Journal of Organometallic Chemistry, 296 (1985) 393–404
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ORGANOMETALLIC SULFUR COMPLEXES

II *. SYNTHESIS AND CHARACTERIZATION OF ORGANOMETALLIC SULFANE COMPLEXES ($(\mu$-$S_x)[M(\eta^5$-$C_5H_5)(CO)_3]_2$ (M = Mo ($x = 2, 3$); M = W ($x = 2$)) AND NEW ROUTES TO $[Cr(\eta^5$-$C_5H_5)(CO)_2]_2S$

MAHMOUD A. EL-HINNAWI ** and ARAB K. EL-QUASEER

Department of Chemistry, Yarmouk University, Irbid (Jordan)

(Received May 30th, 1985)

Summary

The binuclear, disulfur- and trisulfur-bridged organomolybdenum complexes, $(\mu$-$S_x)[Mo(\eta^5$-$C_5H_5)(CO)_3]_2$ ($x = 2$ and 3) were prepared by the reaction of $Na[Mo(\eta^5$-$C_5H_5)(CO)_3]$ with S_2Cl_2 at −97°C and by reaction of Li_2S_x ($x = 2$, 3, and 4) with $Mo(CO)_3(\eta^5$-$C_5H_5)Cl$ at room temperature. Similarly the binuclear, disulfur bridged organotungsten complex, $(\mu$-$S_2)[W(\eta^5$-$C_5H_5)(CO)_3]_2$ was prepared by the reaction of $Na[W(\eta^5$-$C_5H_5)(CO)_3]$ with S_2Cl_2 at −97°C. No reaction was observed between $W(\eta^5$-$C_5H_5)(CO)_3Cl$ and Li_2S_x ($x = 2$, 3 and 4) at room temperature or in boiling THF. The sulfur chromium complex, $[Cr(\eta^5$-$C_5H_5)(CO)_2]_2S$ was the major product of the reaction of $Na[Cr(\eta^5$-$C_5H_5)(CO)_3]$ with S_2Cl_2 and $SOCl_2$ at room temperature or −97°C. The reaction of $[Cr(\eta^5$-$C_5H_5)(CO)_2]_2S$ with I_2 in $CDCl_3$ in 1/1 molar ratio yielded, $Cr(\eta^5$-$C_5H_5)(CO)_3I$.

Introduction

Transition metal-sulfur complexes are of current interest owing in part to their potential as models for biological [2,3] and heterogeneous catalysts [4–6]. Additionally, in the area of metal-cluster chemistry, sulfur ligands have proved to be very versatile in the construction of transition metal cluster complexes including heteronuclear clusters of potential catalytic utility [7]. The coordination chemistry of polysulfide, S_x^{2-} ($x = 1, 2, 3, 4$...etc.) is of particular interest because of their large variety of modes of coordination [8,9]. A number of ionic disulfide bridging complexes have been reported, $[(NH_3)_5RuSSRu(NH_3)_5]^{4+}$ [10], $[(CN)_5CoS_2Co$-

---

[*] For part I see ref. 1.

[**] To whom correspondence should be addressed.

0022-328X/85/$03.30

$(CN)_5]^{6-}$ [11], and $[(H_2O)_5CrS_2Cr(H_2O)_5]^{4+}$ [12]. Simple neutral binuclear complexes of the type $L_nMS_xML_n$ (metallosulfanes) in which polysulfide, S_x^{2-} ($x = 1, 2, 3 \ldots$ etc.), serves as a bidentate bridging ligand are infrequent. Metallomonosulfanes ($x = 1$), are known for d^{10} and d^{8} metals [13]; an example is $(C_2H_5)_3PAuSAu$-$P(C_2H_5)_3$ [14]. Among derivatives of typical transition metals, the Co^I complex, $[(nP_3)CoSCo(nP_3)]$ (nP_3 = tri(2-diphenyl-phosphinoethyl)amine) was prepared by the reaction of sodium ethoxide with $[CoSH(nP_3)]BPh_4$ in THF [15]. The binuclear sulfur-bridged organotungsten complex, $(\mu\text{-}S)[W(\eta^5\text{-}C_5H_5)(CO)_3]_2$ was prepared from the reaction of $(\eta^5\text{-}C_5H_5)(CO)_3WH$ with bis(dimethylamino)sulfane, $S(NMe_2)_2$. The $(\mu\text{-}S)[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$ was prepared analogously and found to be less stable than the tungsten analogue, losing a sulfur atom to give the dimer $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$ [16]. The complex $(\mu\text{-}S)[Re(\eta^5\text{-}C_5H_5)(CO)_2]_2$ was prepared by the reaction of photolytically generated $Re(\eta^5\text{-}C_5H_5)(CO)_2$ with either elemental sulfur or COS. The complex contains a Re–Re bond in addition to bridging sulfur [17].

We previously prepared a series of binuclear, sulfur or polysulfur bridged organoiron complexes, $(\mu\text{-}S_x)[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ ($x = 1$–4) by substitution reaction involving either organoiron or sulfur nucleophiles or redox reactions; the structures of $(\mu\text{-}S_3)[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $\mu\text{-}S_4[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ were determined by X-ray diffraction [1]. Since no such neutral organometallic sulfane complexes are known for chromium, and only the monosulfanes, $(\mu\text{-}S)[M(\eta^5\text{-}C_5H_5)(CO)_3]_2$ for Mo and W, we decided to untertake systematic synthesis of organometallic sulfanes of chromium, molybdenum and tungsten.

