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Cyclopentadienyl chromium chalcogenide complexes. Synthesis of $[CpCr(EPh)]_2E$ (E = S, Se) and their $Cr(CO)_5$ adducts. Crystal structures of $[CpCr(SePh)]_2Se \cdot 1/2C_6H_6$ and $[CpCr(SePh)]_2Se[Cr(CO)_5]$

Lai Yoong Goh, Meng S. Tay, Yau Y. Lim, Wei Chen
Department of Chemistry, University of Malaya, 59100 Kuala Lumpur (Malaysia)

Zhong-Yuan Zhou and Thomas C.W. Mak
Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories (Hong Kong)

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Abstract

$[CpCr(EPh)]_2E$ (**1**, E = S; **2**, E = Se) reacts with $Cr(CO)_5THF$ to give the adducts $[CpCr(EPh)]_2E[Cr(CO)_5]$ (**3**, E = S; **4**, E = Se) in *ca.* 83% and 72% yields, respectively. In the presence of PPh_3 as a $Cr(CO)_5$ scavenger, **3** and **4** were converted back to **1** and **2**, respectively. The molecular structures of **2** and **4** as determined by X-ray crystallography are compared.

Introduction

The function of metal complexes as ligands in the synthesis of multinuclear aggregates has been extensively investigated in recent years [1]. It is well established that the uncoordinated electron pairs on the sulphido ligands of complexes are especially capable of coordinating to transition metal carbonyl fragments or generating higher nuclearity complexes by the coupling of small clusters [2–5]. In his extensive work on metal–metal bonded antiferromagnetic complexes, Pasynskii has successfully utilized the sulphido ligand in $[CpCr(\mu\text{-}SCMe_3)]_2S$ to generate a large variety of tri- and tetra-nuclear clusters [6], "bow-tie" penta-nuclear clusters [7], and recently octanuclear heterometallic clusters [8].

The use of selenium as a useful bridge in cluster build-up is much less documented, although Adams' work on some Os carbonyl complexes indicates a similarity in the role of Se and S in cluster synthesis [9].

Correspondence to: Dr. L.Y. Goh, Dr. W. Chen or Dr. T.C.W. Mak.

In the course of our study on the reaction of $[CpCr(CO)_3]_2$ with Ph_2E_2, we have isolated $[CpCr(\mu\text{-}EPh)]_2E$ (**1**, E = S [10]; **2**, E = Se [11]) as thermolysis products. Here we report the results of an investigation on the reactivity of these complexes with the $Cr(CO)_5$ fragment together with the molecular structures of **2** and its adduct $[CpCr(\mu\text{-}SePh)]_2Se[Cr(CO)_5]$ (**4**).

Experimental

General procedures and physical measurements

Inert-atmosphere manipulation techniques, and preparation of reagents and solvents were as previously described [12]. Ph_2E_2 (E = S, Se) were purchased from Fluka and used as supplied. Proton and ^{13}C NMR spectra were measured on a JEOL FX100 100-MHz spectrometer, and chemical shifts are relative to residual C_6H_6 in C_6D_6, $CHCl_3$ in $CDCl_3$ or to $SiMe_4$. IR spectra were measured on a Perkin–Elmer 1330 instrument. Elemental analyses were made by the Analytical Unit of the Research School of Chemistry, Australian National University, except for Cr, which we analysed as CrO_4^{2-} [13].

Preparation of $[CpCr(EPh)]_2E$

Complex 1 (E = S). This was synthesised in *ca.* 25% yield from the reaction of $[CpCr(CO)_3]_2$ with Ph_2S_2 at 80°C, as previously described [10].

Complex 2 (E = Se). This complex was isolated in 45.6% yield, from the reaction of $[CpCr(CO)_3]_2$ (200 mg, 0.50 mmol) with Ph_2Se_2 (155.3 mg, 0.50 mmol) in toluene (20 ml) at 60°C [11].

