

(Pentamethylcyclopentadienyl)selenium Derivatives. 5.¹ Bis(pentamethylcyclopentadienyl)selenium and Its Reactions with Transition-Metal Carbonyls

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The first cyclopentadienylselenium derivative, $\text{Se}(\text{C}_5\text{Me}_5)_2$ (**1**), has been prepared by the reaction of LiC_5Me_5 with selenium bis(diethylthiocarbamate). Steric crowding about the selenium atom in **1** results in long Se–C bonds and an expanded C–Se–C angle, giving rise to unprecedented reactivity. Treatment of **1** with sources of $\text{M}(\text{CO})_5$ fragments yields the terminal diselenide complexes $[\text{M}(\text{CO})_5\{\text{Se}_2(\text{C}_5\text{Me}_5)_2\}]$ ($\text{M} = \text{Cr}, \text{W}$) via reduction within the transition-metal coordination sphere. Reaction of **1** with $[\text{Fe}_2(\text{CO})_9]$ leads to loss of both C_5Me_5 groups and formation of $[\text{Fe}_3\text{Se}_2(\text{CO})_9]$.

Introduction

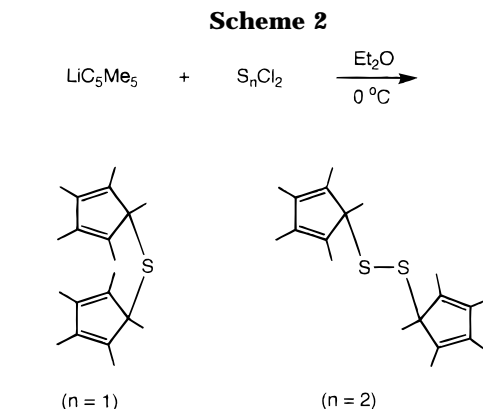
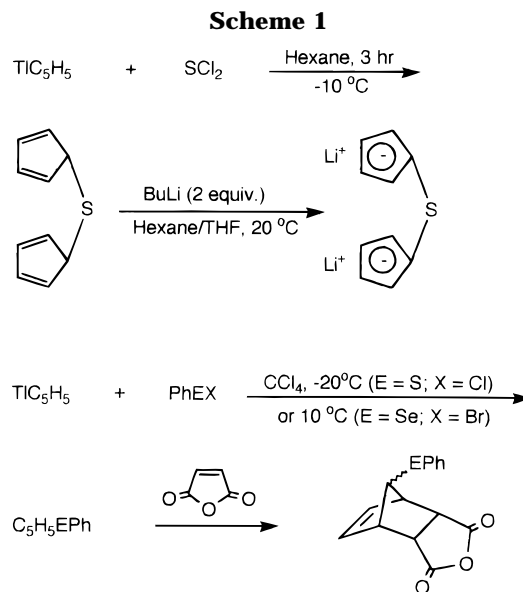
Although cyclopentadienyl derivatives of main-group elements have attracted considerable attention in recent years,² compounds of the group 16 elements (the chalcogens) are still rare. The unsubstituted compound $\text{S}(\text{C}_5\text{H}_5)_2$ is known as a thermally unstable oil but may be deprotonated to a dianion suitable for forming sulfur-bridged metallocenophanes.³ Diels–Alder adducts of the intermediates $\text{S}(\text{C}_5\text{H}_5)\text{Ph}$ and $\text{Se}(\text{C}_5\text{H}_5)\text{Ph}$ have also been prepared⁴ (Scheme 1).

Permethylation of the cyclopentadienyl ring generally facilitates the isolation of such compounds: bis(pentamethylcyclopentadienyl)sulfur has been prepared⁵ as a crystalline solid by the reaction of LiC_5Me_5 with SCl_2 . The disulfide $\text{S}_2(\text{C}_5\text{Me}_5)_2$ may be made by an analogous route (Scheme 2).

A number of mono(pentamethylcyclopentadienyl)sulfur derivatives is also known (Scheme 3).⁶

More recently, the ionic species $[\text{S}(\text{C}_5\text{Me}_5)_2\text{Me}_2]^+[\text{BF}_4]^-$ has been produced by trapping the antiaromatic cation in pentamethylcyclopentadienyl tetrafluoroborate, $[\text{C}_5\text{Me}_5]^+[\text{BF}_4]^-$, with the nucleophile SMe_2 (Scheme 4).⁷

The corresponding selenium and tellurium chemistry has not previously been explored. We now report the preparation of the first thermally stable cyclopentadienylselenium derivative, $\text{Se}(\text{C}_5\text{Me}_5)_2$ (**1**), and its reactivity toward some zerovalent metal carbonyls. Preliminary communications of parts of this work have already been published.^{8,9}