Experimental

Material and methods

All reactions were conducted under nitrogen with Schlenk glassware [18]. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Petroleum ether was purified by vacuum transfer from CaH_2. Methylene chloride was vacuum transferred from P_4O_{10}. Deuterated NMR solvents, acetone-d_6 and chloroform-d_1, were dried over activated 4-A molecular sieves and vacuum distilled. The sulfur monochloride (S_2Cl_2) used contained a few drops of PCl_3 which had been added to the 500 ml bottle to inhibit decomposition, and was stored at 0–5°C. Thionyl chloride ($SOCl_2$) was used as purchased and stored in a refrigerator. Chromium hexacarbonyl, $Cr(CO)_6$, molybdenum hexacarbonyl, $Mo(CO)_6$, and tungsten hexacarbonyl, $W(CO)_6$ were purchased from Aldrich. Anhydrous THF solutions of lithium sulfides Li_2S, Li_2S_2, Li_2S_3, and Li_2S_4 were prepared by treating $Li(C_2H_5)_3BH$ with elemental sulfur as described by Gladysz [19]. For column chromatography, silica particle size 0.063–0.200 mm (70–230 mesh ASTM) EM reagent, was employed. For preparative thin-layer chromatography (PTLC), silica gel 60 layer thickness 0.5 mm, EM reagent was employed. For thin-layer chromatography (TLC), silica gel 60 F_{254}, 0.2 mm EM reagent was employed. Chromatographic separations involved elution of silica columns or preparative thin layer plates with a petroleum ether/diethyl ether mixture, diethyl ether alone, or a diethyl ether/THF mixture. Infrared spectra were recorded on Pye-Unicam SP3-100 spectrometer with KBr cells for solution samples and KBr disks for solid samples. ^1H NMR spectra were recorded on Bruker WP 80 SY spectrometer with TMS as internal standard. Mass spectra were recorded on 7070E VG Analytical organic mass spectrometer. Melting points were determined on a capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Mikroanalytisches Labor Pascher, Busch-str. 54 Bonn 1, West Germany and Spang Microanalytical Laboratory, Eagle Harbor, Michigan 49951.

Procedures

(a) Chromium reactions

1. Reaction of Na[Cr(η^5-C_5H_5)(CO)$_3$] with S_2Cl_2 at −97°C. A solution of S_2Cl_2 (2.7 g, 20 mmol) in THF was added dropwise (15 min) to a rapidly stirred THF solution (150 ml) containing (8.7 g, 40 mmol) of Na[Cr(η^5-C_5H_5)(CO)$_3$] [20] cooled to −97°C (methylene chloride slush bath [18]). The colour changed rapidly to brown. When the addition was complete the mixture was stirred for 1 h at −97°C and then allowed to warm slowly to room temperature with stirring. Solvent was removed in vacuo, the residue was extracted with diethyl ether (150 ml), and the extract was filtered. The volume of the filtrate was reduced in vacuo to 30 ml, and 6 ml portions were transferred to the top of the silica gel column. The column was eluted with 10% diethyl ether in petroleum ether, to give a broad olive-green band which was collected under nitrogen and kept under vacuum to give dark green crystals (0.88 g, 65% yield based on Cr) of [(η^5-C_5H_5)Cr(CO)$_2$]$_2$S (compound I). Anal. Found: C, 45.13; H, 2.95; S, 8.50; Cr, 27.80. $C_{14}H_{10}Cr_2O_4S$ calcd.: C, 44.45; H, 2.67; S, 8.48; Cr, 27.50%. IR (petroleum ether): ν(CO) 1998s, 1958vs, 1932s and 1925s cm^{-1}. IR (THF): ν(CO) 1990s, 1942vs and 1915s (br) cm^{-1}. ^{1}H NMR ($CDCl_3$): strong singlet at δ 4.90 ppm (5H, C_5H_5). The melting point was 114–115°C. R_f (10% diethyl ether in petroleum ether) was 0.30. The data are consistent with those reported for [(η^5-C_5H_5)(CO)$_2$]$_2$S [21].

2. Reaction of Na[Cr(η^5-C_5H_5)(CO)$_3$] with S_2Cl_2 at room temperature. A THF solution of S_2Cl_2 (1.62 g, 12 mmol) was added dropwise (15 min) to a rapidly stirred THF solution (100 ml) containing (5.40 g, 24 mmol) of Na[Cr(η^5-C_5H_5)(CO)$_3$] at room temperature. The colour changed rapidly to green. The mixture was then stirred for 30 min and the IR spectrum was recorded. This revealed the ν(CO) bands 2005m, 1948s, 1925s and 1910sh cm^{-1}; these are characteristic of the chromium tricarbonyl cyclopentadienyl dimer, [Cr(η^5-C_5H_5)(CO)$_3$]$_2$ [22].

When the reaction mixture was continuously stirred for 2 h it became dark olive-green. TLC examination of this olive-green solution showed the presence of the sulfur complex, [Cr(η^5-C_5H_5)(CO)$_2$]$_2$S, R_f (10% diethyl ether in petroleum ether) 0.30. The sulfur complex was isolated by column chromatography (2.75 g, 66% yield) and characterized by IR, ^{1}H NMR and melting point.

