Chromium Chalcogen Complexes. Insertion of Elemental Sulphur into $[\{Cr(cp)(CO)_2\}_2Se]$ and $[Cr(cp)_2(CO)_4Se_2]$ (cp = η-C_5H_5)

Lai Yoong Goh
Department of Chemistry, University of Malaya, 59100 Kuala Lumpur, Malaysia

The facile insertion of elemental sulphur into the cumulated linear triple bond Cr≡Se≡Cr, of $[Cr_2(cp)_2(CO)_4Se]$ (cp = η-C_5H_5) resulted in the isolation of $[Cr_2(cp)_2(CO)_4Se_2]$, $[Cr_2(cp)_2(CO)_4S_2]$, and $[Cr_2(cp)_2(CO)_4S]$, with relative yields dependent on the reaction conditions, as well as the sulphur selenides S_7Se and S_6Se_2. Detailed n.m.r. and t.l.c. studies indicated that the transformation occurred *via* dichalcogen species of the type $[Cr_2(cp)_2(CO)_4S(Se)]$ and $[Cr_2(cp)_2(CO)_5S(Se)]$. It was demonstrated that $[Cr_2(cp)_2(CO)_4Se_2]$ also can undergo a rapid reaction with elemental sulphur to give $[Cr_2(cp)_2(CO)_4S]$ as the ultimate product.

Since the first discovery of the cumulated triple bond Cr≡S≡Cr in $[\{Cr(cp)(CO)_2\}_2S]$ (cp = η-C_5H_5) (**1b**) by Legzdins and co-workers[1] in 1979 and its alternative synthesis in our laboratory in 1983,[2] followed by the synthesis of the analogous Se complex $[\{Cr(cp)(CO)_2\}_2Se]$ (**1a**), [3–5] further information is currently emerging on the reactivity of these complexes. Thus the thermolytic degradation[6] and photoinduced sulphur insertion[7] of the sulphur complex (**1b**) have been reported. Herrmann *et al.*[4] added small alkylidene (CR_2) groups[4] and the organometallic fragment $Fe(CO)_3$ across the Cr≡Se bond[8] and very recently succeeded in reacting (**1a**) with potassium hyperoxide, KO_2, and $[Co(cp)_2]$ to yield the anionic species $[Cr(cp)(CO)_2Se_2]^-$ and $[\{Cr(cp)(CO)_2\}_3Se]^-$, respectively.[9] Recent studies have shown that the formation of $[Cr_2(cp)_2(CO)_4Se_2]$ (**2a**) and $[Cr_2(cp)_2(CO)_5Se_2]$ (**3a**) from the reaction of $[\{Cr(cp)(CO)_2\}_2Se]$ with elemental selenium occurs *via* the insertion of a Se atom into the Cr≡Se bond of (**1a**).[10] Herein, I describe the facile insertion of elemental sulphur, followed by an intermolecular transformation into (**2a**), $[Cr_2(cp)_2(CO)_4S_2]$ (**2b**), and $[Cr_2(cp)_2(CO)_4S]$ (**1b**). The rapid conversion of (**2a**) into (**1b**) in the presence of S_8 is also demonstrated.

Experimental

All reactions were carried out using either conventional Schlenk techniques or in an argon or nitrogen atmosphere in a Vacuum Atmospheres Dribox equipped with a model HE493 Dri-Train.

The compound $[Cr(CO)_6]$ was obtained from Strem Chemicals, Inc. Cyclo-octasulphur was 'S sublime' from B.D.H. Black selenium powder was Hopkin and Williams AnalaR grade. The compounds $[\{Cr(cp)(CO)_3\}_2]$,[11] $[Cr_2(cp)_2(CO)_4E]$ (E = S[12] or Se[3]), $[Cr_2(cp)_2(CO)_4E_2]$ and $[Cr_2(cp)_2(CO)_5E_2]$ (E = S[12] or Se[10]) were synthesised as described before. Solvents were dried over sodium–benzophenone and distilled before use. T.l.c. plates (5 × 10 cm) were Whatman K6 silica gel. N.m.r. spectra were measured on a JEOL FX100 spectrometer, with chemical shifts referenced to residual C_6H_6 in C_6D_6 or to $SiMe_4$ in $[^2H_8]$toluene. Infrared spectra were recorded in the range 4 000—200 cm^{-1} on a Perkin-Elmer 1330 or Beckman IR 4240 instrument. Electron-impact mass spectra were measured on a Kratos AEI MS3074 instrument. Elemental analyses were performed by the Analytical Unit of the Australian National University.

Reactions of $[Cr_2(cp)_2(CO)_4Se]$ (**1a**) *with Elemental Sulphur.*—(*a*) *With* 1 *mol equivalent.* An orange-brown solution of compound (**1a**), prepared *in situ* from $[Cr_2(cp)_2(CO)_6]$ (100 mg, 0.25 mmol) and Se_8 (110 mg, 1.39 mmol) in toluene (5 cm^3), was filtered through Celite into a flask containing S_8 (9.3 mg, 0.29 mmol S), and the mixture stirred for 3 h at ambient temperature. The resultant yellow-brown solution was filtered to remove a small amount of a reddish black precipitate, and then concentrated to *ca.* 1 cm^3. Addition of a little n-hexane, followed by cooling at −30 °C for 30 min, gave dark needle-like crystals of $[Cr_2(cp)_2(CO)_4Se_2]$ (**2a**) (42 mg, 0.083 mmol, 33% yield), in admixture with *ca.* 10% of $[Cr_2(cp)_2(CO)_4S]$ (**1b**). A second crop of the latter complex (40 mg, 0.11 mmol, 44% yield) was subsequently obtained after 15 h at −30 °C.