Experimental Section

All reactions were performed using standard Schlenk techniques and predried solvents under an atmosphere of dinitrogen. ¹H and ¹³C NMR spectra: Bruker AC400; tetramethylsilane as internal standard. ⁷⁷Se NMR spectra: Bruker WM250; dimethyl selenide as external standard. IR spectra: Perkin-Elmer 1725X. UV/vis spectra: Perkin-Elmer Lambda 9. Cyclic voltammetry: EG & G Model 273 scanning poten-

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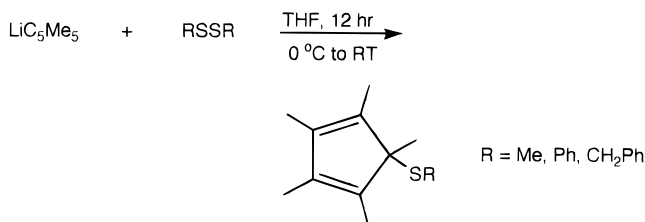
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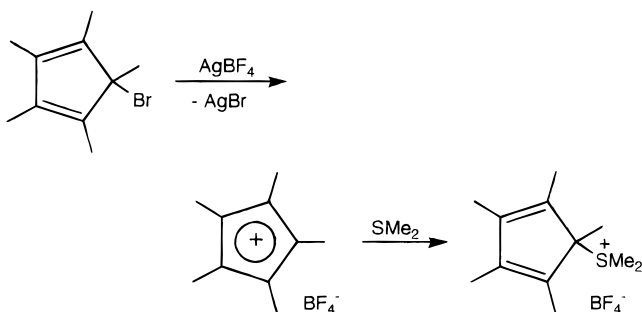
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Scheme 3



Scheme 4

Table 1. ¹H NMR Spectra

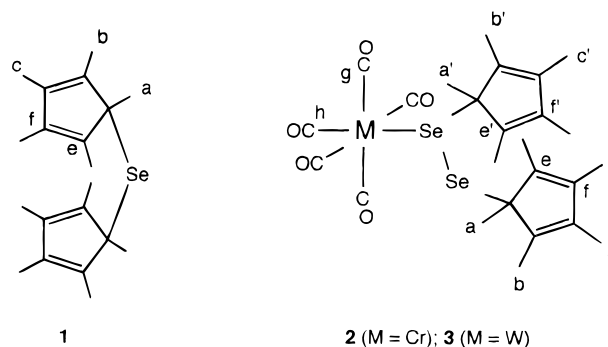
compd (solvent)	chem shift (δ) ^a
1 (CDCl ₃)	0.96 (s, 6, Me _a ; ³ J(¹ H- ⁷⁷ Se) = 20.4 Hz), 1.65 (s, 12, Me _b), 1.73 (s, 12, Me _c)
2 (C ₆ D ₆) ^b	1.05 (s, 3, Me _a), 1.10 (s, 3, Me _a), 1.65 (s, 12, Me _{b,b'}), 1.69 (s, 12, Me _{c,c'})
3 (CDCl ₃)	1.26 (s, 3, Me _a), 1.34 (s, 3, Me _a), 1.74 (s, 12, Me _{b,b'}), 1.87 (s, 6, Me _c), 1.90 (s, 6, Me _c)

^a In parentheses: multiplicity, integral, assignment. For assignment lettering, see Chart 1; a, a' etc. may be transposed.

tiostat; Pt working and auxiliary electrodes; Ag/Ag⁺ (0.1 M AgNO₃ in CH₃CN) as reference electrode; 0.1 M [NBu₄][ClO₄] in CH₃CN as supporting electrolyte; under these conditions [Fe(C₅H₅)₂]/[Fe(C₅H₅)₂]⁺ has *E*_{1/2} = +0.27 V vs Ag/Ag⁺. Mass spectra were recorded by the EPSRC Mass Spectrometry Centre, using electron impact (EI) or fast atom bombardment (FAB). LiC₅Me₅ was prepared from equimolar amounts of pentamethylcyclopentadiene¹⁰ and butyllithium (1.7 M in hexanes) in petroleum ether (bp 40–60 °C). [M(CO)₅THF],¹¹ [M(CO)₄(nbd)]¹² (nbd = norbornadiene), [M(CO)₃(CH₃CN)₃]¹³ (M = Cr, Mo, W), and Se(S₂CNEt₂)₂¹⁴ were prepared as described in the literature.