Reaction with $Cr(CO)_5THF$

Preparation of $[CpCr(SPh)]_2S[Cr(CO)_5]$ (3). A solution of $Cr(CO)_5THF$ (15.8 ml, 0.206 mmol), prepared as described by Strohmeier *et al.* [14], was added to a purple solution of $[CpCr(SPh)]_2S$ (**1**) (100 mg, 0.206 mmol) in THF (8 ml), and the mixture was stirred at ambient temperature. After 5 min, the solution had turned to greenish-brown, but the reaction was allowed to proceed for a further 30 min. The solution was then concentrated to dryness and the residue redissolved in *ca.* 1 ml toluene and chromatographed on a silica gel column (1 × 6 cm) prepared in n-hexane. Two fractions were collected: (i) a greenish-brown eluate in toluene (15 ml) which on concentration to *ca.* 2 ml and addition of n-hexane and cooling at −25°C yielded $[CpCr(SPh)]_2S[Cr(CO)_5]$ (**3**) (100 mg, 0.15 mmol, 71.6%). Anal. Found: C, 50.43; H, 3.31; S, 13.24; Cr, 21.26. $[CpCr(SPh)]_2S[Cr(CO)_5](1/2C_6H_6)$ calc.: C, 50.39; H, 3.25; S, 13.44; Cr, 21.79%. IR (nujol): ν(CO) 2050vs, 1990s, 1950ssh, 1935m, 1925wsh, 1915s, 1895vs cm^{-1}. ^1H NMR (C_6D_6): δ(cp) 20.79 ($\nu_{1/2}$ 180 Hz); $\delta(C_6H_5)$ obscured by solvent peaks. ^{13}C NMR ($CDCl_3$): δ(cp) 101.83 ($\nu_{1/2}$ 30 Hz), δ(CO) 207.78, 211.42, 238.98. FAB^+ mass spectrum: *m/e* 676 $\{[CpCr(SPh)]_2S[Cr(CO)_5]\}$, 536 $\{[CpCr(SPh)]_2SCr\}$, 485 $\{[CpCr(SPh)]_2S\}$, 375 $\{[Cp_2Cr_2(SPh)]S\}$, 226 $\{CpCr(SPh)\}$, and (ii) a purple fraction in ether (5 ml) which on dryness gave unreacted $[CpCr(SPh)]_2S$ (10 mg, 0.02 mmol, 10%).

Preparation of $[CpCr(SePh)]_2Se[Cr(CO)_5]$ (4). To a bluish purple solution of **2** (100 mg, 0.16 mmol) in THF (10 ml) was added a THF solution of $Cr(CO)_5THF$ (12.3 ml, 0.16 mmol). The mixture was stirred at ambient temperature for 30 min, although it had attained a permanent greenish-brown colour after 5 min. The solution was then concentrated to dryness, redissolved in toluene (*ca.* 1 ml) and loaded onto a silica gel column (1.5 × 5 cm) prepared in n-hexane. Chromatography gave two fractions: (i) a greenish-brown solution in toluene (20 ml), which yielded after concentration to *ca.* 2 ml, followed by addition of n-hexane and cooling at −35°C, brown crystals of $[CpCr(SePh)]_2Se[Cr(CO)_5]$ (**4**) (108 mg, 0.13 mmol, 82.6%) and (ii) a bluish-purple fraction in ether (5 ml) which on dryness gave unreacted $[CpCr(SePh)]_2Se$ (5 mg, 0.006 mmol, 5%). Data for (**4**): Anal. Found: C, 40.05; H, 3.26; Cr, 19.63. $[CpCr(SePh)]_2Se[Cr(CO)]_5$ calc.: C, 39.68; H, 2.47; Cr, 19.08%. IR (nujol): ν(CO) 2055vs, 1980s, 1930m, 1915m, 1890vs cm^{-1}. ^1H NMR (C_6D_6): δ(cp) 25.57 ($\nu_{1/2}$ 210 Hz); $\delta(C_6H_5)$ obscured by solvent peaks. ^{13}C NMR ($CDCl_3$): δ(cp) 99.52 ($\nu_{1/2}$ 36 Hz); δ(CO) 190.0, 190.4, 229.6. FAB^+ mass spectrum: *m/e* for ^{80}Se, 820 {$[CpCr(SePh)]_2Se[Cr(CO)_5]$}, 708 {$[CpCr(SePh)]_2Se[Cr(CO)]$}, 680 {$[CpCr(SePh)]_2SeCr$}, 628 {$[CpCr(SePh)]_2Se$}.

