

## Mono- and Di-selenium Complexes of Chromium. Syntheses and Crystal Structures of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{Se}$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{Se}_2$

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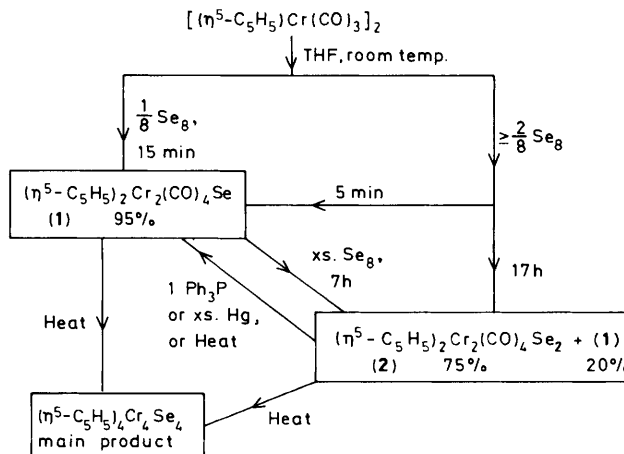
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The reaction of dicyclopentadienylhexacarbonyldichromium with elemental selenium at ambient temperature provides a simple route to  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{Se}$  (**1**) and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{Se}_2$  (**2**) in high yields.

There has been increasing interest recently in the syntheses, structure determinations, and reactivity of transition metal-chalcogen complexes.<sup>1-12</sup> However, examples of selenium complexes of the transition metals, first synthesised in 1958,<sup>4</sup> remain rare, and their syntheses from elemental selenium are very uncommon, with only a few known examples to date.<sup>5-7</sup> In particular, chromium-selenium complexes were unknown until the recent reports on  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{Se}$ .<sup>11,12</sup> We describe here the facile reactions (Scheme 1) of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$  with  $\text{Se}_8$  to give  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{Se}$  (**1**) and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{Se}_2$  (**2**), as well as their structures.

A deep-green stirred suspension in tetrahydrofuran (THF) of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$  and grey  $\text{Se}_8$  in 1/8 molar proportion per chromium dimer reacted completely under argon within 15 min at ambient temperature to give a red-brown homogeneous solution from which was isolated (**1**) as dark red-brown crystals in 95% yield (see Scheme 1). With a 2/8 molar proportion of  $\text{Se}_8$  per chromium dimer, (**1**) was again isolated in 95% yield after 5 min. With longer reaction times, (**2**) was formed at the expense of (**1**) and after 17 h at ambient temperature a mixture of (**1**) (18%) and (**2**) (74%) was obtained. When complex (**1**) was stirred with excess of  $\text{Se}_8$  powder during 7 h (**2**) was also obtained in 75% isolated yield. Compounds (**1**) and (**2**) were separated by fractional crystalli-

sation from toluene-n-hexane, and (**2**) was obtained as black-brown needles. One of the Se atoms in (**2**) was removed instantaneously by 1 equiv. of  $\text{Ph}_3\text{P}$  or slowly during 24 h by excess of Hg to give (**1**) quantitatively.