Bis(pentamethylcyclopentadienyl)selenium (1). Selenium bis(diethylthiocarbamate) (3.00 g, 8 mmol) was dissolved in toluene (50 cm³) and added to a stirred solution of LiC₅Me₅ (2.27 g, 16 mmol) in toluene (50 cm³) at room temperature. After 30 min a yellow solution and a white precipitate of lithium diethylthiocarbamate had formed. The solution was filtered, reduced in volume by evaporation under reduced pressure and passed through a short silica column using petroleum ether (bp 40–60 °C) as eluent to yield a yellow solution. This was concentrated and cooled to -10 °C to give pale yellow crystals of **1**. Yield: 0.84 g (30%). NMR: see Tables 1–3. MS (EI, ⁸⁰Se; *m/e*): 350 (42%, M⁺); 270 (10%, C₂₀H₃₀⁺); 215 (52%, C₁₀H₁₅Se⁺); 135 (100%, C₁₀H₁₅⁺). IR (KBr disk; cm⁻¹): 2960 (s), 2914 (s), 2852 (s), 1438 (br), 1376 (s), 1362 (br), 1049 (br), 709 (m), 596 (m). UV/vis (10⁻³ M in hexane; nm): 210 (ε = 1800 dm³ mol⁻¹ cm⁻¹); 190 (ε = 230 dm³ mol⁻¹ cm⁻¹). Details of the crystal structure determina-

Chart 1

Table 2. ¹³C NMR Spectra

compd (solvent)	chem shift (δ) ^a
1 (CDCl ₃)	10.6 (C _a), 11.5 (C _b), 21.1 (C _c), 62.3 (C _d), 132.6 (C _e), 137.4 (C _f)
2 (C ₆ D ₆) ^b	9.4 (C _a), 10.5 (C _{a'}), 11.3 (C _b), 11.7 (C _{b'}), 17.7 (C _c), 21.3 (C _{c'}), 211.5 (C _g), 215.9 (C _h)
3 (C ₆ D ₆) ^c	10.8 (C _a), 11.3 (C _{a'}), 11.4 (C _b), 11.7 (C _{b'}), 16.9 (C _c), 19.5 (C _{c'}), 66.4 (C _d), 67.2 (C _{d'}), 197.7 (C _g , ¹ J(¹³ C- ¹⁸³ W) = 128 Hz), 199.6 (C _h)

^a For assignment lettering, see Chart 1; a, a' etc. may be transposed. ^b Signals for C_{d,d'}, C_{e,e'}, and C_{f,f'} not observed. ^c Signals for C_{e,e'} and C_{f,f'} not observed.

Table 3. ⁷⁷Se NMR Spectra

compd (solvent)	chem shift (δ)
1 (C ₇ D ₈)	324 (septet, ³ J(⁷⁷ Se- ¹ H) = 21.8 Hz)
2 (C ₆ D ₆)	616, 636
3 (C ₇ D ₈)	515, 675

Table 4. Crystal Data and Details of Data Collection and Refinement

	1	2	3
formula	C ₂₀ H ₃₀ Se	C ₂₅ H ₃₀ CrO ₅ Se ₂	C ₂₅ H ₃₀ O ₅ Se ₂ W
<i>M</i> _r	349.42	620.43	752.28
cryst syst	monoclinic	monoclinic	triclinic
<i>a</i> /Å	10.313(2)	8.916(4)	9.049(4)
<i>b</i> /Å	11.116(1)	15.647(9)	11.322(6)
<i>c</i> /Å	16.332(2)	20.119(10)	14.930(9)
α/deg	90	90	99.28(5)
β/deg	92.08(1)	96.34(4)	95.89(5)
γ/deg	90	90	109.91(4)
<i>V</i> /Å ³	1871	2790	1399
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1
<i>Z</i>	4	4	2
<i>D</i> _f /(g cm ⁻³)	1.240	1.477	1.786
μ/cm ⁻¹	19.8 (Mo Kα)	67.5 (Cu Kα)	68.2 (Mo Kα)
cryst size/mm ³	0.25 × 0.20 × 0.20	0.20 × 0.50 × 0.50	0.40 × 0.40 × 0.60
θ range for data/deg	2.2–29.8	3.0–55.0	2.5–27.0
total no. of unique data	3575	6969	6071
total no. of obsd data	3116	3029	4680
no. of params	310	328	328
<i>R</i>	0.0244	0.067	0.053
<i>R</i> _w	0.0285	0.082	0.059

tion carried out by Prof. M. B. Hursthouse and Dr. K. M. A. Malik in Cardiff are given in Table 4. Measurements were carried out with a FAST area detector diffractometer using Mo Kα radiation (λ = 0.710 69 Å). A significance test of *F*_o > 4σ(*F*_o) was used and an absorption correction applied by DIFABS.¹⁵ Solution was by direct methods (SHELX-76) and refinement by full-matrix least squares using SHELX-80. All the hydrogen atoms were located from the difference map and refined freely with individual isotropic temperature factors.

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[M(CO)₅{Se₂(C₅Me₅)₂}] (2 (M = Cr), 3 (M = W)). Stirring a mixture of **1** (0.20 g, 0.6 mmol) and [M(CO)₅THF] (M = Cr, 0.16 g, 0.6 mmol; M = W, 0.24 g, 0.6 mmol) in THF (50 cm³) at room temperature led overnight to a gradual darkening of the solution. This was reduced in volume by evaporation under reduced pressure and the residue was passed through a silica column using petroleum ether (bp 30–40 °C) as eluent. The first yellow band (which contained (C₅Me₅)₂) was followed by a trace of unreacted **1** and then an orange-red band which was collected and concentrated. Cooling to –10 °C produced dark orange crystals of **2** (M = Cr, 0.03 g, 16% yield) or orange-red crystals of **3** (M = W, 0.04 g, 18% yield). NMR: see Tables 1–3.