3. Reaction of Na[Cr(η^5-C_5H_5)(CO)$_3$] with $SOCl_2$ at −97°C. A solution of $SOCl_2$ (1.43 g, 12 mmol) in THF was added dropwise (15 min) to a rapidly stirred THF solution (100 ml) containing (5.40 g, 24 mmol) of Na[Cr(η^5-C_5H_5)(CO)$_3$] cooled to −97°C. The colour changed rapidly to brown. The mixture was then stirred for 1 h at −97°C and subsequently allowed to warm slowly to room temperature with stirring. Solvent was removed in vacuo, the residue was extracted with diethyl ether (100 ml), and the extract was filtered. The volume of the filtrate was reduced in vacuo to 10 ml, and 5 ml portions were transferred to the top of the silica gel column. The column was eluted with 10% diethyl ether in petroleum ether, to give a broad olive-green band. This band was collected under nitrogen and kept under vacuum to give a dark-green crystalline solid (0.66 g, 63% yield) identified by IR, ^{1}H NMR and melting point as $[Cr(\eta^5\text{-}C_5H_5)(CO)_2]_2S$.

When $Na[Cr(\eta^5\text{-}C_5H_5)(CO)_3]$ was treated with $SOCl_2$ at room temperature, the results were similar to those obtained at room temperature with S_2Cl_2: the chromium sulfur complex was isolated by column chromatography (2.75 g, 66% yield).

4. Reaction of $[Cr(\eta^5\text{-}C_5H_5)(CO)_3]_2$ with elemental sulfur. A solution of sulfur (3.07 g, 12 mmol) in THF (50 ml) was added to a rapidly stirred THF solution (80 ml) containing (2.01 g, 5 mmol) of $[Cr(\eta^5\text{-}C_5H_5)(CO)_3]_2$ [23]. The mixture was kept at 40–50°C under nitrogen for 2 h during which the colour changed from green to dark olive-green. The mixture was allowed to cool to room temperature, then the solvent was removed in vacuo, the residue was extracted with diethyl ether (100 ml), and the extract was filtered. The volume of the filtrate was reduced in vacuo to 15 ml, and 5 ml portions were transferred to the top of a silica gel column. The column was first eluted with petroleum ether to remove elemental sulfur. Elution with 10% diethyl ether in petroleum ether afforded a broad olive-green band, which was collected under nitrogen. Solvent was removed under vacuum to give dark-green crystals of the sulfur complex, $[Cr(\eta^5\text{-}C_5H_5)(CO)_2]_2S$, (0.28 g, 45% yield). The complex was characterized by IR and ^{1}H NMR spectroscopy and melting point.

5. Reaction of the sulfur compound $[Cr(\eta^5\text{-}C_5H_5)(CO)_2]_2S$, with iodine. A $CDCl_3$ solution of iodine (0.051 g, 0.20 mmol) was added to a $CDCl_3$ solution (0.080 g, 0.20 mmol) of $[Cr(\eta^5\text{-}C_5H_5)(CO)_2]_2S$ in an NMR tube under nitrogen. Gas evolution was observed and the colour of the mixture changed from dark olive-green to light green. The ^{1}H NMR spectrum of the mixture was recorded 10 min after mixing the reactants: a new strong singlet at δ 5.22 ppm had appeared, and the singlet of the sulfur compound at δ 4.90 ppm had disappeared. When the ratio of reactants $[Cr(\eta^5\text{-}C_5H_5)(CO)_2]_2S/I_2$ was 2/1, the ^{1}H NMR spectrum of the reaction mixture after 10 min showed two singlets, one for the product at δ 5.22 and the other at δ 4.90 ppm for the starting sulfur compound. The infrared spectrum of the product was recorded in $CDCl_3$ and in CCl_4; IR ($CDCl_3$): ν(CO) 2025s, 1970vs and 1951s(br) cm^{-1}. IR (CCl_4): ν(CO) 2028s, 1974vs and 1951m cm^{-1}. The IR bands in the carbonyl region are at the positions reported for $Cr(\eta^5\text{-}C_5H_5)(CO)_3I$ [24].

(b) Molybdenum reactions

1. Reaction of $Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$ with S_2Cl_2. A THF solution of $Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$ was prepared by refluxing (14 h) solid $Mo(CO)_6$ (7.85 g, 30 mmol) with a THF solution (150 ml) of sodium cyclopentadienide (1.95 g, 30 mmol) [25]. Slow addition (20 min) of a solution of S_2Cl_2 (2.03 g, 15 mmol) in 40 ml THF to a rapidly stirred solution of $Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$ (8.04 g, 30 mmol) in THF (150 ml) cooled to −97°C gave a dark brown solution. This was stirred for a further 1 h at −97°C then warmed to room temperature with stirring. The solvent was removed in vacuo and the residue extracted with diethyl ether (200 ml). The extracts were filtered, reduced in vacuo to ca. 50 ml, and column chromatographed. The column was first eluted with 10% diethyl ether in petroleum ether which gave a purple red band; this was collected under nitrogen and evaporated to give the characteristic purple-red crystalline solid $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$. IR ($CH_2Cl_2$) ν(CO): 2015 m, 1962vs and 1915s cm^{-1}. ^{1}H NMR ($CDCl_3$): strong singlet at δ 5.26 ppm (5H, C_5H_5) [26]. The column was then eluted with 30% diethyl ether in