Reaction of $Cr(CO)_5$ adducts with PPh_3

(i) To a brownish-purple solution of $[CpCr(SPh)]_2S[Cr(CO)_5]$ (**3**) (4 mg, 0.0059 mmol) in THF (3 ml) was added PPh_3 (3.1 mg, 0.012 mmol) and the mixture stirred at ambient temperature for 24 h. The reaction solution was examined at intervals by TLC on Merck Kieselgel 60 (0.25 mm) plates. The chromatogram of the resulting brownish-purple solution at the end of 24 h showed mainly $[CpCr(SPh)]_2S$ (**1**) ($R_f = 0.25$) with a trace of unreacted (**3**) ($R_f = 0.69$) with toluene as eluent.

(ii) To a greenish-brown solution of $[CpCr(SePh)]_2Se[Cr(CO)_5]$ (**4**) (4 mg, 0.0049 mmol) in THF (3 ml) was added PPh_3 (2.56 mg, 0.010 mmol) and the mixture stirred at ambient temperature. Similar monitoring of the reaction as above showed that after 24 h, the resulting brownish-purple solution contained mainly $[CpCr(SePh)]_2Se$ (**2**) and a trace of unreacted **4** ($R_f = 0.37$ and 0.40, respectively, with n-hexane/toluene (1 : 1) as eluent).

Crystal structure determination

Deep-purple diffraction-quality cuboidal-shaped crystals of $[CpCr(SePh)]_2Se$ (**2**) were obtained from a solution in benzene/ether after 2 days at room temperature. Brown thick rectangular plates of $[CpCr(SePh)]_2Se[Cr(CO)_5]$ (**4**) were obtained from a solution in toluene/ether after a day at −30°C.

Data collection and processing. Details of crystal parameters, data collection and structure refinement are given in Table 1.

Crystal (2). The crystal was coated with epoxy glue to prevent decomposition by air.

Accurate cell dimensions and space group data were obtained from 25 strong reflections in the $28° < 2\theta < 32°$ shell. A total of 3616 reflections were collected on an Enraf–Nonius CAD4 four-circle diffractometer at ambient temperature (299 K) and were processed. Lorentz polarization, linear decay and absorption corrections [15] were applied. Two Se atoms were located from a Patterson map and the remaining non-hydrogen atoms from successive difference Fourier maps, and were refined anisotropically. The hydrogen atoms were generated geometrically at C–H = 0.95 Å and allowed to ride on their respective parent C atoms with $B = 1.3$ times that of the parent atom. A benzene molecule was found trapped in the crystal at the centre of inversion.

Table 1

Data collection and processing parameters

	2	4
Molecular formula	$(C_6H_5Se)_2Se(C_5H_5Cr)_2 \cdot \frac{1}{2}C_6H_6$	$(C_6H_5Se)_2[SeCr(CO)_5]$-$(C_5H_5Cr)_2$
Molecular weight	664.33	817.35
Colour and habit	Black plate	Black plate with (100) well-developed
Unit cell parameters		
a (Å)	9.566(2)	10.115(5)
b (Å)	10.240(2)	18.022(5)
c (Å)	13.205(3)	15.807(5)
V (Å^3)	1213.1(5)	2870(2)
Z	2	4
α (°)	102.85(2)	
β (°)	101.39(2)	95.14
γ (°)	98.07(2)	
$F(000)$	646	1584
Density (calc.) (g cm^{-3})	1.82	1.89
Space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
Radiation	Graphite-monochromatized Mo-K_α, $\lambda = 0.71073$ Å	graphite-monochromatized Mo-K_α, $\lambda = 0.71073$ Å
Standard reflections	$(\bar{2}\bar{4}\bar{2})(0\bar{5}\bar{2})(\bar{1}\bar{5}\bar{2})$	(041), (002)
Intensity variation	–	±1%
R_{int} (from merging of equiv. reflections)	–	0.020
Absorption coefficient (cm^{-1})	53.47	48 92
Crystal size (mm^3)	< 0.3	0.44×0.34×0.08
Mean μ_r	–	0.70
Transmission factors	–	0.282–0.784
Scan type and rate	ω–2θ	ω-scan; 3.005–15.625 deg min^{-1}
Scan range	–	0.60° below K_{α_1} to 0.80° above K_{α_2}
Background counting	–	Stationary counts for one-fifth of scan time at each end of scan range
Collection range	$h, k, \pm l$ $2\theta_{max} = 46°$	$h, k, \pm l$; $2\theta_{max} = 50°$
Unique data measured	3370	4051
Obs. data, n	2284 with $I \geq 3\sigma(I)$	2395 with $\lvert F_o \rvert \geq 6\sigma(\lvert F_o \rvert)$
No. of variables, p	271	343
$R_F = \Sigma \lVert F_o - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0 040	0.051
Weighting scheme	$w = [\sigma^2(F) + 0.0004F^2 + 1]^{-1}$	$w = [\sigma^2(F_o) + 0.0004 \lvert F_o \rvert^2]^{-1}$
$R_G = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w \lvert F_o \rvert^2]^{1/2}$	0.046	0.057
$S = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / (n - p)]^{1/2}$	0.616	1.730
Residual extrema in final difference map (e Å^{-3})	0.79 (max)	+1.00– –0.53