2: MS (FAB; ⁸⁰Se, ⁵²Cr; *m/e*): 622 (5%, M⁺); 487 (45%, Cr(CO)₅Se₂C₅Me₅⁺); 459 (25%, Cr(CO)₄Se₂C₅Me₅⁺); 407 (25%, Cr(CO)₃Se₂C₅Me₅⁺); 347 (100%, CrSe₂C₅Me₅⁺). IR (Nujol mull; cm⁻¹): 2062 (w), 1944 (s), 1925 (m). UV/vis (10⁻³ M in hexane; nm): 440 (ε = 25 dm³ mol⁻¹ cm⁻¹); 230 (ε = 510 dm³ mol⁻¹ cm⁻¹); 210 (ε = 550 dm³ mol⁻¹ cm⁻¹).

3: MS (FAB; ⁸⁰Se, ¹⁸⁴W; *m/e*): 617 (26%, W(CO)₅Se₂C₅Me₅⁺); 589 (100%, W(CO)₄Se₂C₅Me₅⁺); 535 (56%, W(CO)₃Se₂C₅Me₅⁺); 507 (28%, W(CO)₂Se₂C₅Me₅⁺); 455 (42%, W(CO)₂SeC₅Me₅⁺); 429 (28%, WSe₂C₅Me₅⁺). IR (Nujol mull; cm⁻¹): 2070 (w), 1940 (vs), 1923 (s). UV/vis (10⁻³ M in hexane; nm): 415 (ε = 40 dm³ mol⁻¹ cm⁻¹); 320 (ε = 120 dm³ mol⁻¹ cm⁻¹); 210 (ε = 830 dm³ mol⁻¹ cm⁻¹).

Details of the crystal structure determinations carried out by Prof. M. Di Vaira in Florence are given in Table 4. Measurements were carried out with an Enraf-Nonius CAD4 diffractometer using Cu Kα radiation (λ = 1.5418 Å) for **2**, Mo Kα radiation (λ = 0.71069 Å) for **3**, and ω/2θ scans. A significance test of *I* ≥ 3σ_{*I*} was used and an empirical absorption correction applied. Solution was by Patterson and Fourier methods and refinement using SHELX-76 (anisotropic W, Se, O, C; H atoms in calculated positions with C–H = 0.96 Å and rigid CH₃ groups).

[Fe₃Se₂(CO)₉] (4). Diiron nonacarbonyl (0.29 g, 0.8 mmol) was suspended in petroleum ether (bp 40–60 °C, 50 cm³), in which it was insoluble. Compound **1** (0.28 g, 0.8 mmol) was slowly added, upon which the solution became black almost immediately. The mixture was stirred at room temperature overnight and the solvent then removed by evaporation under reduced pressure. The residue was chromatographed on a silica column using petroleum ether (bp 30–40 °C) as eluent. The first product to be eluted was (C₅Me₅)₂, and the second was a violet band, which when concentrated and cooled to –10 °C afforded violet crystals. These were identified as [Fe₃Se₂(CO)₉] by comparison of mass and infrared spectra with those of an authentic sample. Yield: 0.33 g (72%). MS (EI, ⁸⁰Se; *m/e*): 578 (M⁺). IR (KBr disk; cm⁻¹): 2058 (vs), 2039 (vs), 2011 (vs), 1992 (vs), 1973 (m).

Results and Discussion

Synthesis and Characterization of Bis(pentamethylcyclopentadienyl)selenium (1). The synthesis of the sulfur compound S(C₅Me₅)₂ was achieved by the reaction of sulfur dichloride with 2 equiv of lithiated pentamethylcyclopentadiene. The analogous reaction involving selenium could not be carried out, as selenium dihalides are known only in the vapour phase; attempts to isolate them as solids or liquids result in disproportionation. A suitable alternative precursor for the production of Se(II) compounds was found in the form of selenium bis(diethylthiocarbamate). This is an easily prepared, air-stable crystalline solid, which is readily soluble in organic solvents.¹⁴

The room-temperature reaction of Se(S₂CNET₂)₂ with 2 equiv of LiC₅Me₅ in toluene led to the formation of