TABLE 1

LOW RESOLUTION MASS SPECTRUM DATA FOR $(\mu\text{-}S_2)[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$ (II) [a]

m/e	Tentative assignments	Relative abundance	*m/e*	Tentative assignments	Relative abundance
311	$(C_5H_5)Mo(CO)_3S_2^+$	23.6	196	Mo_2^+	63.7
283	$(C_5H_5)Mo(CO)_2S_2^+$	8.4	195	$(C_5H_5)MoS^+$	100.0
279	$(C_5H_5)Mo(CO)_3S^+$	20.8	190	$(CO)MoS_2^+$	100.0
255	$(C_5H_5)Mo(CO)S_2^+$	53.9	179	$(C_5H_5)Mo_2S^{2+}$	6.2
251	$(C_5H_5)Mo(CO)_2S^+$	100.0	163	$(C_5H_5)Mo^+$	29.9
247	$(C_5H_5)Mo(CO)_3^+$	16.4	162	MoS_2^+	10.2
246	$Mo(CO)_3S_2^+$	73.0	130	MoS^+	11.9
228	Mo_2S^+	4.0	65	$(C_5H_5)^+$	8.6
227	$(C_5H_5)MoS_2^+$	10.5			
218	$(CO)_2MoS_2^+$	28.5			
214	$(CO)_3MoS^+$	10.5			

[a] The assignments involve the most abundant naturally isotopes in each fragment (^{98}Mo isotope for molybdenum).

petroleum ether, to give a broad greenish-orange band which was collected under nitrogen. TLC examination of this eluate indicated the presence of two compounds with R_f (33% diethyl ether in petroluem ether) 0.17 (orange) and 0.24 (green); These were separated by preparative thin-layer chromatography (PTLC) using 40% diethyl ether in petroleum ether as eluant. The compound with R_f value 0.17 was isolated as an orange-red crystalline solid (0.95 g, 56% yield) and identified by elemental analysis, infrared and ^1H NMR spectroscopy, and melting point as $Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl$ [25]. Anal. Found: C, 34.26; H, 1.91; Cl, 12.81. $C_8H_5MoO_3Cl$ calcd.: C, 34.3; H, 1.8; Cl, 12.7%. IR (CCl_4) ν(CO): 2055s, 1980vs and 1958vs cm^{-1}. ^1H NMR ($CDCl_3$): strong singlet at δ 5.64 ppm (5H, C_5H_5) melting point: 135–136°C.

The compound with R_f value 0.24 was isolated as a green crystalline solid (0.67 g, 20% yield) and characterized by elemental analysis, infrared spectra, ^1H NMR, mass spectra and melting point, 69–70°C, as $(\mu\text{-}S_2)[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$ (II). Anal. Found: C, 34.46; H, 1.95; Mo, 34.93; S, 11.71. $C_{16}H_{10}Mo_2O_6S_2$ calcd.: C, 34.67; H, 1.82; Mo, 34.62; S, 11.57%. IR (petroleum ether) ν(CO): 2040s, 1972vs and 1949vs cm^{-1}. ^1H NMR ($CDCl_3$): strong singlet at δ 5.56 ppm (5H, C_5H_5). In the mass spectrum the molecular ion was not observed; significant mass fragments were observed for the molybdenum isotopes (see Table 1).

When the reaction of $Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$ with S_2Cl_2 was carried out at room temperature the products were mainly the molybdenum dimer $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$, the chloromolybdenum derivative $Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl$, and elemental sulfur.

2. *Reaction of* $Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl$ *with* Li_2S. A THF solution (20 ml) of Li_2S (0.092 g, 2 mmol) was added slowly under nitrogen to a rapidly stirred solution of $Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl$ (1.12 g, 4 mmol), which had been made by reaction of $Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$ with S_2Cl_2 in 50 ml THF at room temperature. The mixture was stirred for 24 h at room temperature and TLC examination then indicated the presence of two compounds with R_f values (33% diethyl ether in petroleum ether) of 0.56 and 0.17. The compounds were identified as $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$ and unreacted $Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl$ by comparison with authentic samples.

3. Reaction of $Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl$ *with* Li_2S_2. A THF solution (30 ml) of Li_2S_2 (0.156 g, 2 mmol) was added to a rapidly stirred solution of $Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl$ (1.12 g, 4 mmol) in THF (100 ml) at room temperature under nitrogen. The mixture was stirred for 24 h, solvent was removed in vacuo, and the solid residue was extracted with 100 ml of petroleum ether. The extract was filtered under nitrogen and reduced to 30 ml in vacuo. TLC examination of the extract indicated the presence of four compounds with R_f values (33% diethyl ether in petroleum ether) 0.56 purple-red; 0.42 reddish-pink; 0.24 light-green and 0.17 orange-red. These were separated by preparative thin-layer chromatography (40% diethyl ether in petroleum ether) and extracted with diethyl ether. The compound with R_f 0.56 was identified as $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$. The product with R_f 0.42 was a reddish-pink solid (compound III) with IR (petroleum ether) $\nu(CO)$: 2048m, 1982vs and 1955s cm^{-1}. ^1H NMR ($CDCl_3$) singlet at δ 5.61. Anal. Found: S, 16.64. $C_{16}H_{10}Mo_2O_6S_3$ $(\mu\text{-}S_3)[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2S_3$ calcd.: S, 16.38%. The compound with R_f 0.24 was a green crystalline solid, identified as compound II, $(\mu\text{-}S_2)[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$. The compound with R_f 0.17 appeared as reddish-orange crystals, and was identified as the unreacted $Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl$. In solution compound III is reddish-pink and is gradually converted into compound II and the dimer, $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$, as shown by ^1H NMR spectroscopy and by TLC R_f values.