(*b*) *With excess.* (*i*) *With* 5.76 *mol equivalents at low temperature.* A solution of compound (**1a**), prepared as above, was cooled to −30 °C and S_8 (46 mg, 1.44 mmol) added. The suspension was mixed by swirling the flask, while allowing it to warm to 10 °C, and then immediately filtered through Celite before concentration to *ca.* 1 cm^3 (total work-up time 24 min). On addition of n-hexane, followed by cooling to −30 °C for 30 min, the muddy green-brown solution yielded dark green-brown crystals (44 mg), the n.m.r. spectrum of which indicated mainly (**2a**) (δ 4.08) with traces at δ 5.13 and 4.36. T.l.c. on SiO_2 plates showed the presence of (**2a**), $[Cr_2(cp)_2(CO)_4(SSe)]$, (**2c**), and (**1a**), as brown, light brown, and orange spots possessing R_f values of 0.36, 0.39, and 0.69 respectively when eluted with n-hexane–toluene (1:1), or 0.23, 0.26, and 0.49 with n-hexane–toluene (8:5). From the mother-liquor was obtained a subsequent crop of dark brown crystals (63 mg), consisting of unreacted (**1a**) contaminated with traces of (**2a**) and its S analogue, (**2b**).

(*ii*) *With* 31.2 *mol equivalents.* A solution of compound (**1a**), prepared from $[Cr(cp)_2(CO)_6]$ (200 mg, 0.50 mmol) was treated with S_8 (500 mg, 15.6 mmol S), as described under (*a*). The excess of S_8 was filtered off and the yellowish green filtrate concentrated to *ca.* 5 cm^3, whereupon golden yellow crystals of S_8 (136 mg) formed on cooling [*m*/*z* 256 (S_8), 224 (S_7), 192 (S_6), 160 (S_5), 128 (S_4), 96 (S_3), and 64 (S_2)]. Further concentration of the mother-liquor to 2 cm^3, followed by cooling to −30 °C, gave yellow-brown crystals (75 mg), the mass spectrum of which showed the fragmentation pattern of a mixture of S_8, S_7Se, and S_6Se [*m*/*z* 352 (S_6Se_2), 320 (S_5Se_2), 304 (S_7Se), 288 (S_4Se_2), 272 (S_6Se), 256 (S_3Se_2, S_8), 240 (S_5Se), 224 (S_2Se_2, S_7), 208 (S_4Se), 192 (SSe_2, S_6), 176 (S_3Se), 160 (Se_2, S_5), 144 (S_2Se), 128 (S_4), 112 (SSe), 96 (S_3), and 64 (S_2)]. The n.m.r. spectrum showed that these crystals were contaminated with traces of $[Cr_4(cp)_4S_4]$ (δ 4.90) and $[Cr_4(cp)_4Se_4]$ (δ 5.13). The mother-liquor possessed cp resonances at δ 4.3 and 4.1, with a relative intensity of 5:1. Addition of n-hexane, followed by cooling overnight at −30 °C, yielded one macro-sized crystal of (**1b**) (70 mg, 0.185 mmol, 37%), together with fine dark needles (60 mg, 0.146 mmol, 29%)

Table 1. Reaction conditions[a] and products of the reaction $[Cr_2(cp)_2(CO)_4Se]$ (**1a**) + *n*S ⟶

n	Reaction time (min)	Products (%)	Identification methods
1	180	(**2a**) (33[b]), (**1b**) (44[c])	N.m.r., i.r. of isolated crystals
5.76	*ca.* 5[d]	Mixture of (**2a**), (**2b**), (**2c**), and unreacted (**1a**)	T.l.c. of isolated crystals
31.2	180	S_7Se, S_6Se_2	Mass spectrometry
		$[Cr_4(cp)_4S_4]$, $[Cr_4(cp)_4Se_4]$ (traces)	N.m.r.
		(**1b**) ($\geqslant 37$[c] + 32[b])	N.m.r., i.r., and t.l.c. of isolated crystals
		(**2b**) ($\leqslant 29$[b])	
		(**3c$_1$**) and (**3c$_2$**) (traces)	
100	60	S_7Se, S_6Se_2	Mass spectrometry
		(**1b**) (94,[e] 53[c])	N.m.r. and i.r.
		(**2a**) (6[e])	

[a] At ambient temperature, unless otherwise stated. [b] Impure isolated crystals. [c] Pure isolated crystals. [d] Temperature allowed to increase from −30 to 10 °C during reaction. [e] In solution by n.m.r. estimation.

of (**2b**) (δ 4.135), contaminated with some (**1b**). These components were confirmed by t.l.c. which also indicated a trace amount of $[Cr_2(cp)_2(CO)_5E_2]$ (E = S or Se). A subsequent crop (60 mg, 0.16 mmol, 32%) consisting mainly of (**1b**) was also obtained.

(*iii*) *With* 100 *mol equivalents.* A similar reaction with S_8 (1.6 g, 50 mmol S) for 1 h resulted in a dark muddy green product mixture, consisting of $[Cr_2(cp)_2(CO)_4S]$ and $[Cr_2(cp)_2(CO)_4Se_2]$ in the molar proportion 16:1, in addition to a rust-red precipitate (380 mg) of S_8, S_7Se, and S_6Se_2. The mother-liquor yielded deep green chunky crystals of $[Cr_2(cp)_2(CO)_4S]$ (*ca.* 100 mg, 53%).

Identification of Products and Intermediates.—(*a*) *Proton n.m.r. spectral studies. Reaction of* $[Cr_2(cp)_2(CO)_4Se]$ (**1a**) *with* S_8. A 0.05 mol dm^{-3} solution of compound (**1a**) was prepared *in situ* from $[Cr_2(cp)_2(CO)_6]$ (10 mg, 0.025 mmol) and Se_8 (2.2 mg, 0.028 mmol Se) in C_6D_6 (0.5 cm^3) and filtered into a 5-mm n.m.r. tube. After an initial n.m.r. spectrum, S_8 (4.5 mg, 0.141 mmol S) was added to the frozen orange-brown solution. After rapid mixing at *ca.* 8 °C, the tube was returned to the n.m.r. probe maintained at 8 °C. The rapid changes in the first 30 min, recorded by continuous consecutive scans, are illustrated in Figure 1, which also includes spectra for the subsequent slower changes. These changes are described in detail in the Results and Discussion section. A similar study was performed at ambient temperature, as well as under 1 atm (*ca.* 10^5 Pa) of CO at both 8 °C and ambient temperature.