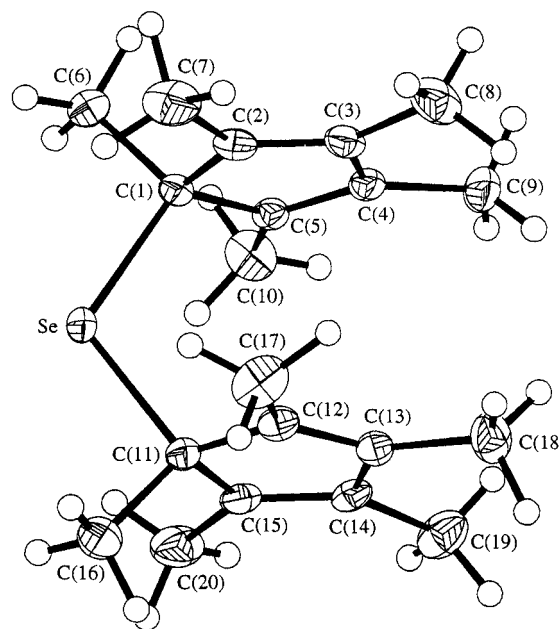
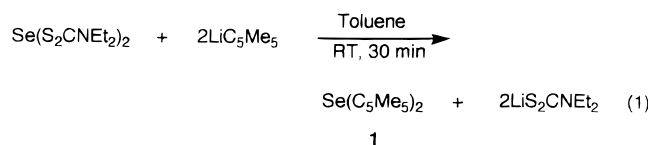


Figure 1. Molecular structure of Se(C₅Me₅)₂ (**1**).

the novel compound bis(pentamethylcyclopentadienyl)selenium (**1**) (eq 1). The product crystallised from



hexane at –10 °C as pale yellow monoclinic crystals in 30% yield. In the solid state **1** is stable to air at room temperature for a number of days but decomposed rapidly when heated above 60 °C; it is best stored in the dark at –10 °C under an inert atmosphere.

Analogous treatment of tellurium bis(diethylthiocarbamate) with LiC₅Me₅ produced a precipitate of LiS₂CNET₂, indicating that the reaction had proceeded in a similar fashion. All attempts to isolate the tellurium-containing product, however, resulted in decomposition and the precipitation of tellurium powder. This observation has very recently been confirmed by Sladky and co-workers, who have succeeded for the first time in isolating a homoleptic cyclopentadienyltellurium compound by utilizing the stabilizing effect of trimethylsilyl substituents.¹⁶

The NMR spectroscopic data for **1** are summarized in Tables 1–3. The two C₅Me₅ rings are attached in a η¹ fashion to the selenium atom, giving rise to three signals in the ¹H NMR spectrum at room temperature. The thermal sensitivity of the compound precludes the observation of spectra at higher temperatures, but its behavior appears to parallel that of the analogous sulfur compound, which is nonfluxional. This is in contrast with the behavior of most other η¹-cyclopentadienyl derivatives.¹⁷

The molecular structure of **1** has been confirmed by X-ray diffraction (see Figure 1).⁸ Selected bond lengths and angles are given in Table 5. Each C₅Me₅ group is bonded to the selenium atom through a single carbon

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Table 5. Selected Bond Lengths (Å) and Angles (deg) for Se(C₅Me₅)₂ (1)

C(1)–Se	1.995(4)	C(11)–Se	2.004(4)
C(6)–C(1)	1.533(5)	C(2)–C(1)	1.509(5)
C(7)–C(2)	1.497(4)	C(3)–C(2)	1.338(4)
C(8)–C(3)	1.497(4)	C(4)–C(3)	1.478(4)
C(9)–C(4)	1.499(4)	C(5)–C(4)	1.339(4)
C(10)–C(5)	1.491(4)	C(5)–C(1)	1.508(5)
C(11)–Se–C(1)	109.6(2)	C(2)–C(1)–Se	112.6(2)
C(5)–C(1)–Se	113.3(2)	C(5)–C(1)–C(2)	103.5(3)
C(6)–C(1)–Se	102.7(2)	C(6)–C(1)–C(2)	112.4(3)
C(6)–C(1)–C(5)	112.8(3)	C(3)–C(2)–C(1)	108.9(3)
C(4)–C(3)–C(2)	109.3(3)	C(5)–C(4)–C(3)	109.6(3)
C(4)–C(5)–C(1)	108.7(3)		

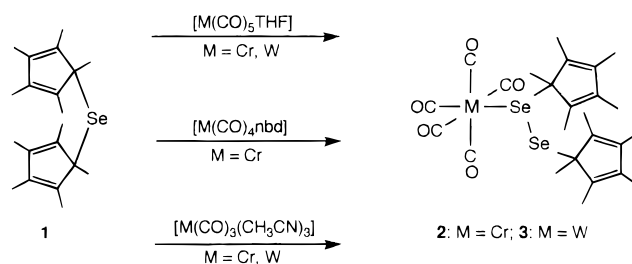
atom and exhibits two short C–C distances consistent with the presence of isolated double bonds. The Se–C bond lengths (average 2.000 Å) are much larger than the sum of the covalent radii (1.930 Å), and the C–Se–C angle (109.6°) is the largest known for a simple diorgano selenide.¹⁸ These data imply considerable distortion of the bonding about selenium as a consequence of the size of the pentamethylcyclopentadienyl groups.