4. Reaction of $Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl$ *with* Li_2S_3. Slow addition under nitrogen of THF solution (30 ml) of Li_2S_3 (0.220 g, 2 mmol) to a solution of $Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl$ (1.12 g, 4 mmol) in THF (100 ml) at room temperature, followed by 24 h stirring gave after the usual work-up (see experiment(3)) mainly compound III, which is gradually converted in solution into compound II and the dimer $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$.

5. Reaction of $Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl$ *with* Li_2S_4. Slow addition of a solution of Li_2S_4 (0.280 g, 2 mmol) in THF (30 ml) to a solution of $Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl$ (1.12 g, 4 mmol) in THF (100 ml) under nitrogen at room temperature, followed by 24 h stirring gave, after the usual work-up (see experiment (3)) mainly III, II, and the dimer $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$.

Tungsten reactions

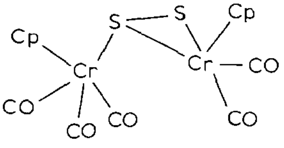
1. Reaction of $Na[W(\eta^5\text{-}C_5H_5)(CO)_3]$ *with* S_2Cl_2. A solution of S_2Cl_2 (2.71 g, 10 mmol) in THF (40 ml) was added slowly (20 min) to a rapidly stirred solution of $Na[W(\eta^5\text{-}C_5H_5)(CO)_3]$ [25], (7.12 g, 20 mmol) in THF (150 ml) at −97°C. The colour changed rapidly to greenish-brown. The mixture was subsequently stirred for 1 h at −97°C and then allowed to warm slowly to room temperature with stirring. The solvent was removed in vacuo and the residue was extracted with diethyl ether (200 ml). The volume of the extract was reduced in vacuo to 15 ml, and column chromatographed. The column was first eluted with 60% diethyl ether in petroleum ether, to give an orange-red band. The band was collected under nitrogen and solvent was removed in vacuo to give an orange-red crystalline solid (0.92 g, 37% yield), which was identified from its IR and ^1H NMR spectra and melting point (136–137°C, dec.) as $W(\eta^5\text{-}C_5H_5)(CO)_3Cl$ [26]. IR (CCl_4) $\nu(CO)$: 2043s, 1962vs and 1943s cm^{-1}. ^1H NMR ($CDCl_3$): strong singlet at δ 5.76 ppm (5H, C_5H_5). The column was then eluted with 10% THF in diethyl ether, to give a deep brownish-green band, which was collected under nitrogen. TLC examination showed that the eluate gave one major green spot with R_f value 0.42 (50% THF in petroleum ether) and an unidentified minor brown spot with R_f value 0.30. The eluate was then reduced in vacuo to 10 ml and subjected to preparative TLC. Elution with 35% THF in petroleum ether and extraction with THF gave a pure green crystalline solid, compound IV m.p. 182–184°C (decomp.). IR (CH_2Cl_2) ν(CO): 2025m, 1945sh, 1926s (br) and 1885 sh cm^{-1}. ^1H NMR ($CDCl_3$): singlet at δ 5.62 ppm (5H, C_5H_5). R_f (50% THF in petroleum ether) 0.42. Anal. Found: S, 9.03. $C_{16}H_{10}W_2O_6S_2$, (μ-S_2)[W(η^5-C_5H_5)(CO)$_3$]$_2S_2$ calcd.: S, 8.77%.

When the reaction of Na[W(η^5-C_5H_5)(CO)$_3$] with S_2Cl_2 was carried out at room temperature, the products were mainly the dimer, [W(η^5-C_5H_5)(CO)$_3$]$_2$, and the chloro derivative W(η^5-C_5H_5)(CO)$_3$Cl.

When W(η^5-C_5H_5)(CO)$_3$Cl was treated separately with THF solution of Li_2S, Li_2S_2, Li_2S_3, or Li_2S_4 at room temperature or in boiling THF, no reaction was observed, and the starting material, W(η^5-C_5H_5)(CO)$_3$Cl stayed intact. Mainly similar results were obtained when boiling toluene was used, but in this case an unidentified precipitate was also observed.

Results and discussion

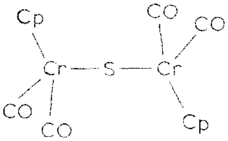
In neutral organometallic sulfanes each terminal sulfur atom acts as simple two electron σ-donor, and each sulfur atom retains two uncoordinated lone pair which should be available for further complexation. The procedures used for the preparation of the organometallic sulfanes involved mild conditions in order to avoid decarbonylation and further complexation. From previous work [1], it was known that the organoiron trisulfane, (μ-S_3)[Fe(η^5-C_5H_5)(CO)$_2$]$_2$ was the most stable iron sulfane. In the present work, the most commonly encountered product from the chromium reactions was the dark-green crystalline chromium sulfur complex I, in ~ 65% yield, [Cr(η^5-C_5H_5)(CO)$_2$]$_2$S. This was the final major product from the reaction of Na[Cr(η^5-C_5H_5)(CO)$_3$] with S_2Cl_2 and $SOCl_2$ at room temperature or at −97°C. Reaction of the chromium dimer with elemental sulfur also gave the chromium sulfur complex I. The reaction of chromium dimer, [Cr(η^5 − C_5H_5)(CO)$_3$]$_2$ with elemental sulfur was previously shown to produce the chromium sulfur complex (η^5-C_5H_5)$_2$Cr$_2$(CO)$_5$S$_2$ as dark brown crystals having the following structure [27,28]:



Cp =(η^5-C_5H_5)

This disulfur complex undergoes CO-elimination and desulfurization slowly at ambient temperature to produce the chromium sulfur complex I. We observed formation of a brown color on addition of S_2Cl_2 or $SOCl_2$ to Na[Cr(η^5-C_5H_5)(CO)$_3$] at −97°C, this gradually changed to dark olive green, the color of complex I upon warming up to room temperature; we think that the development of the brown color at low temperatures may indicate the formation of chromium sulfane, (μ-S_x)[Cr(η^5-C_5H_5)(CO)$_3$]$_2$, which at room temperature undergoes CO elimination and desulfurization, and is finally converted into the stable chromium sulfur complex I. Complex I was first obtained by Legzdins [21], in 34% yield, from the reaction of Na[(η^5-

$C_5H_5)(CO)_3]$ with trithiazyl chloride, $S_3N_3Cl_3$, in an attempt to prepare the thionitrosyl chromium complex, $(\eta^5\text{-}C_5H_5)(CO)_2CrNS$. The molecular structure of complex I has been also reported [21], and involves $Cr(\eta^5\text{-}C_5H_5)(CO)_2$ units bridged by a sulfur atom with a short Cr–S bond distance (2.074 Å), suggesting multiple bond character in the essentially linear Cr–S–Cr linkage. The structure of complex I is shown.



Cp = $(\eta^5\text{-}C_5H_5)$

The sulfur chromium complex I, $[Cr(\eta^5\text{-}C_5H_5)(CO)_2]_2S$, reacts with an equimolar amount of I_2 in $CDCl_3$ to give the iodo derivative $Cr(\eta^5\text{-}C_5H_5)(CO)_3I$. The behaviour of the sulfur chromium complex in this reaction is similar to that of the dimer, $[Cr(\eta^5\text{-}C_5R_5)(CO)_2]_2$, (R = H, Me) (which contains a Cr–Cr triple bond), which reacts with I_2 to give $Cr(\eta^5\text{-}C_5R_5)(CO)_3I$ [29–31].

In the molybdenum reactions, the anion $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]^-$ reacts with S_2Cl_2 at −97°C to a give purple-red crystalline solid of the dimer $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$, the orange-red crystalline solid of the chloro-derivative, $Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl$ (56% yield) and the new green crystalline solid molybdenum disulfane $(\mu\text{-}S_2)[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$ (20% yield), II. Isolation of these products was achieved by column chromatography and preparative thin-layer chromatography. The ν(CO) infrared spectrum of the molybdenum disulfane, II, in petroleum ether (Fig. 1) showed three strong bands at 2040s, 1972vs and 1949vs cm^{-1} which are attributed to terminal carbonyl ligands. The same pattern of IR bands is found in complexes of the formula $Mo(\eta^5\text{-}C_5H_5)(CO)_3X$ (X = Cl, Br, I, $Mo(\eta^5\text{-}C_5H_5)(CO)_3$) [26]. In addition, the iron trisulfane, $(\mu\text{-}S_3)[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$, [1] has IR spectral features, similar to those of the iron derivative, $(\eta^5\text{-}C_5H_5)(CO)_2FeX$ (X = Cl, Br, I, CH_3) [26] as expected since the metallosulfane compounds each have two identical carbonyl containing units on each terminal sulfur of the sulfur chain S_x (x = 2, 3, or higher) and the different rotomers of the sulfur-bridged compound are expected to undergo interconversion very rapidly in solution at room temperature, the barrier to rotation about a single S–S bond being only ca. 5 kcal mol^{-1} [32,33]. The above reasoning would also suggest that the two cyclopentadienyl rings in the metallosulfane compound are magnetically equivalent on the NMR time at ambient temperature, and consequently the metallosulfane compound exhibits a single resonance due to the two $(\eta^5\text{-}C_5H_5)$ rings; the new molybdenum disulfane compound, $(\mu\text{-}S_2)[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$ gives a sharp singlet at δ 5.56 ppm in $CDCl_3$ as does the iron trisulfane, $(\mu\text{-}S_3)[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ (sharp singlet at δ 5.18 ppm ($CDCl_3$)) [1].

Details of the mass spectrum of $(\mu\text{-}S_2)[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$ are shown in Table 1. Although the molecular ion was not observed, the fragment ions observed in the spectrum strongly support the formation of the disulfur-bridged molybdenum compound. We found that the disulfur-bridged molybdenum compound undergoes slow desulfurization under nitrogen at room temperature to give the molybdenum dimer $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$. This was confirmed by the ^1H NMR spectrum and by R_f values.

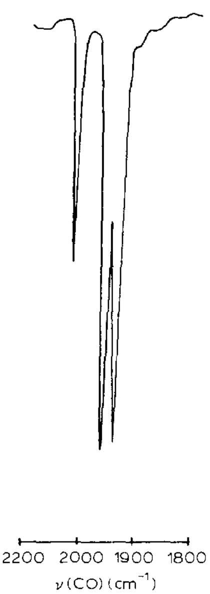


Fig. 1. ν(CO) infrared spectrum of (μ-S_2)[Mo(η^5-C_5H_5)(CO)$_3$]$_2$ in petroleum ether.