Reaction of $[Cr_2(cp)_2(CO)_4Se_2]$ (**2a**) *with* S_8. To a mixture of compound (**2a**) (10 mg, 0.02 mmol) and S_8 (3.6 mg, 0.113 mmol S) in a 5-mm n.m.r. tube was added C_6D_6 (0.45 cm^3). The proton spectrum monitored at 8 °C showed no change in the cp resonance at δ 4.05 after 1.5 h. The tube was therefore taken out of the n.m.r. probe and shaken up at ambient temperature (28 °C) to hasten the reaction. The spectral changes, scanned at intervals at 8 °C, are shown in Figure 2.

(*b*) *Low-temperature* ^1H *and* ^{13}C *n.m.r. spectral studies.* To a mixture of compound (**1a**) (16.3 mg, 0.038 mmol) and S_8 (7.5 mg, 0.23 mmol) in a capped 5-mm n.m.r. tube was added [$^2H_8$]toluene (0.4 cm^3) and the tube shaken for 5 min in an ice–water bath. The ^1H n.m.r. spectrum immediately scanned at −90 °C showed *ca.* 10% completion of reaction. The ^{13}C spectrum was next recorded at −90 °C. The sample was taken out of the probe, allowed to warm up to achieve 20% completion of reaction, as indicated by the ^1H spectrum, and another ^{13}C spectrum was taken at −68 °C to look for the presence of $[Cr_2(cp)_2(CO)_4S_2]$ (**2b**) [δ 91.29 (cp) and 258.88 (CO)]. The same reaction sample was subsequently allowed to proceed to 70% completion of reaction and the ^{13}C spectrum scanned again at −68 and −90 °C, as above. The resonances observed together with their assignments are given in Table 4, which also lists the chemical shift data for relevant authentic complexes for ease of comparison.

(*c*) *Thin-layer chromatographic* (*t.l.c.*) *separation. Reaction of* $[Cr_2(cp)_2(CO)_4Se]$ (**1a**) *with* S_8. A mixture of compound (**1a**) (2 mg, 0.005 mmol) and S_8 (2 mg, 0.006 mmol S) was triturated in toluene (*ca.* 0.1 cm^3), and drops were spotted on to 5 × 10 mm t.l.c. silica plates at periodic intervals up to 25 min, alongside spots of authentic samples of $[Cr_2(cp)_2(CO)_4E]$, $[Cr_2(cp)_2(CO)_4E_2]$, and $[Cr_2(cp)_2(CO)_5E_2]$ (E = S or Se). The plates were developed in n-hexane–toluene (4:6) and the R_f values are given in Table 2. After reaction for 2 min, in addition to an orange spot pertaining to (**1a**), two weak light brown spots were detected in the region of $[Cr_2(cp)_2(CO)_5E_2]$ with R_f 0.06—0.07 and 0.13—0.14 respectively, the former decreasing and the latter increasing in intensity with time. Also observed were two other spots in the region of $[Cr_2(cp)_2(CO)_4E_2]$, attributed to (**2a**) and the hitherto unknown species (**2c**).

Reaction of $[Cr_2(cp)_2(CO)_4Se_2]$ (**2a**) *with* S_8. A similar reaction was carried out for compound (**2a**). Immediately after mixing of (**2a**) and S_8, a t.l.c. spot of the product mixture showed the complete absence of (**2a**), but a strong orange-brown immovable spot (R_f = 0) together with low-intensity spots of (**1b**) (yellowish green), (**2b**) (muddy green), and an unknown species (light yellow, R_f 0.70). The intensity of the spots with R_f = 0 and 0.70 decreased with time and were no longer discernible after *ca.* 20 min, at which time only (**1b**) (yellow) and a brown spot with an R_f equal to that of (**2a**) were present.

Results and Discussion

Reaction with Sulphur.—Elemental sulphur reacts readily with $[Cr_2(cp)_2(CO)_4Se]$ (**1a**) under heterogeneous conditions to give a mixture of products, the composition of which varies with the conditions, as shown in Table 1. Thus a reaction for 3 h with 1 mol equivalent of sulphur resulted in the isolation of $[Cr_2(cp)_2(CO)_4Se_2]$ (**2a**) and $[Cr_2(cp)_2(CO)_4S]$ (**1b**) in 33 and 44% yield, respectively, whereas 31.2 mol equivalents of sulphur yielded (**1b**) (*ca.* 69%) and $[Cr_2(cp)_2(CO)_4S_2]$ (**2b**) (*ca.* 29%) as major products contaminated with a trace of a $[Cr_2(cp)_2(CO)_5E_2]$ species (E_2 = SSe), detectable by t.l.c. With 100 mol equivalents of sulphur, a 16:1 mixture of (**1b**) and (**2a**) was obtained in 1 h. In the last two reactions, a rust-red precipitate, consisting of a mixture of S_8, S_7Se, and S_6Se_2, identified by their mass spectra, was also obtained.

The nature and composition of the organometallic products described above indicate that the mechanistic pathway for the conversion of the selenium complex (**1a**) into its sulphur

Table 2. R_f Values in n-hexane–toluene (4:6)

Compound	E = Se	E = S	Observed species and assignments
$[Cr_2(cp)_2(CO)_4E]$	(**1a**) 0.60 (orange)	(**1b**) 0.60 (yellowish green)	(**1a**) Initially (orange) and (**1b**) finally (yellowish green)
$[Cr_2(cp)_2(CO)_4E_2]$	(**2a**) 0.34 (brown)	(**2b**) 0.38 (green)	(**2a**) 0.34 (light brown) (**2c**) 0.36 (green)
$[Cr_2(cp)_2(CO)_5E_2]$	(**3a**) 0.15 (brown)	(**3b**) 0.10 (pale brown)	(**3c$_1$**)[a] 0.06—0.07 (light brown)[b] (**3c$_2$**)[a] 0.13—0.14 (light brown)

[a] Assigned to E_2 = SSe. [b] Decreases in intensity with reaction time.