From a theoretical standpoint it has been noted¹⁹ that perhapto attachment of carbocyclic rings in bent-sandwich molecules is to be expected when the total of ring π plus main group element electrons is 14. The structures of bis(pentamethylcyclopentadienyl)tin(II)²⁰ and the bis(pentamethylcyclopentadienyl)arsenic(III) cation²¹ exemplify this principle. Among group 16 compounds, therefore, bis- η^5 attachment of the C₅Me₅ rings may be expected in the dications [E(C₅Me₅)₂]²⁺. The oxidation of **1** in acetonitrile solution was investigated electrochemically using cyclic voltammetry. The process was found to be irreversible, with $E_{ox} = +0.40$ V vs [Fe(C₅H₅)₂]/[Fe(C₅H₅)₂]⁺. The oxidation of **1** thus occurs at a lower potential than those of both C₅Me₅H²² and S(C₅Me₅)₂.⁵ Nevertheless, it appears that the HOMO is associated with the ring π orbitals rather than the selenium atom, making the chances of isolating simple cations remote.

Reactions of **1** with Group 6 Metal Carbonyls.

A few examples of group 6 metal (Cr, Mo, W) carbonyls with a single selenium-bound ligand acting as a σ -donor are known. They are usually prepared either by irradiation of a mixture of the selenide (e.g. Se(M'Me₃)₂; M' = Ge, Sn, Pb²³) and the metal hexacarbonyl or by reaction of the THF adduct [M(CO)₅THF] (e.g. with SePh₂²⁴). Complexes in which a dialkyl selenide bridges two metals have been synthesized by a similar method.²⁵

The complex [Cr(CO)₅(SeEt₂)] has been produced via a different route.²⁶ Chromium hexacarbonyl yields the anion [Cr(CO)₅(SeH)]⁻ on photochemical or thermal

Scheme 5

reaction with Na₂Se in alcohols. This may be isolated as its [(Ph₃P)₂N]⁺ salt. On alkylation with [Et₃O][BF₄]⁻ the dialkyl selenide complex was formed.

Treatment of a THF solution of [M(CO)₅THF] (M = Cr, Mo, W) with an equimolar quantity of **1**, followed by stirring overnight at room temperature, led to a gradual darkening of the mixture. On subsequent column chromatography using silica and petroleum ether (bp 30–40 °C) as eluent, the first band was yellow (C₅Me₅)₂. The orange-red band which followed was reduced in volume and cooled to –10 °C, affording when M = Cr dark orange crystals of **2** and when M = W orange-red crystals of **3**. No product could be isolated when M = Mo, highlighting the generally lower stability of molybdenum complexes of this type. The products were found to be moderately air-stable in the solid state but to decompose rapidly in aerated solution at room temperature.

The reactions of **1** (2 equiv) with [M(CO)₄(nbd)] (nbd = bicyclo[2.2.1]hepta-2,5-diene) and of **1** (3 equiv) with [M(CO)₃(CH₃CN)₃] (M = Cr, Mo, W) were also investigated. Stirring overnight in THF solution led to a gradual darkening of the mixtures. Subsequent workup by column chromatography using silica and petroleum ether (bp 30–40 °C) again yielded **2** for the reactions of [Cr(CO)₃(CH₃CN)₃] and [Cr(CO)₄(nbd)], and **3** for the reaction of [W(CO)₃(CH₃CN)₃]. The reactions conducted with [W(CO)₄(nbd)] and both molybdenum complexes did not afford tractable products. These results are summarized in Scheme 5. That the same product is formed regardless of the number of carbonyl ligands present in the starting material is unusual but not unprecedented and implies that carbonyl redistribution in this system occurs quite readily.

The NMR spectroscopic data for **2** and **3** are summarized in Tables 1–3. They show that in neither compound has **1** coordinated intact. It has been transformed into the diselenide Se₂(η^1 -C₅Me₅)₂, which is terminally bound to the metal pentacarbonyl fragment, leading to six distinct methyl environments. The mechanism of this transformation is unclear, but the thermal decomposition of **1** or its reaction with elemental selenium can be ruled out as intermediate steps, as neither of these processes takes place in the absence of the transition metal under the conditions employed. Also, **2** and **3** could not be prepared by the reaction of metal carbonyl derivatives with a mixture, Se_n(C₅Me₅)₂, containing bis(pentamethylcyclopentadienyl)diselenium ($n = 2$).²⁷ We therefore conclude that the selenide-to-diselenide reduction has taken place within the transition-metal coordination sphere.

