\text{S}_2\text{C}_4\text{H}_3)]_2\text{S}$ ($\mathbf{12}$). Prolong thermolysis of $\mathbf{12}$ was completely converted to $\text{Cp}_4\text{Cr}_4\text{S}_4$, as final thermolytic product. The reaction of $\mathbf{4}$ with one equimolar of Thienyl Disulfide at ambient and elevated temperature had led to a pair of isomeric products, *trans-syn*

$[\text{CpMo}(\text{CO})(\text{C}_4\text{H}_3\text{S}_2)]_2$ (**13a**) , *trans-anti* $[\text{CpMo}(\text{CO})(\text{C}_4\text{H}_3\text{S}_2)]_2$ (**13b**) dan $[\text{CpMo}(\text{O})(\text{C}_4\text{H}_3\text{S}_2)]_2\text{O}$ (**14**).

ABSTRAK

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

Semua produk telah dikenalpasti dengan menggunakan IR, ^1H , ^{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 $60\text{ }^\circ\text{C}$ selama 60 jam telah menghasilkan produk utama iaitu $[\text{CpCr}(\text{CO})_2]_2\text{S}$ (**5**) diikuti dengan produk $[\text{CpCr}(\text{SC}_6\text{H}_{11})]_2\text{S}$ (**6**) yang kehilangan semua karbon dioksida. Selepas pemanasan **6** telah ditukar menjadi $\text{Cp}_4\text{Cr}_4\text{S}_4$ (**7**) sebagai hasil kehilangan karbon dioksida yang lengkap. Tindak balas yang melibatkan **4** pada suhu yang lebih tinggi dengan dicyclohexyl disulfide telah memberi hasil isomerik *trans-syn* dan *trans-anti* $[\text{CpMo}(\text{CO})(\text{SC}_6\text{H}_{11})]_2$ (**8**), $[\text{Cp}_2\text{Mo}_2(\text{CO})(\text{O})(\text{SC}_6\text{H}_{11})_2]$ (**9**) dan $[\text{Cp}_3\text{Mo}_3(\text{CO})_4(\mu_3\text{-O})(\text{SC}_6\text{H}_{11})]$ (**10**) sebagai hasil utama. Kajian thermolitic diikuti dengan ^1H NMR membuktikan **8** mengalami proses kehilangan karbon dioksida dan pengoksidaan untuk hasil **9** dan **10**.

(ii) Tindak balas yang mudah iaitu antara $[\text{CpCr}(\text{CO})_3]_2$ (**1**) dengan Thienyl Disulfide pada suhu bilik telah menghasilkan $\text{CpCr}(\text{CO})_3\text{H}$ (**11**) dan $[\text{CpCr}(\text{CO})_2]_2\text{S}$ (**5**) sebagai hasil produk utama. Tindak balas ini melibatkan radikal monomer $\text{CpCr}(\text{CO})_3\cdot$ daripada terma belahan ikatan antara Cr-Cr. Pada suhu tinggi, produk $[\text{CpCr}(\text{CO})_2]_2\text{S}$ (**5**) and $[\text{CpCr}(\text{S}_2\text{C}_4\text{H}_3)]_2\text{S}$ (**12**) telah dihasilkan. Proses degradasi telah memberi $[\text{CpCr}(\text{S}_2\text{C}_4\text{H}_3)]_2\text{S}$ (**12**) sebagai hasil kehilangan karbon dioksida yang lengkap.

Reaksi thermolitic yang sepenuhnya telah menukar **12** to $\text{Cp}_4\text{Cr}_4\text{S}_4$ sebagai produk thermolytic. Tindak balas antara **4** dengan setara molar Thienyl Disulfide pada suhu bilik dan suhu tinggi menghasilkan produk isomerik iaitu *trans-syn* $[\text{CpMo}(\text{CO})(\text{C}_4\text{H}_3\text{S}_2)]_2$ (**13a**) , *trans-anti* $[\text{CpMo}(\text{CO})(\text{C}_4\text{H}_3\text{S}_2)]_2$, dan $[\text{CpMo}(\text{O})(\text{C}_4\text{H}_3\text{S}_2)]_2\text{O}$ (**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