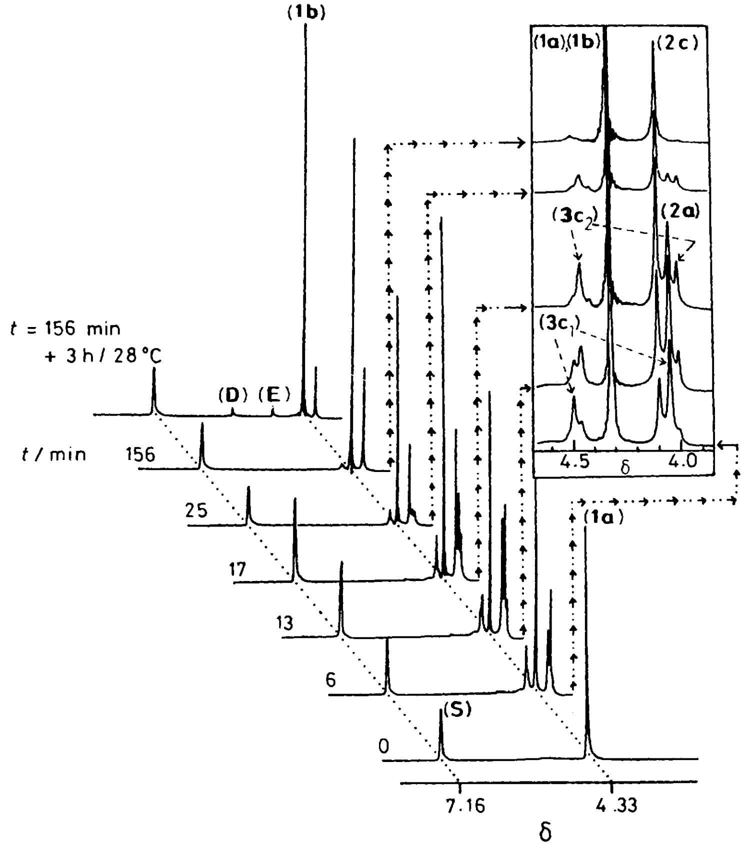


Figure 1. Time-dependent ^1H n.m.r. spectra for the reaction of a 0.05 mol dm^{-3} solution of $[Cr_2(cp)_2(CO)_4Se]$ (**1a**) in C_6D_6 with 5.6 mol equivalents of sulphur at 8 °C. Peaks are assigned as (S) = solvent (δ 7.16) and for the products, as in the text: (**1b**), $[Cr_2(cp)_2(CO)_4S]$ (δ 4.33); (**2a**), $[Cr_2(cp)_2(CO)_4Se_2]$ (δ 4.05); (**2c**), $[Cr_2(cp)_2(CO)_4(SSe)]$ (δ 4.11); (**3c$_1$**) and (**3c$_2$**), isomers $[Cr_2(cp)_2(CO)_5(SSe)]$ (δ 4.52, 4.05 and 4.48, 4.02 respectively); (**D**), $[Cr_4(cp)_4(CO)_2S_2]$ (δ 5.71) and (**E**), $[Cr_4(cp)_4S_4]$ (δ 4.90)

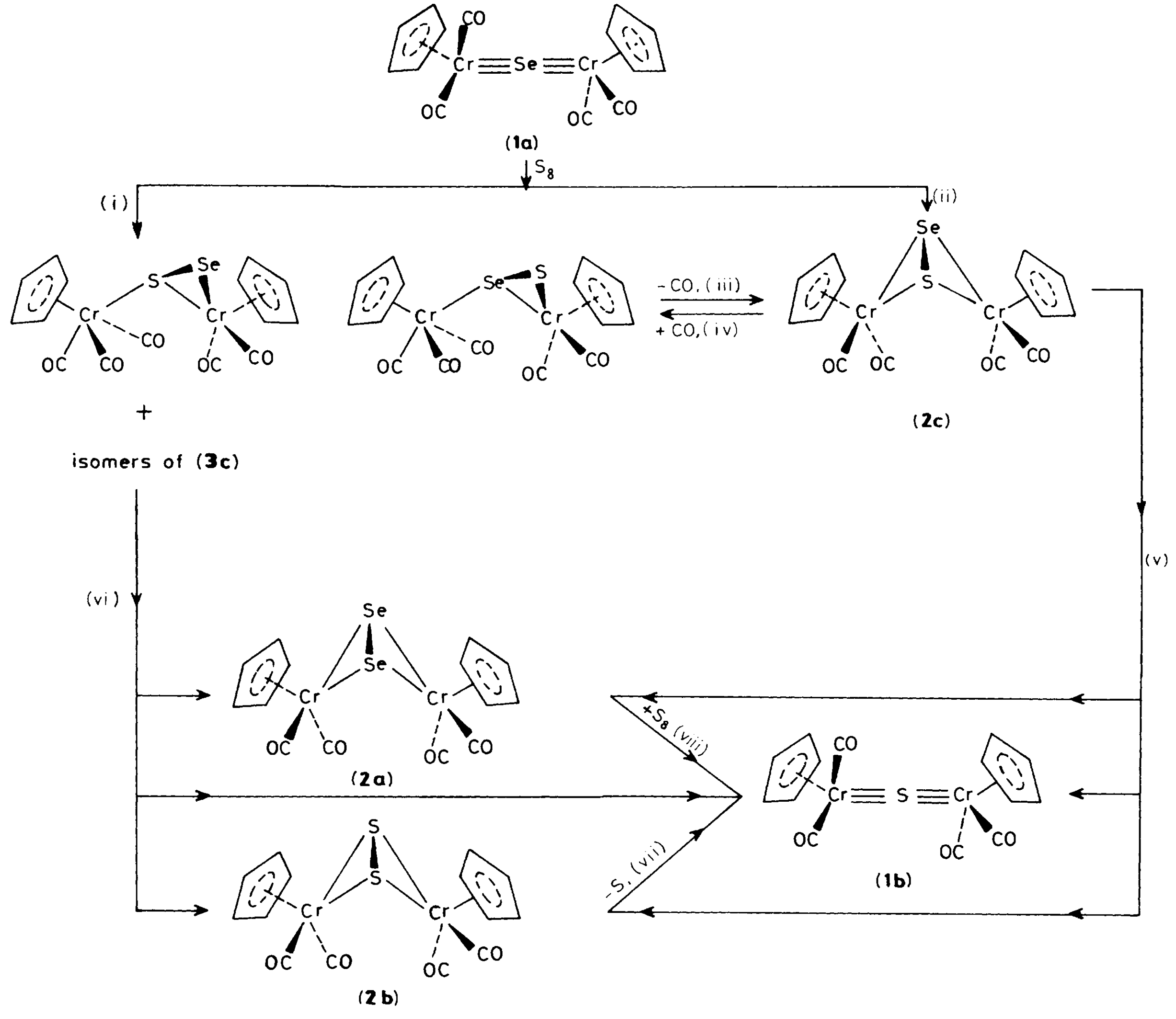
analogue (**1b**) as the ultimate product involves the formation of a sulphur-insertion complex which then disproportionates to (**2a**) and (**2b**), and/or undergoes an intermolecular rearrangement to (**2a**) and (**1b**) with loss of an S atom. Unfortunately, this S-inserted complex defied all attempts at isolation, even at low temperatures. Thus, as indicated in Table 1, a rapid reaction with 5.76 mol equivalents of sulphur at −30 to 10 °C resulted in *ca.* 40% conversion of (**1a**) into an isolated mixture, found by t.l.c. to consist of (**2a**), (**2b**), and the apparent S-insertion product (**2c**). Therefore in an attempt to gain some insight into the nature of this S-inserted intermediate and thence the mechanism of the reaction, detailed n.m.r. and diagnostic t.l.c. investigations were undertaken.