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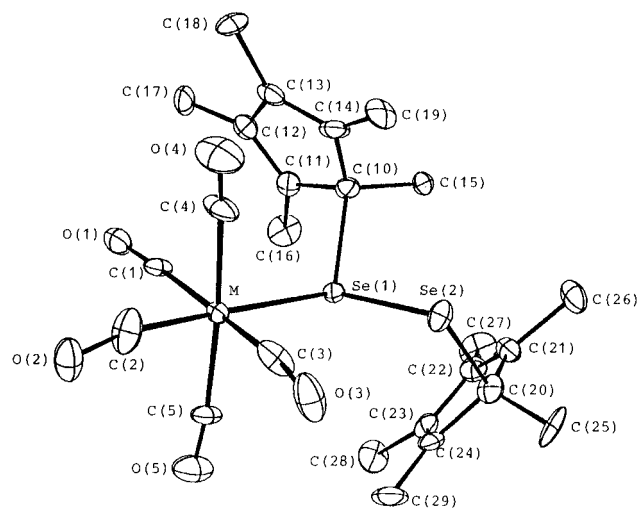


Figure 2. Molecular structure of $[M(CO)_5\{Se_2(C_5Me_5)_2\}]$ ($M = Cr$ (**2**), W (**3**, shown)).

Table 6. Selected Bond Lengths (Å) for $[M(CO)_5\{Se_2(C_5Me_5)_2\}]$

	2 ($M = Cr$)	3 ($M = W$)
M–Se(1)	2.545(1)	2.671(1)
M–C(1)	1.874(9)	2.022(10)
M–C(2)	1.828(9)	1.968(11)
M–C(3)	1.880(9)	2.032(12)
M–C(4)	1.896(8)	2.019(13)
M–C(5)	1.875(9)	2.013(12)
Se(1)–Se(2)	2.327(1)	2.330(1)
Se(1)–C(10)	2.033(7)	2.038(9)
C(10)–C(11)	1.494(10)	1.520(13)
C(11)–C(12)	1.294(11)	1.329(14)
C(12)–C(13)	1.448(12)	1.463(15)
C(13)–C(14)	1.334(11)	1.311(14)
C(14)–C(10)	1.505(10)	1.479(13)
Se(2)–C(20)	2.023(8)	2.034(10)
C(20)–C(21)	1.479(11)	1.474(14)
C(21)–C(22)	1.320(10)	1.323(14)
C(22)–C(23)	1.455(11)	1.446(16)
C(23)–C(24)	1.326(12)	1.311(16)
C(24)–C(20)	1.509(12)	1.523(16)

Table 7. Selected Bond Angles (deg) for $[M(CO)_5\{Se_2(C_5Me_5)_2\}]$

	2 ($M = Cr$)	3 ($M = W$)
Se(1)–M–C(1)	90.9(3)	91.1(3)
Se(1)–M–C(2)	172.9(3)	173.2(4)
Se(1)–M–C(3)	92.4(3)	91.6(3)
Se(1)–M–C(4)	98.9(3)	98.6(3)
Se(1)–M–C(5)	86.2(3)	87.0(3)
M–Se(1)–Se(2)	109.7(1)	107.1(1)
M–Se(1)–C(10)	114.9(2)	114.2(3)
Se(2)–Se(1)–C(10)	103.9(2)	103.7(3)
Se(1)–C(10)–C(11)	109.3(5)	108.1(7)
C(10)–C(11)–C(12)	108.8(7)	106.4(9)
C(11)–C(12)–C(13)	111.2(7)	111.1(9)
C(12)–C(13)–C(14)	108.8(7)	108.7(9)
C(13)–C(14)–C(10)	108.1(7)	110.0(9)
C(14)–C(10)–C(11)	103.0(6)	103.8(8)
Se(1)–Se(2)–C(20)	99.1(2)	100.3(3)
Se(2)–C(20)–C(21)	102.9(6)	103.8(8)
C(20)–C(21)–C(22)	108.9(7)	108.7(1.0)
C(21)–C(22)–C(23)	109.4(7)	109.9(1.0)
C(22)–C(23)–C(24)	110.4(7)	110.4(1.0)
C(23)–C(24)–C(20)	107.1(7)	107.5(1.0)
C(24)–C(20)–C(21)	104.0(7)	103.5(9)

The constitution of **2** and **3** has been confirmed by X-ray diffraction (see Figure 2).⁹ Selected bond lengths and angles are given in Tables 6 and 7. The two complexes have essentially the same molecular structure, although the packing is different in each case. The

bond lengths in the $M(CO)_5$ fragments are normal and show typical shortening of the M–C bond *trans* to the non-carbonyl ligand. There appear to be no comparable data available for chromium selenide complexes, but the W–Se distance (2.671 Å) is similar to that in $[W(CO)_5\{Se(CPh_2CH_2CMe=CH_2)\}]$ (2.674 Å)²⁸ and only slightly shorter than that in $[W(CO)_5\{Se(SnMe_3)_2\}]$ (2.736 Å).²⁹ Each selenium atom is bonded to a single carbon of one C_5Me_5 ring, the Se–C distances (average 2.036, 2.028 Å) being the longest thus far reported, much larger than the sum of the covalent radii (1.930 Å).¹⁸ The bonding within the C_5Me_5 groups is as expected for σ coordination, with two short C–C distances indicating the presence of isolated double bonds.