Computations were performed using the MOLEN program package [16] on a DEC MicroVAX-II Computer. Analytic expressions of neutral atom scattering factors were employed and anomalous dispersion corrections were incorporated

[17]. Atomic coordinates and their equivalent isotropic displacement parameters of the non-hydrogen atoms are given in Table 2A.

Crystal (4). Raw intensities collected on a Nicolet R3m/V four-circle diffractometer at room temperature (294 K) were processed with the profile-fitting procedure of Diamond [18] and corrected for absorption using ψ-scan data [15]. Patterson superposition yielded the position of the three chromium and three selenium atoms of **4**. The coordinates of the other non-hydrogen atoms were derived from successive difference Fourier syntheses. The non-hydrogen atoms were subjected to anisotropic refinement and the H atoms were generated geometrically (C–H bonds fixed at 0.96 Å) and assigned the same isotropic temperature factor of $U = 0.08$ Å^2. Computations were performed using the SHELXTL-PLUS program package [19] on a DEC MicroVAX-II computer. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated [16]. The atomic coordinates are given in Table 2B.

Table 2A

Positional parameters and their estimated standard deviations for **2**

Atom	x	y	z	B_{eq} [a]
Se1	0.0208(1)	0.2082(1)	0.47961(8)	3.90(2)
Se2	0.2231(1)	0.4330(1)	0.40245(8)	3.55(2)
Se3	0.1220(1)	0.1225(1)	0.21745(7)	3.02(2)
Cr1	0.2319(2)	0.1931(2)	0.4120(1)	3.19(4)
Cr2	−0.0132(2)	0.2750(2)	0.3170(1)	2.91(3)
C1	0.311(1)	0.076(1)	0.525(1)	6.3(3)
C2	0.393(1)	0.201(1)	0.5588(9)	5.5(3)
C3	0.468(1)	0.226(1)	0.4856(9)	5.3(3)
C4	0.434(1)	0.112(1)	0.401(1)	5.5(3)
C5	0.335(1)	0.016(1)	0.426(1)	7.8(4)
C6	−0.252(1)	0.209(1)	0.253(1)	5.3(3)
C7	−0.224(1)	0.327(1)	0.335(1)	6.2(3)
C8	−0.149(1)	0.429(1)	0.307(1)	6.5(4)
C9	−0.127(1)	0.377(1)	0.206(1)	6.2(3)
C10	−0.193(1)	0.243(1)	0.1746(9)	5.7(3)
C11	0.409(1)	0.423(1)	0.2519(9)	4.8(3)
C12	0.468(1)	0.467(1)	0.1773(9)	5.8(3)
C13	0.419(1)	0.563(1)	0.134(1)	6.5(3)
C14	0.310(2)	0.622(1)	0.1664(9)	6.6(4)
C15	0.250(1)	0.59(1)	0.243(1)	5.3(3)
C16	0.301(1)	0.4801(9)	0.2875(7)	3.5(2)
C17	−0.057(1)	−0.117(1)	0.2445(8)	4.2(3)
C18	−0.138(1)	−0.245(1)	0.2116(8)	5.1(3)
C19	−0.157(1)	−0.321(1)	0.1097(9)	5.4(3)
C20	−0.092(1)	−0.268(1)	0.0426(9)	5.1(3)
C21	−0.006(1)	−0.138(1)	0.0759(8)	4.1(3)
C22	0.010(1)	−0.0602(9)	0.1814(7)	3.1(2)
C23	0.441(2)	−0.027(1)	0.080(1)	8.3(4)
C24	0.404(1)	0.070(1)	0.034(1)	8.0(4)
C25	0.461(1)	0.098(1)	−0.044(1)	7.3(4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

Table 2B

Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors [a] ($Å^2 \times 10^4$ for Se and Cr; $\times 10^3$ for other atoms) for **4**