Identification of Intermediates and Products.—(*a*) *N.m.r. Studies.* (*i*) *Reaction of* $[Cr_2(cp)_2(CO)_4Se]$ (**1a**) *with* S_8. A time-dependent proton n.m.r. study of the reaction of a 0.05 mol dm^{-3} solution of compound (**1a**) in C_6D_6 with 5.6 mol equivalents of S at 8 °C is illustrated in Figure 1. The observed spectral changes can be interpreted with the help of t.l.c. data (Table 2) and low-temperature n.m.r. spectral data (Tables 3 and 4) for the product solutions in comparison with those for authentic samples of alternative dichalcogen complexes. Thus the first spectrum scanned at 6 min after mixing of the reactants showed the resonances of the reactant $[Cr_2(cp)_2(CO)_4Se]$ (**1a**) (δ 4.33), two possible isomers of $[Cr_2(cp)_2(CO)_5(SSe)]$ (**3c$_1$**) (δ 4.52 and 4.05) and (**3c$_2$**) [δ 4.48 (sh) and 4.02 (sh)], $[Cr_2(cp)_2(CO)_4Se_2]$ (**2a**) (δ 4.05), and $[Cr_2(cp)_2(CO)_4(SSe)]$ (**2c**) (δ 4.11) which could obscure the presence of a trace of $[Cr_2(cp)_2(CO)_4S_2]$ (**2b**) (δ 4.11). {The alternative assignments to $[Cr_2(cp)_2(CO)_5Se_2]$ (**3a**) (δ 4.48 and 4.05) and $[Cr_2(cp)_2(CO)_5S_2]$ (**3b**) (δ 4.52 and 4.11) were ruled out by both t.l.c. and low-temperature n.m.r.

Table 3. Proton n.m.r. chemical shift data (δ) in C_6D_6 at 8 °C

Compound	E = Se	E = S	Assignments of observed intermediates or products
$[Cr_2(cp)_2(CO)_4E]$	(**1a**) 4.33	(**1b**) 4.33	(**1b**) 4.33
$[Cr_2(cp)_2(CO)_4E_2]$	(**2a**) 4.05	(**2b**) 4.11	(**2a**) 4.05 (**2c**) 4.11
$[Cr_2(cp)_2(CO)_5E_2]$	(**3a**) 4.48, 4.05	(**3b**) 4.52, 4.11	(**3c**$_1$)[a] 4.52 and 4.05 (**3c**$_2$)[a] 4.48 and 4.02
Others			(**D**) 5.71 $[Cr_4(cp)_4(CO)_2S_2]$[b] (**E**) 4.90 $[Cr_4(cp)_4S_4]$[b]

[a] Assigned to E_2 = SSe, but may obscure trace amounts of (**2b**) seen in low-temperature n.m.r. studies described in Table 4. [b] As reported in ref. 6.



Scheme.

observations discussed below.} The total intensity of the product resonances is seen to peak at 13—17 min. The resonance at δ 4.52, one of the cp resonances pertaining to (**3c**$_1$), decayed rapidly within this time, accompanied by a concurrent growth at δ 4.48, one of the cp resonances ascribed to (**3c**$_2$). Simultaneously the resonances at δ 4.05 of (**2a**) and δ 4.11 of (**2c**) also increased, with intensities peaking at 13 and 17 min respectively. Subsequently, all these resonances, with the exception of that at δ 4.11, rapidly decayed, reaching zero intensity by 156 min. The peak at δ 4.11 however persisted for more than 3 h at 30 °C. At this time, the solution was the characteristic muddy green of the sulphur complex $[Cr_2(cp)_2(CO)_4S]$ (**1b**). Decomposition products, $[Cr_4(cp)_4S_4]$ (δ 4.90) and $[Cr_4(cp)_4(CO)_2S_2]$ (δ 5.71), derived from (**1b**),[6] had also started to form.