Two previous examples of a terminal diselenide ligand have been reported:³⁰ $[M(CO)_5\{Se_2(CH_2SiMe_3)_2\}]$ and $[M(CO)_5\{SeSeCH_2CMe_2CH_2\}]$ ($M = Cr, Mo, W$). Variable-temperature NMR spectroscopy of these complexes has shown that they undergo a number of fluxional processes, including a 1,2-shift, in which the metal moves from one selenium atom to the other. Similar behavior has been observed for **2** and **3**. The results of these studies will be reported separately.³¹

Three carbonyl stretching vibrations were observed in the region 1920–2070 cm^{-1} for both complexes. This result is typical for complexes of the type $[M(CO)_5L]$, where L is a point ligand. The stretching vibrations are assigned as $2A_1$ and E.³² A band is present in the UV/vis spectrum in the region of 400–450 nm for both compounds. This probably corresponds to an absorption by the Se–Se bond.

Although a true “coordination shift” cannot be calculated from the ⁷⁷Se NMR spectra of **2** and **3**, it is notable that the chemical shift difference between the coordinated and free selenium atoms is much greater in **3** than in **2**. This suggests an increased Se–M interaction when $M = W$, further evidenced by the generally greater stability of the tungsten complex.

Reaction of 1 with $[Fe_2(CO)_9]$. Derivatives of $[Fe(CO)_5]$ containing dialkyl selenide ligands appear to be unknown, although the chemistry of the related cationic complexes $[C_5H_5Fe(CO)_{3-n}(SeMe_2)_n]^+$ ($n = 1–3$) is well-developed.³³ There is also an extensive series of compounds based on the complex $[Fe_2Se_2(CO)_6]$, first prepared³⁴ in 1958 from $[Fe(CO)_5]$ and elemental gray selenium. This has been found to demonstrate reactivity typical of organic diselenides.³⁵

When Cowley and co-workers performed the reaction of $[Fe_2(CO)_9]$ with bis(pentamethylcyclopentadienyl)sulfur in *n*-hexane,⁵ a dark red crystalline material was produced. Spectral evidence indicated the absence of any C_5Me_5 rings, and closer investigation revealed the identity of the product to be $[Fe_3S_2(CO)_9]$, as prepared

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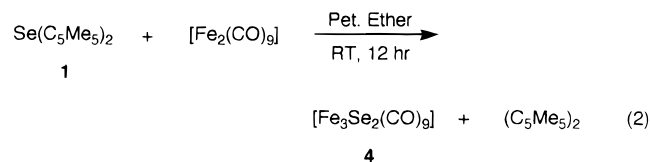
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by Hieber and Gruber³⁴ and subsequently structurally characterized by Dahl and Sutton³⁶ in 1963. Although it is not mechanistically clear how the product is formed, it seems that the desulfurization of organic sulfides by iron carbonyls is a fairly common occurrence.³⁷

A mixture of $[\text{Fe}_2(\text{CO})_9]$ and **1** was stirred overnight at room temperature under an inert atmosphere using petroleum ether (bp 40–60 °C) as solvent. An almost immediate darkening of the solution was observed, to generate a dark violet colored solution, from which a violet crystalline material was isolated in 72% yield (eq 2). Infrared and mass spectroscopic investigation re-



vealed the identity of the product to be $[\text{Fe}_3\text{Se}_2(\text{CO})_9]$ (**4**), also originally prepared by Hieber,³⁴ which is analogous to the product of the reaction with bis-(pentamethylcyclopentadienyl)sulfur.

Five infrared absorption maxima were recorded in the carbonyl stretching region, although Hieber reported only three stretching frequencies for this complex, corresponding to the three groups of terminal carbonyls.

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This we ascribe to the use of higher resolution equipment than was available in 1958. As the product was eluted as a single well-defined band from the column and was consequently obtained in crystalline form, it is extremely unlikely that the additional peaks in the infrared spectrum are due to an impurity.

Conclusion

The reactions of **1** with zerovalent metal carbonyls reported here all proceed with cleavage of at least one selenium–carbon bond. This novel reactivity can be associated with the steric crowding at the selenium atom, which facilitates the loss of the bulky C_5Me_5 group. Studies are now in progress to examine further the chemistry of **1** and its analogues.

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Supporting Information Available: Listings of the atomic coordinates, thermal parameters, and bond lengths and angles associated with the crystal structure determinations reported for **1–3** (13 pages). Ordering information is given on any current masthead page. This material has also been deposited at the Cambridge Crystallographic Data Centre.

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