Reactions of Mo(η^5-C_5H_5)(CO)$_3$Cl with Li_2S_x ($x = 1$, 2, 3, and 4) in THF solution in 2/1 molar ratio respectively were carried out separately at room temperature. The Li_2S reaction yielded only the molybdenum dimer, [Mo(η^5-C_5H_5)(CO)$_3$]$_2$ whereas the Li_2S_2 reaction gave the molybdenum dimer, the molybdenum disulfane, (μ-S_2)[Mo(η^5-C_5H_5)(CO)$_3$]$_2$, and a new reddish-pink solid compound, III, which was identified as (μ-S_3)[Mo(η^5-C_5H_5)(CO)$_3$]. These compounds were separated by preparative thin-layer chromatography under nitrogen. The solution (petroleum ether) infrared spectrum in the ν(CO) region of compound III is shown in Fig. 2. The spectrum shows three bands at 2048m, 1982vs and 1955s cm^{-1}, which are attributed to terminal carbonyl ligands. The ^{1}H NMR spectrum of compound III shows a sharp singlet at 5.61 ppm due to the cyclopentadienyl ring protons. Compound III dissociates slowly at room temperature in solution to give the molybdenum dimer [Mo(η^5-C_5H_5)(CO)$_3$]$_2$ and the molybdenum disulfane,

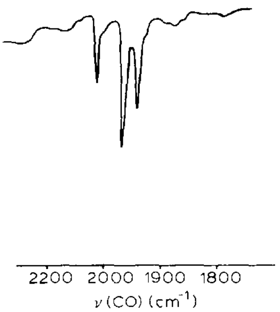


Fig. 2. ν(CO) infrared spectrum of (μ-S_3)[Mo(η^5-C_5H_5)(CO)$_3$]$_2$ in petroleum ether.

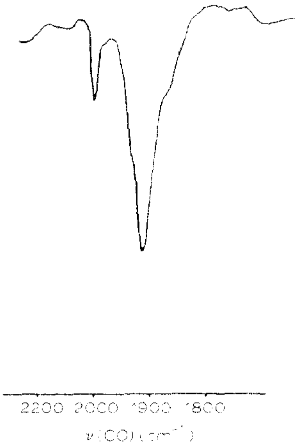


Fig. 3. ν(CO) infrared spectrum of $(\mu\text{-}S_2)[W(\eta^5\text{-}C_5H_5)(CO)_3]_2$ in CH_2Cl_2.

$(\mu\text{-}S_2)[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$; these two dissociation products were identified by their ^{1}H NMR spectra, color, and R_f values. The formation of the molybdenum trisulfane in addition to the disulfane in the Li_2S_2 reaction could be attributed to the presence of the S_3^{2-} associated with the following equilibrium [34]:

$$2S_2^{2-} \rightleftharpoons S_3^{2-} + S^{2-}$$

The reaction of $Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl$ with THF solution of Li_2S_3 and Li_2S_4 separately at room temperature produced the molybdenum dimer and compound III; no other sulfur molybdenum compounds were formed at room temperature, but when the reaction mixture in THF was refluxed for a few hours a precipitate was formed, but this was not characterized. It appears from the results that molybdenum disulfane, $(\mu\text{-}S_2)[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$ is more stable than the mono- and tri-sulfane.

In the tungsten reaction, the anion, $[W(\eta^5\text{-}C_5H_5)(CO)_3]^-$, reacts with S_2Cl_2 in THF at room temperature to give the tungsten dimer $[W(\eta^5\text{-}C_5H_5)_3]_2$ and the chloro derivative, $W(\eta^5\text{-}C_5H_5)(CO)_3Cl$; these were identified by their IR and ^{1}H NMR spectra properties [26]. When the anion was treated with S_2Cl_2 in THF at -97°C the chloro derivative, $W(\eta^5\text{-}C_5H_5)(CO)_3Cl$ and a new green cyrstalline solid, compound IV were isolated by column chromatography and/or by preparative thin-layer chromatography under nitrogen. Compound IV was identified as the tungsten disulfane $(\mu\text{-}S_2)[W(\eta^5\text{-}C_5H_5)(CO)_3]_2$; its ν(CO) bands (CH_2Cl_2) are shown in Fig. 3. The spectrum shows bands at 2025m, 1945sh, 1926s (br) and 1885sh cm^{-1} which are attributed to terminal carbonyl ligands. The reported ν(CO) infrared spectrum of the recently prepared tungsten monosulfane, $(\mu\text{-}S)[W(\eta^5\text{-}C_5H_5)(CO)_3]_2$ [16] showed similar bands, 2030w, 2005s, 1935vs (br) and 1910(sh). The ^{1}H NMR spectrum ($CDCl_3$) of compound IV exhibits a singlet at δ 5.62 ppm attributable to the cyclopentadienyl ring protons. IR and ^{1}H NMR data are shown in Table 2.