It is important to note that $[Cr_2(cp)_2(CO)_4Se_2]$ (**2a**) and $[Cr_2(cp)_2(CO)_4S]$ (**1b**) are formed very early in the transformation process, and are observed when only 10% of (**1a**) has reacted. This, together with the absence of (**2b**) at this stage (see Table 4), suggests that (**1b**) together with (**2a**) is derived directly

Table 4. Low-temperature n.m.r. chemical shift data in [$^2H_8$]toluene

Authentic complexes	^1H (δ) E = Se	^1H (δ) E = S	^{13}C (δ) E = Se	^{13}C (δ) E = S	Temperature (°C)
[$Cr_2(cp)_2(CO)_4E$]	(**1a**) 3.98	(**1b**) 4.06	(**1a**) 88.85, 250.5	(**1b**) 89.32, 247.6	−90
	4.07	4.13	88.77, 250.3	89.32, 247.4	−68
[$Cr_2(cp)_2(CO)_4E_2$]	(**2a**) 3.83	(**2b**) 3.87	(**2a**) 90.69, 259.3	(**2b**) 91.26, 259.2	−90
	3.88	3.95	90.61, 259.0	91.29, 258.9	−68
[$Cr_2(cp)_2(CO)_5E_2$]	(**3a**) 3.61, 4.31	(**3b**) 3.73, 4.37	(**3a**) 89.83, 92.01 235.8, 239.2, 245.6, 255.8, 265.7	(**3b**) 90.69, 92.63 233.8, 239.8, 246.6, 256.3, 266.6	−90
		(**3b**) 3.84, 4.42		(**3b**) 90.72, 92.82 234.0, 239.5, 246.6, 256.1, 266.5	−68
Intermediates and products					
At 10% conversion	3.98 (**1a**) and unresolved resonances [3.83 (**2a**), 3.89,[a] 4.04 (sh, vw) (**1b**)], 4.36,[a] 4.49 (vw)[a]		88.85, 250.5 (**1a**); 90.69, 259.3 (**2a**); 89.44, 247.7 (**1b**); and weak CO signals at 256.4, 262.5, 265.5, 268.4, 272.8		−90
At 20% conversion	4.02 (**1a**), 3.84 (**2a**), 4.08 (sh) (**1b**) with approximate relative intensity of 12:2:1[b]		88.85, 250.5 (**1a**); 90.65, 259.2 (**2a**); 89.40, 247.8 (**1b**)		−90
	4.07 (**1a**), 3.88 (**2a**), 4.13w (sh) (**1b**) with approximate relative intensity of 12:2:1		88.77, 250.3 (**1a**); 90.61, 259.0 (**2a**); 89.36, 247.5 (**1b**)		−68
At 70% conversion	3.98 (vw) (**1a**), 3.83 (**2a**), 4.05 (**1b**), the latter two with relative intensity of 1:1, 3.88 (sh) (**2b**), 4.10 (w, sh),[a] 4.50 (vw)[a]		88.81, 250.5 (**1a**); 90.61, 259.2 (**2a**); 89.40, 247.7 (**1b**); 91.27 (vw), 259.2 (**2b**); and very weak CO resonances at 234.5, 235.7, 246.4, 262.6, 268.9		−90
	4.07 (sh) (**1a**), 3.89 (**2a**), 4.13 (**1b**) with relative intensity 1:4:4 and very weak unresolved resonances [3.92 (w),[a] 3.95 (vw) (**2b**)], 4.53[a]		88.74 (**1a**); 90.61, 259.0 (**2a**); 89.32, 247.5 (**1b**); 91.23, 259.0 (**2b**); 91.93 (vw)[a]		−68

[a] New and ascribed to S-inserted complexes; v = very, w = weak, sh = shoulder. [b] At −80 °C.

from an intermolecular rearrangement of the S-inserted intermediate rather than *via* (**2b**), since the latter is known to be converted into (**1b**) at a much lower rate ($t_{\frac{1}{2}}$ *ca.* 2 h at 30 °C).[12] In fact, as indicated in Table 4, compound (**2b**) has only been observed in trace amounts at 70% conversion of (**1a**), when (**2a**) and (**1b**) are present in approximately equal amounts. It appears that (**2b**) is only formed in substantial quantity by a low-temperature degradation of the S-inserted intermediate, as observed in the reaction with 31.2 mol equivalents of S, which gave a 29% yield of (**2b**). The resonances of [$Cr_2(cp)_2(CO)_5E_2$] (**3a**; E = Se) and (**3b**; E = S) are not observed at all in the low-temperature spectra (Table 4) of the product mixture at 10, 20, and 70% conversion of (**1a**). The unassigned proton resonances, *viz.* δ 4.36 and 4.49 (−90 °C) at 10% conversion, δ 4.10 and 4.50 (−90 °C) at 70% conversion, and δ 3.92 and 4.53 (−68 °C) at 70% conversion, can be attributed to the hitherto unknown species [$Cr_2(cp)_2(CO)_4(SSe)$] and [$Cr_2(cp)_2(CO)_5(SSe)$]. The five weak CO signals in the ^{13}C spectrum at −90° C lend support to the presence of the latter pentacarbonyl complex.

Under 1 atm CO, a study at 8 °C showed that the conversion of compound (**1a**) into (**1b**) is retarded by a factor of 2—3. Also in contrast to the immediate formation of [$Cr_2(cp)_2(CO)_5(SSe)$] under argon, it is now observed that its formation is greatly inhibited. In fact, the resonance δ 4.46—4.48, assignable to the isomers of this species, is barely visible and only as a broad peak, with intensity increasing just slightly over 5 h. The only dominant product resonance was that at δ 4.05 of [$Cr_2(cp)_2(CO)_4Se_2$] (**2a**) with that at δ 4.11 of [$Cr_2(cp)_2(CO)_4S_2$] (**2b**) and/or [$Cr_2(cp)_2(CO)_4(SSe)$] (**2c**) becoming noticeable at 3 h. As expected, this inhibitory effect of CO was observed at ambient temperature, when the transformation process took 1 h to go to completion, instead of 20 min as observed under argon. The resonance at δ 4.08 of (**2a**) reaches a peak at 20 min with intensity half that of the resonance at δ 4.36. As at 8 °C, a weak broad band at δ 4.49, (**3c**), and a shoulder at δ 4.14, (**2b**), were observed from 4 min. In addition, an unidentified resonance was