Atom	x	y	z	U_{eq}
Se(1)	1607(1)	528(1)	2477(1)	478(4)
Se(2)	342(1)	2322(1)	1745(1)	524(4)
Se(3)	2627(1)	2076(1)	3531(1)	485(4)
Cr(1)	394(2)	1563(1)	3056(1)	467(6)
Cr(2)	2529(2)	1698(1)	2022(1)	451(6)
Cr(3)	2854(2)	−303(1)	3667(1)	538(7)
O(1)	55(11)	−860(6)	3798(5)	78(4)
O(2)	3194(10)	−1504(6)	2370(5)	87(4)
O(3)	5553(10)	340(7)	3373(6)	97(5)
O(4)	2689(11)	721(5)	5200(5)	82(4)
O(5)	4068(13)	−1407(6)	4913(6)	106(5)
C(1)	−1285(14)	851(9)	3392(8)	76(6)
C(2)	−1805(15)	1532(12)	3073(9)	87(7)
C(3)	−1334(16)	2098(9)	3620(11)	90(7)
C(4)	−488(15)	1742(9)	4282(8)	78(6)
C(5)	−493(13)	1008(8)	4121(7)	61(5)
C(6)	3982(21)	2452(10)	1463(13)	99(9)
C(7)	4655(16)	1930(15)	1919(9)	96(8)
C(8)	4375(18)	1254(10)	1563(12)	90(7)
C(9)	3480(18)	1348(11)	865(10)	88(8)
C(10)	3225(17)	2092(14)	808(9)	94(8)
C(11)	−381(13)	1181(7)	463(6)	58(5)
C(12)	−1256(15)	849(8)	−144(7)	74(6)
C(13)	−2540(16)	1107(10)	−266(7)	82(7)
C(14)	−2994(15)	1670(10)	180(8)	82(6)
C(15)	−2099(13)	2014(8)	778(7)	71(6)
C(16)	−806(11)	1774(7)	922(6)	50(4)
C(17)	1481(13)	3575(7)	3430(7)	62(5)
C(18)	1574(15)	4345(8)	3438(7)	71(6)
C(19)	2774(14)	4688(7)	3534(6)	63(5)
C(20)	3900(14)	4268(8)	3549(8)	73(6)
C(21)	3853(13)	3489(7)	3546(7)	61(5)
C(22)	2611(13)	3158(6)	3493(6)	49(4)
C(23)	1122(14)	−658(7)	3771(7)	56(5)
C(24)	3046(13)	−1024(8)	2839(6)	62(5)
C(25)	4552(14)	103(8)	3490(7)	67(5)
C(26)	2744(14)	358(8)	4598(7)	65(5)
C(27)	3584(16)	−968(8)	4447(7)	74(6)

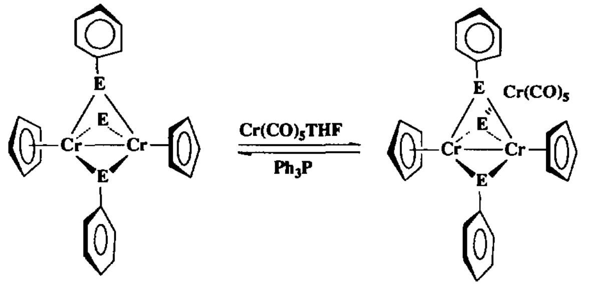
[a] U_{eq} defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and discussion

Reaction with $Cr(CO)_5THF$

$[CpCr(EPh)]_2E$ (E = S, Se) reacts readily at ambient temperature with $Cr(CO)_5THF$ to give adducts $[CpCr(EPh)]_2E[Cr(CO)_5]$ (**3**, E = S; **4**, E = Se) as black crystals in *ca.* 72 and 83% yields, respectively (eq. 1).

By means of diagnostic TLC, it was demonstrated that PPh_3 will abstract the $Cr(CO)_5$ fragment from **3** and **4** resulting in their reversion to **1** and **2**, respectively.