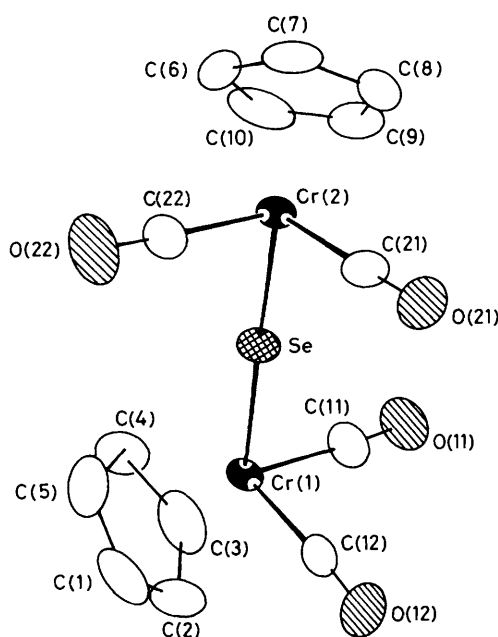


Scheme 1

**Table 1.** Spectral characteristics of (1) and (2).

Complex	N.m.r.		I.r., $\text{v}/\text{cm}^{-1}$ (KBr)	
	$^1\text{H}$ ( $\delta$ ) <sup>a</sup>	$^{13}\text{C}$ ( $\delta$ ) <sup>a</sup>	CO	Other
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{Se}$ (1) <sup>c</sup>	4.36 (s)	88.85 (s, $\text{C}_5\text{H}_5$ ), 249.05 (s, CO)	1975s, 1943s, sh, 1925vs, 1910vs, sh, 1892vs, 1868vs	3110vw, 1428m, 1067w, 915vw, 822s, 615m, 550s, sh, 527m, 487m
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{Se}_2$ (2) <sup>d</sup>	4.08 (s)	90.92 (s, $\text{C}_5\text{H}_5$ ), 224.6 (br.) <sup>b</sup>	2000vw, sh, 1945vs, 1900vs, 1890vs, 1833m	3100w, 2950w, 2920w, 1425m, 1350vw, 1120vw, 1065vw, 1015m, 860w, sh, 825s, 635m, 570s, 535m, 475m, 405w

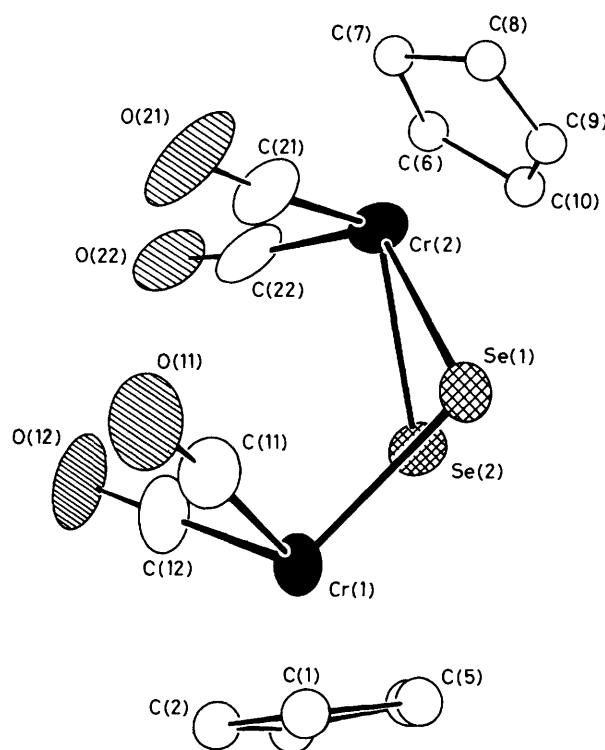
<sup>a</sup> Chemical shifts referred to  $\text{Me}_4\text{Si}$  in  $\text{C}_6\text{D}_6$ . <sup>b</sup> Line-width  $\sim 5$  p.p.m. (125 Hz). <sup>c</sup> Low-resolution mass spectrum:  $m/z$  425.853,  $(\eta^5\text{-C}_5\text{H}_5)_2^{52}\text{Cr}_2(\text{CO})_4^{80}\text{Se}$  (calc. 425.856); 369.85,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_2^{80}\text{Se}$ ; 341.87,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})^{80}\text{Se}$ ; 313.88,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2^{80}\text{Se}$ ; 248.84,  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}_2^{80}\text{Se}$ ; 183.79,  $\text{Cr}_2^{80}\text{Se}$ ; 182.01,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}$ ; 116.98,  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}$ ; and 131.85,  $\text{Cr}^{80}\text{Se}$ . <sup>d</sup>  $m/z$  for  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{Se}_2$  not observed. Under electron-impact conditions, spectrum shows decomposition and further reaction of the fragments.

**Figure 1.** Molecular structure of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{Se}$  (1). Bond angle at Se  $178.28(5)^\circ$ .

In solution under an inert atmosphere, (2) undergoes extrusion of a Se atom at ambient or elevated temperatures to yield initially (1) and finally a species identified so far only by its low resolution mass spectrum as  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_4\text{Se}_4$  ( $m/z$  788, calc. 787.6). Identical observations have been made with the S analogue of (1) and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_5\text{S}_2$ .<sup>13</sup> Complexes (1) and (2) are air-stable in the crystalline state and have been characterised by elemental analyses and X-ray crystallography. Spectral characteristics are given in Table 1.

Diffraction-quality polyfaceted crystals of (1) were obtained from THF-*n*-hexane-diethyl ether at  $-23^\circ\text{C}$  after a few hours. Fine needles of (2) were obtained overnight from toluene-*n*-hexane at  $-28^\circ\text{C}$ .