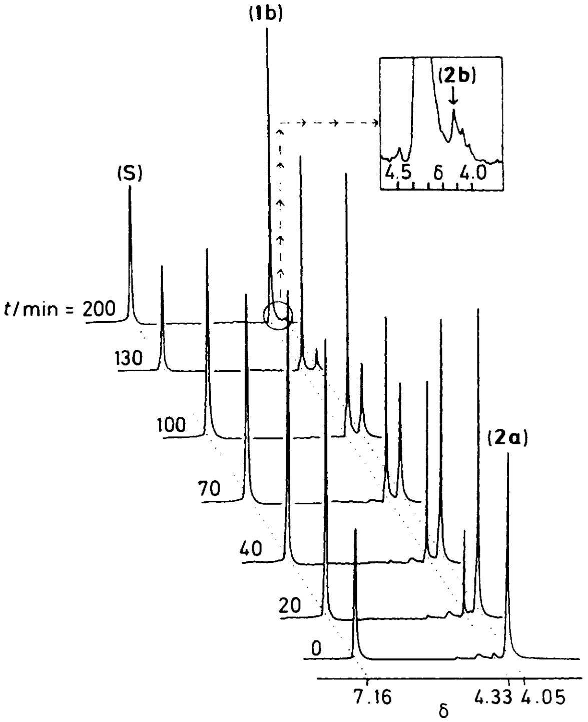


Figure 2. Time-dependent ^1H n.m.r. spectra for the reaction of a 0.044 mol dm^{-3} solution of [$Cr_2(cp)_2(CO)_4Se_2$] (**2a**) in C_6D_6 with 5.6 mol equivalents of sulphur at ambient temperature. Peaks were assigned as follows: (S) = solvent (δ 7.16); (**2a**), [$Cr_2(cp)_2CO)_4Se_2$] and/or its S-insertion intermediate (δ 4.05); (**1b**), [$Cr_2(cp)_2(CO)_4S$] (δ 4.33); (**2b**), [$Cr_2(cp)_2(CO)_4S_2$] (δ 4.11). Spectral scans at 8 °C. The spectrum at *t* = 0 was taken after 1.5 h at 8 °C

observed as a shoulder at δ 4.30. These observations imply that, under CO, the conversion of (**1a**) into (**1b**) occurs *via* a different pathway, which will be elaborated later.

(*ii*) *Reaction of* [$Cr_2(cp)_2(CO)_4Se_2$] (**2a**) *with* S_8. The time-dependent proton n.m.r. spectral changes (scanned at 8 °C) for the ambient-temperature reaction of a 0.044 mol dm^{-3} solution of compound (**2a**) in C_6D_6 with 5.6 mol equivalents of S are illustrated in Figure 2. The resonance at δ 4.05 decayed with $t_{\frac{1}{2}}$ of *ca.* 1 h, accompanied by a concurrent growth at δ 4.33, the cp resonance of [$Cr_2(cp)_2(CO)_4S$] (**1b**), and a simultaneous colour change from dark brown to dark muddy green. At *ca.* 2 h, the peak at δ 4.11 appeared as a shoulder on that at δ 4.05 and was more clearly defined at *ca.* 3 h. This same resonance, appearing as δ 4.135 at 28 °C and attributable to [$Cr_2(cp)_2(CO)_4S_2$] (**2b**), was found to persist up to 24 h when it still formed 12% of the product mixture, together with the degradation products of (**1b**),[6] *viz.* [$Cr_4(cp)_4(CO)_2S_2$] (δ 5.71, 10%) and [$Cr_4(cp)_4S_4$] (δ 4.90, 7%).

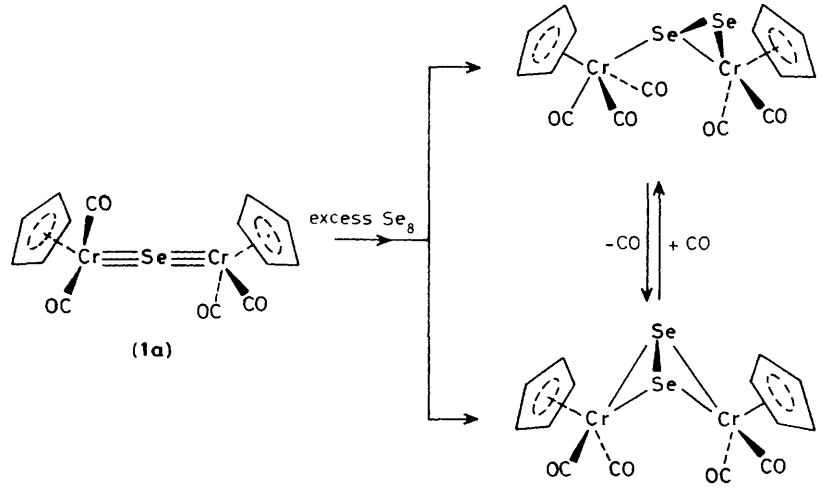
This reaction was found to be immeasurably slower at 8 °C. Hence the rapid decay of the resonance at δ 4.05 at 8 °C in Figure 1 implies that this resonance in the reaction of [$Cr_2(cp)_2(CO)_4Se$] with S_8 does not belong solely to (**2a**) or its S-insertion intermediate (see t.l.c. studies below), but also to (**3c**$_1$).

This conversion of compound (**2a**) into [$Cr_2(cp)_2(CO)_4S$] (**1b**) is consistent with the higher yield of isolated (**1b**) (Table 1) at the expense of (**2a**) at longer reaction times or with a large excess of S. Here again it is unfortunate that the S-inserted complex is not amenable to isolation and unambiguous characterisation, because it seems to possess identical n.m.r. and t.l.c. characteristics to those of (**2a**).