1, E=S
2, E=Se

3, E=S
4, E=Se

(1)

The adducts **3** and **4** are close analogues of $(CpCrSCMe_3)_2SM(CO)_5$ (M = Cr, Mo and W), formed from the photochemical reaction of $(CpCrSCMe_3)_2S$ with $M(CO)_6$ [20]. As in the case of the $SCMe_3$ complex, the additional coordination of the thiolate bridge S atoms to $Cr(CO)_4$ to form a chelate complex, has not been observed to occur. Pasynskii had attributed this finding to the large M–S (sulphide) distance leading to the large M $\cdots$ S (thiolate) separation, and to the repulsion between S and two nearest equatorial CO groups around the octahedrally coordinated M atoms. In fact, the intact S (thiolate) group has not been observed to coordinate at all in any of Pasynskii's complexes, e.g. $[CpCr(SCMe_3)]_2SMn(CO)_nCp$ ($n = 2, 3$) [6a] and $[CpCr(SCMe_3)]_2SMn_2(CO)_9$ [21]. The SR group only coordinates as S(sulphide) after cleavage of R, to form for instance $[(MeCp)_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2]$ M, where $M = Fe(CO)_3$ [22], $M = Co(CO)_2$ [21,23] and $Mn(CO)_3$ [23], $M = RhL_2$ for $L = \pi\text{-}C_8H_{12}$ or $(CO)_2$ [24], the heterometallospirane clusters $[Cp_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2]_2M$ where M = Cr [25], M = Mn [7], $M = Mn^{II}$ and Fe^{II} [26] and the "butterfly" clusters, $[Cp_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)]M$ where both SR groups have been cleaved, $M = Cp_2Ni_2$ [27] and $M = Co_2(CO)_4$ [6c].

Structures

The bonding parameters of **2** and **4** are given in Table 3 and the perspective view of their structures given in Figs. 1 and 2. The complex **2** is isostructural with its S analogue **1** [10]. As shown in Table 4, their unit cell dimensions are almost identical, with those of **2** just slightly expanded in all three axes. The structure of **1** which closely resembles that of the analogous bis(μ-t-butylthiolate) complex [28], has been previously described in detail [10]. As in these earlier examples, the Cr–Cr bond distance (2.762 Å) in **2** is significantly shorter than the Cr–Cr single bond distance in the related dinuclear $[CpCr(\mu\text{-}SR)(NO)]_2$ complexes (2.906 Å for $R = {}^tBu$ [29]; 2.950 Å for R = Ph [30]). This is in agreement with the existence of a M≡M triple bond as required by the demands of the 18-electron rule. Similarly, as in the structure of **1**, the Cr–Se (selenido) distance (av. 2.373 Å) is shorter than the Cr–Se (selenolato) distance (av. 2.484 Å). The difference (0.11–0.12 Å) between the Cr–S and Cr–Se distances merely reflects the difference between the covalent radii of S and Se (0.15 Å). The Cr–Cp distance in **2** (2.20 Å) is unexpectedly much longer than that in **1** (1.88 Å). Although steric overcrowding around the Cr_2Se_3

Table 3

Selected bond lengths (Å) and bond angles (°) of **2** and **4** [a]