**Crystal data:** (1)  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2]_2\text{Se}$ ,  $M = 425$ . Orthorhombic, space group  $Pbca$ ,  $a = 12.228(3)$ ,  $b = 12.692(4)$ ,  $c = 19.980(5)$  Å;  $U = 3101$  Å<sup>3</sup>;  $Z = 8$ ,  $\mu(\text{Mo-K}\alpha) = 39.9$  cm<sup>-1</sup>. (2)  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2]_2\text{Se}_2$ ,  $M = 504$ . Monoclinic, space group  $P2_1/c$ ,  $a = 10.566(2)$ ,  $b = 12.983(3)$ ,  $c = 11.964(2)$  Å;  $\beta =$

**Figure 2.** Molecular structure of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{Se}_2$  (2). Bond angles at Se: Cr(1)-Se(1)-Cr(2)  $100.2(1)$ , Cr(1)-Se(1)-Se(2)  $63.6(1)$ , Cr(2)-Se(1)-Se(2)  $63.1(2)$ , Cr(1)-Se(2)-Cr(2)  $100.3(1)$ , Cr(1)-Se(2)-Se(1)  $63.3(1)$ , Cr(2)-Se(2)-Se(1)  $63.7(1)$ ; at Cr: Se(1)-Cr(1)-Se(2)  $53.1(1)$ , Se(1)-Cr(2)-Se(2)  $53.1(2)^\circ$ .

$101.05(3)^\circ$ ;  $U = 1611$  Å<sup>3</sup>;  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 62.7$  cm<sup>-1</sup>. † 1989 Unique reflections for (1) [ $F_o^2 > 3\sigma(F_o^2)$ ,  $1.5^\circ < 2\theta < 60^\circ$ , Mo-K $\alpha$ ] and 1119 unique reflections for (2) [ $F_o^2 > 3\sigma(F_o^2)$ ,  $1.5^\circ < 2\theta < 54^\circ$ , Mo-K $\alpha$ ] were measured on a Enraf-Nonius CAD-4 diffractometer. Both structures were solved by Patterson and Fourier synthesis and refined by

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

full-matrix least-squares<sup>14</sup> to  $R = 4.6\%$ ;  $R_w = 7.0\%$  for (1) and  $R = 5.5\%$ ,  $R_w = 6.0\%$  for (2). Their structures are shown in Figures 1 and 2.

The complex (1), containing an essentially linear Cr-( $\mu$ -Se)-Cr group, is structurally analogous to  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{S}$ ,<sup>1,3</sup> which possesses a three-legged piano stool arrangement of ligands around each Cr atom. The short Cr-Se distances (2.208–2.211 Å), compared with the sum of the covalent radii ( $r_{\text{Cr}} 1.18$ ,  $r_{\text{Se}} 1.17$  Å),<sup>15</sup> are consistent with multiple bonding that has been postulated for such systems.<sup>3,16</sup> They are also in agreement with the Cr-S distance in the S analogue, after allowing for the 0.13 Å difference in the covalent bond radii of S (1.04 Å) and Se (1.17 Å). The significance of this structural analysis is that this chromium-selenium complex also belongs to the family of MEM multiple-bond systems, which now also include complexes with  $M = V$  ( $E = S, \text{Se}, \text{or Te}$ ).<sup>8</sup>

The structure of (2) shows a  $\mu$ -Se<sub>2</sub> ligand bridging two metal atoms, the first instance of its kind for Cr and for a cyclopentadienylcarbonyl complex. The only other reported example is  $\text{Fe}_2(\text{CO})_6\text{Se}_2$ <sup>4,10</sup> to which it is structurally similar. Both complexes possess  $C_{2v}$  symmetry. However, the Cr-Se-Cr angle,  $100.25^\circ$  av., is much larger than the equivalent angle,  $66.1^\circ$  av., in the Fe complex. The effect of this difference is reflected in the greater bending of the CO ligands towards the Se<sub>2</sub> group in the Cr complex when compared to the distorted tetragonal pyramidal arrangement around the Fe atom. The Se-Se distance (2.277 Å) of the  $\mu$ -Se<sub>2</sub> group, like that in  $\text{Fe}_2(\text{CO})_6\text{Se}_2$  (2.293 Å), lies between that of a normal Se-Se single bond (2.336 Å) and that of an Se=Se double bond (2.19 Å).<sup>17</sup> The Cr atoms achieve the noble gas configuration, if we assume that the  $\mu$ -Se<sub>2</sub> ligand, like  $\mu$ -S<sub>2</sub> in  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cr}_2\text{S}_5$ , acts as a 6e donor.<sup>18</sup>

From the reactivity point of view the ability of (1) to cleave and react with cyclo-octaselenium to give (2) is a novel feature not described before for such MEM multiple bonded systems, and the mechanistic implications of this, together with that of the conversion of (1) and (2) to give  $(\eta^5\text{-C}_5\text{H}_5)_4\text{Cr}_4\text{Se}_4$ , are currently under investigation.

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