The reaction of $W(\eta^5\text{-}C_5H_5)(CO)_3Cl$ with Li_2S_x ($x = 1, 2, 3$ and 4) in THF at room temperature did not yield the expected tungsten sulfanes $(\mu\text{-}S_x)[W(\eta^5\text{-}C_5H_5)(CO)_3]_2$, the $W(\eta^5\text{-}C_5H_5)(CO)_3Cl$ remaining unchanged. Similar results were observed when the reactions were carried out in boiling THF or toluene for few

TABLE 2

SOME PROPERTIES OF $(\mu\text{-S}_x)[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$ (M = Mo, $x = 1, 2, 3$; M = W, $x = 1, 2$)

Compound	Colour	M.p. (°C)	R_f	IR ν(CO) (cm^{-1})	^{1}H NMR, δ (ppm) (CDCl$_3$)
$(\mu\text{-S})[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$ [a]	green				5.48
$(\mu\text{-S}_2)[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$	green	69–70	0.24 [b]	2040s, 1972vs and 1949vs [d]	5.56
$(\mu\text{-S}_3)[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$	reddish pink		0.42 [b]	2048m, 1982vs and 1955s [d]	5.61
$(\mu\text{-S})[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$ [a]	green			2030w, 2005s, 1935vs (br) and 1910sh [e]	5.56
$(\mu\text{-S}_2)[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$	green	182–184 (dec.)	0.42 [c]	2025m, 1945sh, 1926s (br) and 1885 sh [f]	5.62

[a] Ref. 16. [b] R_f values were measured in 33% diethyl ether in petroleum ether. [c] R_f value was measured in 50% THF in petroleum ether. [d] In petroleum ether. [e] In CDCl$_3$. [f] In CH$_2$Cl$_2$.

hours, after which the solution contained unreacted, $\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}$ and a precipitate was also present, but this was not characterized.

Acknowledgement

We gratefully acknowledge research grant support from the graduate school at Yarmouk University, and thank Miss Nazek Khouri for help in preparing the manuscript.

References

1 M.A. El-Hinnawi, A.A. Aruffo, B.D. Santarsiero, D.R. McAlister, and V. Schomaker, Inorg. Chem., 22 (1983) 1585.
2 (a) D. Coucouvanis, Acc. Chem. Res., 14 (1981) 201; (b) W. Lovenberg, (Ed.), Iron-Sulfur Proteins, Academic Press, New York.
3 A. Müller, E. Diemann, R. Jostes and H. Bogge, Angew. Chem. Int. Ed. Engl., 20 (1981) 934.
4 M.R. DuBois, M.C. Van Derveer, D.L. DuBois, R.C. Haltiwanger and W.K. Miller, J. Am. Chem. Soc., 102 (1980) 7456.
5 R.D. Adams, Acc. Chem. Res., 16 (1983) 67.
6 R.D. Adams, Z. Dawoodi, D.F. Foust and B.E. Segmüller, Organometallics, 2 (1983) 315.
7 F. Richter and H. Vahrenkamp, Angew. Chem. Int. Ed. Engl., 19 (1980) 65.
8 A. Müller and W. Jaegermann, Inorg. Chem., 18 (1979) 2631.
9 A. Müller, W. Jaegermann and J.H. Enemark, Coord. Chem. Rev., 46 (1982) 245.
13 E. Diemann and A. Müller, Coord. Chem. Rev., 10 (1973) 79.
14 C. Kowala and J.M. Swan, Aust. J. Chem., 19 (1966) 547.
15 C. Mealli, S. Midollini and L. Sacconi, Inorg. Chem., 17 (1978) 632.
16 M. Herberhold, W. Jellen and H.H. Murray, J. Organomet. Chem., 270 (1984) 65.
17 M. Herberhold, D. Reine, K. Ackermann, U. Thewalt and T. Debaerdemacker, Z. Naturforsch. B, 39 (1984) 1199.
18 D.F. Shriver, The Manipulation of Air - Sensitive Compounds, McGraw-Hill, New York, 1969.
19 J.A. Gladysz, V.K. Wong and B.S. Jick, J. Chem. Soc., Chem. Commun., (1978) 838.
20 J.K. Hoyano, P. Legzdins and J.T. Malito, Inorg. Synth., 18 (1978) 126.
21 T.J. Greenhough, B.W.S. Kolthammer, P. Legzdins and J. Trotter, Inorg. Chem., 18 (1979) 3543.
22 P. Hackett, P.S. O'Neill and A.R. Manning, J. Chem. Soc., Dalton Trans., (1974) 1625.

23 R.B. King and F.G.A. Stone, Inorg. Synth., 7 (1963) 104.
24 A.F. Manning and D.J. Thornhill, J. Chem. Soc., A., (1971) 637.
25 T.S. Piper and G.J. Wilkinson, Inorg. and Nucl. Chem., 3 (1956) 104.
26 D.G. Alway and K.W. Barnett, Inorg. Chem., 19 (1980) 1533.
27 L. Yoong Gon, W.T. Hambley and G.B. Robertson, J. Chem. Soc., Chem. Commun., (1983) 1458.
28 W.A. Herrmann, J. Rohrmann and A. Schäfer, J. Organomet. Chem., 265 (1984) C1
29 A.F. Manning and D.J. Thornhill, Chem. Soc., A., (1971) 637.
30 R.B. King, Coord. Chem. Rev., 20 (1976) 155.
31 R.B. King, M.Z. Iqbal and A.D. King Jr., J. Organomet. Chem., 171 (1979) 53.
32 O. Foss, Acta. Chem. Scand., 8 (1954) 469.
33 L. Pauling, Proc. Natl. Sci. U.S., 35 (1949) 495.
34 W. Giggenbach, Inorg. Chem., 11 (1972) 1201.