	2	**4**		**2**	**4**
Se(1)–Cr(1)	2.375(2)	2.454(3)	Se(2)–Cr(1)	2.500(2)	2.478(2)
Se(1)–Cr(2)	2.371(2)	2.439(2)	Se(2)–Cr(2)	2.480(2)	2.485(3)
Se(1)–Cr(3)	–	2.637(2)	Se(2)–C(16)	1.94(1)	1.94(1)
Se(3)–Cr(1)	2.473(2)	2.493(3)	C(23)–C(24)	1.32(2)	–
Se(3)–Cr(2)	2.483(2)	2.475(2)	C(24)–C(25)	1.32(2)	–
Se(3)–C(22)	1.928(9)	1.95(1)	⟨Cr(2)–C(cp)⟩	2.20(1)	2.22(2)
⟨Cr(1)–C(cp)⟩	2.21(1)	2.23(2)	$\langle C–C \rangle_{phenyl}$	1.36(2)	1.38(2)
$\langle C–C \rangle_{cp}$	1.37(2)	1.38(2)			
Cr(1)–Se(1)–Cr(2)	71.2(1)	70.7(1)	Cr(1)–Se(1)–Cr(3)	–	112.9(1)
Cr(2)–Se(1)–Cr(3)	–	122.0(1)	Cr(1)–Se(2)–Cr(2)	67.4(1)	69.6(1)
Cr(1)–Se(2)–C(16)	113.1(3)	104.3(3)	Cr(2)–Se(2)–C(16)	106.5(2)	111.0(4)
Cr(1)–Se(3)–Cr(2)	67.7(1)	69.5(1)	Cr(1)–Se(3)–C(22)	108.7(3)	110.9(4)
Cr(2)–Se(3)–C(22)	106.8(3)	104.3(3)			
Se(1)–Cr(1)–Se(2)	84.1(1)	94.7(1)	Se(1)–Cr(1)–Se(3)	100.5(1)	85.7(1)
Se(2)–Cr(1)–Se(3)	87.1(1)	89.9(1)	Se(1)–Cr(1)–Cr(2)	54.4(1)	54.4(2)
Se(2)–Cr(1)–Cr(2)	56.0(1)	55.3(2)	Se(3)–Cr(1)–Cr(2)	56.3(1)	54.9(2)
Se(1)–Cr(2)–Se(2)	84.6(1)	94.9(1)	Se(1)–Cr(2)–Se(3)	100.4(1)	86.4(1)
Se(2)–Cr(2)–Se(3)	87.4(1)	90.2(1)	Se(1)–Cr(2)–Cr(1)	54.5(1)	54.9(2)
Se(2)–Cr(2)–Cr(1)	56.7(1)	55.1(2)	Se(3)–Cr(2)–Cr(1)	56.0(1)	55.5(2)
Se(1)–Cr(3)–C(23)	–	82.3(4)	C(26)–Cr(3)–C(27)	–	86.4(6)
C(23)–Cr(3)–C(24)	–	88.9(6)	Se(1)–Cr(3)–C(25)	–	93.2(4)
C(23)–Cr(3)–C(25)	–	175.5(5)	C(24)–Cr(3)–C(25)	–	90.7(6)
Se(1)–Cr(3)–C(26)	–	98.0(4)	C(23)–Cr(3)–C(26)	–	91.5(6)
C(24)–Cr(3)–C(26)	–	173.8(5)	C(25)–Cr(3)–C(26)	–	89.4(6)
Se(1)–Cr(3)–C(27)	–	173.1(5)	C(23)–Cr(3)–C(27)	–	92.3(6)
C(24)–Cr(3)–C(27)	–	87.4(6)	C(25)–Cr(3)–C(27)	–	92.1(6)
Se(2)–C(16)–C(15)	118.8(9)	117.1(9)	Se(3)–C(22)–C(17)	126.5(7)	
Se(3)–C(22)–C(21)	115.9(8)	115.0(9)	C(23)–C(24)–C(25)	121.0(1)	
Se(2)–C(16)–C(11)	122.4(8)	123.5(9)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

skeleton is probably a contributing factor for this large difference, the real basis for this observation remains unclear.

As shown in Table 4, the $Cr(CO)_5$ adducts, **3** and **4**, each possesses very different unit cell dimensions, which are in turn very different from those of their parent compounds, **1** and **2**, respectively. The Cr–Cr distance (2.833 Å) in **4**, although longer than those in **1** and **2**, is still shorter than previously observed Cr–Cr single bond distances [29,30] and therefore indicative of some degree of Cr–Cr multiple bonding. The narrower range of values for bonding parameters observed in **4** shows a structure more regular than that of the parent complex (**2**). The data in Table 4 show that the differences in the measured Cr–E^c, Cr–E^d, E–Ph and E–$Cr(CO)_5$ distances for each pair of related S and Se complexes (*i.e.* in comparing **1** with **2** and **3** with **4**) are entirely consistent with the difference in covalent radii (1.17 − 1.02 = 0.15 Å) of the S and Se atoms.