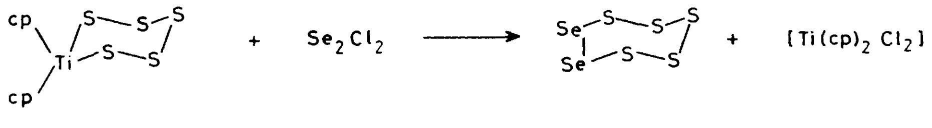
(*b*) *T.l.c. studies.* The spectral assignments given above were supported by a comparative t.l.c. study, alongside authentic dichalcogen complexes, as shown in Table 2. It was found that a reaction of (**1a**) for 2 min resulted in four different species, *viz.* two in the region of [$Cr_2(cp)_2(CO)_5E_2$], (**3c**$_1$) and (**3c**$_2$) not equivalent to either (**3a**) or (**3b**), and two in the region of [$Cr_2(cp)_2(CO)_4E_2$], corresponding to (**2a**) and an unknown (**2c**). Coupled with n.m.r. spectral observations discussed above, this behaviour led to the assignment of (**3c**$_1$) and (**3c**$_2$) to the two possible isomers of [$Cr_2(cp)_2(CO)_5(SSe)$] and (**2c**) to [$Cr_2(cp)_2(CO)_4(SSe)$]. This together with the gradual colour change of the spot at R_f 0.60 from orange to yellowish green is consistent with the transformation of (**1a**) to (**1b**), *via* a mechanism represented by the Scheme. All these spots persisted to the end of the observation period of 25 min. A sample after ageing overnight at −30 °C showed the presence of [$Cr_2(cp)_2(CO)_4Se_2$] (**2a**), [$Cr_2(cp)_2(CO)_4S_2$] (**2b**), and [$Cr_2(cp)_2(CO)_4S$] (**1b**). In the reaction of compound (**2a**), t.l.c. indicated an instantaneous complete conversion into an orange-brown immovable spot together with trace amounts of (**1b**), (**2b**), and an unknown with R_f = 0.70. Hence the resonance at δ 4.05 in Figure 2 found after *t* = 0 cannot be ascribed to (**2a**) but rather to an intermediate that is converted into (**2b**) and (**1b**).

Reaction Pathways.—The n.m.r. spectral and t.l.c. findings discussed above indicate reaction pathways represented in the Scheme. There is no doubt that two isomers of [$Cr_2(cp)_2(CO)_5(SSe)$] (**3c**) [recognisable by the similarity of their spectral and t.l.c. characteristics to those of [$Cr_2(cp)_2(CO)_5E_2$] (E = S or Se)] are first formed immediately on mixing of the reactants [pathway (i) in the Scheme]. The compound [$Cr_2(cp)_2(CO)_4(SSe)$] (**2c**) (δ 4.11) can be formed by a concurrent pathway (ii) and/or by decarbonylation [route (iii)] of the pentacarbonyl complexes (**3c**). The formation of (**2c**) is followed by a fairly rapid transformation (v) to [$Cr_2(cp)_2(CO)_4Se_2$] (**2a**), [$Cr_2(cp)_2(CO)_4S_2$] (**2b**), and [$Cr_2(cp)_2(CO)_4S$] (**1b**). The early formation of (**1b**) at ambient temperature, as observed in the t.l.c. studies, shows that it is derived together with (**2a**) mainly from an intermolecular rearrangement of (**2c**) rather than from (**2b**) by loss of an S atom [(vii)], as the latter process has been demonstrated to be much slower ($t_{\frac{1}{2}}$ *ca.* 2 h at 30 °C).[12] However, the transformation to (**1b**) *via* (**2b**) appears to be the preferred pathway at low temperatures, as observed in the product isolation at −30 °C.

As noted earlier, the presence of a CO atmosphere inhibits the rate of transformation of compound (**1a**) to (**1b**). This together with the failure to observe any (**2c**) (δ 4.11) in the n.m.r. spectrum (though a trace is seen in t.l.c.) is indicative of a suppression of route (iii) and supports a reversible process (iv). Under such circumstances, the predominant pathway to (**1b**) must be a slower alternative route (vi) *via* (**3c**) to (**2a**), (**1b**), and (**2b**) and finally to (**1b**) as the sole ultimate product. The inhibition by CO of the formation of (**3c**) seems to suggest that



(ix)



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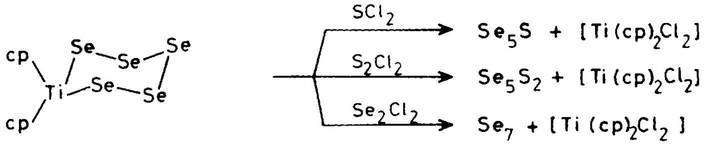

(xi)

the conversion (i) of (**1a**) into (**3c**) involves extensive Cr–CO bond breaking in the rate-determining step. It may be inferred that (i) is the dominant pathway rather than (ii), otherwise the presence of CO would enhance the formation of (**3c**) as observed in the case of $[Cr_2(cp)_2(CO)_4Se_2]$.[10]

The insertion of S into the Cr≡Se≡Cr bond of $[Cr_2(cp)_2(CO)_4Se]$ (**1a**) to form $[Cr_2(cp)_2(CO)_4(SSe)]$ (**2c**) and $[Cr_2(cp)_2(CO)_5(SSe)]$ (**3c**) is in accord with our earlier observations of the much slower insertion of Se into (**1a**) to yield $[Cr_2(cp)_2(CO)_4Se_2]$ and $[Cr_2(cp)_2(CO)_5Se_2]$ [equation (ix)].[10]

As far as we are aware, these examples are the only known cases of the insertion of main-group elements into multiple bonds between transition metals and bare main-group elements. The Cr≡Se triple bond does exhibit a very high reactivity, as is demonstrated by its thermolytic behaviour.[13]

An interesting and perhaps useful complementary result is the facile formation of S_7Se and S_6Se_2, considering that such interchalcogen compounds are often difficult to synthesise and separate.[14,15] A report of the formation of such compounds from organometallics comes from the reaction[16] represented by equations (x) and (xi), which provided a new route to cyclic six- and seven-membered selenium sulphides. The synthesis of cyclic eight-membered Se_4S_4 by similar crossover experiments has been reported very recently.[17]

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