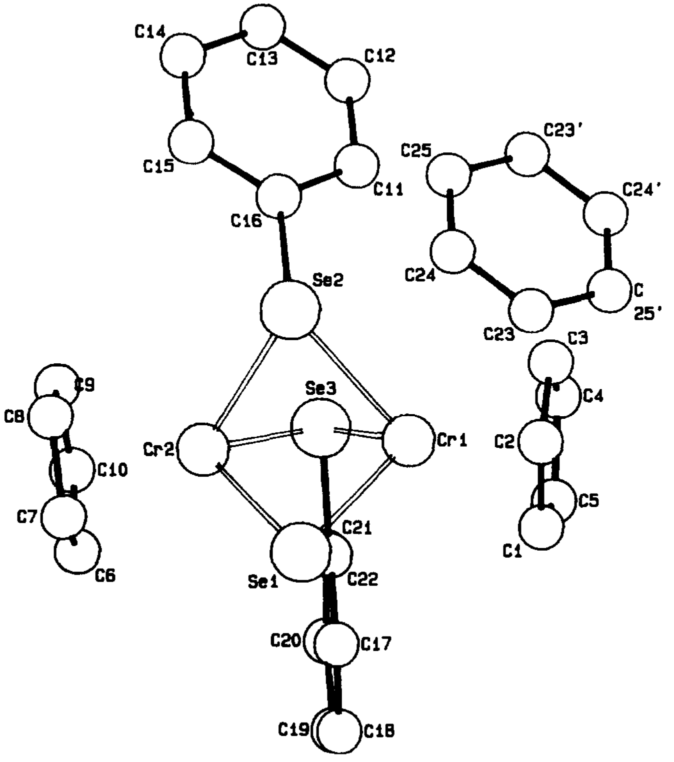


Fig. 1. Perspective view of the molecular structure of $[CpCr(SePh)]_2Se$ $1/2C_6H_6$

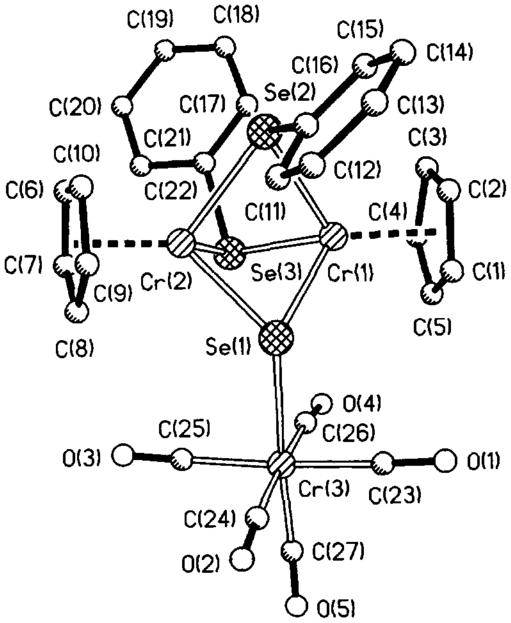


Fig. 2. Perspective view of $Cp_2Cr_2(SePh)_2Se[Cr(CO)_5]$.

Table 4

Space group, unit cell dimensions and some significant bonding parameters of complexes 1–4

	$[CpCr(EPh)]_2E\cdot 1/2C_6H_6$		$[CpCr(EPh)]_2ECr(CO)_5$	
	E = S (1) [a]	E = Se (2)	E = S (3) [b]	E = Se (4)
a (Å)	9.548(1)	9.566(2)	9 9214(9)	10.115(5)
b (Å)	10.122(2)	10.240(2)	10 137(1)	18.022(5)
c (Å)	13.003(1)	13.205(3)	17 210(2)	15.807(5)
α (°)	103.71(1)	102.85(2)	93 506(8)	90
β (°)	100.351(9)	101.39(2)	91.562(8)	95 14(3)
γ (°)	98.62(1)	98.07(2)	114.597(8)	90
V ($Å^3$)	1176.4(3)	1213.1(5)	1568 3(3)	2870(2)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Z	2	2	2	4
Cr–Cr (Å)	2.676(1)	2.762(2)	2.730	2.833(3)
Cr–E (Å) [c]	2.371(1) (2.365–2 383)(1)	2.484(2) (2.473–2.500)(2)	2.355 (2.347–2 361)	2 483(3) (av) (2.475–2.493)(3)
Cr–E (Å) [d]	2.250(1) (2.248, 2.251)(2)	2.373(2) (2.371, 2.375)(2)	2.293 (2.292, 2.294)	2 441(3) (av) (2.439, 2.454)(3)
E–Ph (Å)	1.783(4), 1.791(5)	1.928(9), 1.94(1)	1.785, 1.83 [e]	1.95(1), 1.94(1)
⟨Cr–Cp⟩ (Å)	1.876(6), 1.885(6)	2.20(1), 2.21(1)	2.22, 2 19	2.23(2), 2.22(2)
E–$Cr(CO)_5$ (Å)	–	–	2.49	2.637(2)
E–Cr–E (°)	84.2–98.4(1)	84.05–100.54(6)	83.72–93.53	85.7–94.9(1)
Cr–E–Cr (°)	68.6–73.0(1)	67.37–71.18(6)	70.64–73.04	69.5–70.7(1)

[a] Ref. 10. [b] Unpublished results. [c] Thiolato/selenolato. [d] Sulfido/selenido. [e] Disordered.

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