

Dichalcogenolanes by Ring-expansion of Transition Metal-coordinated Thietanes and Selenetanes

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Pentacarbonyltungsten-coordinated selenetanes react with seleno- and telluro-cyanate by insertion of the chalcogen atom into the Se-C bond of the selenetanes to give 1,2-diselenolanes and -selenatellurolane, respectively; the analogous reaction of $(\text{CO})_5\text{W}[\text{SC}(\text{Ph})\text{HCH}_2\text{C}(\text{OEt})\text{H}]$ with tellurocyanate affords a 1,2-thiatellurolane complex.

The coordination mode and the reactivity of transition metal-coordinated heterocycles such as thiophenes,¹ selenophenes² and thietanes^{3,4} have recently attracted much interest in connection with the hydrodesulfurization process.⁵ For thietane ligands several reaction modes have been observed: (i) thermal, photochemical and nucleophile-promoted ring opening with or without oligomerization,⁴ (ii) insertion of the central metal into the S-C bond and coupling of the resulting metallathiacycles with formation of a disulfide link⁴ and (iii) $\text{Co}_2(\text{CO})_8/\text{Ru}_3(\text{CO})_{12}$ -catalysed regiospecific insertion of CO into the S-C bond of the thietane to give thiobutyrolactones.⁶ We now report the unusually facile, transition metal-promoted selective insertion of the selenium and tellurium atom of seleno- and telluro-cyanates into the X-C bond of thietane and selenetane ligands.

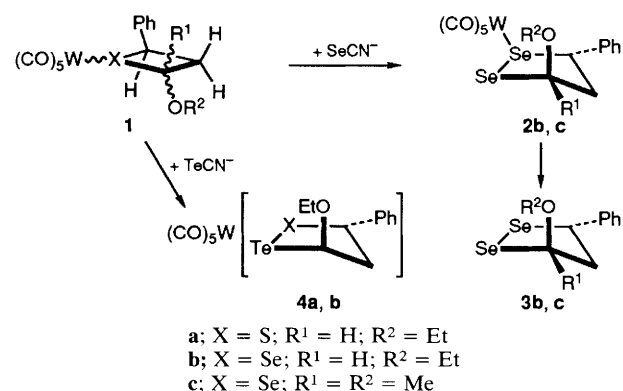
The selenetane complex **1c** reacts with SeCN^- in excess (SeCN^- : **1c** ca. 10:1) even at -40°C within several minutes by insertion of the selenium atom of SeCN^- into an Se-C bond of the selenetane to form the diselenolane **3c** and its pentacarbonyl tungsten complex **2c** (Scheme 1). The progress of the reaction can be followed by IR spectroscopy or by the brightening of the orange colour of the solution to yellow. The structure of **2c** and **3c** was deduced from their spectra,[†] and that of **2c** (although prepared by a different route, *vide infra*) was additionally established by X-ray analysis (Fig. 1).[‡] The diselenolane ring adopts the 'envelope' conformation with a dihedral angle of ca. 127° , the selenium atoms forming the base line. The phenyl and the methoxy group occupy equatorial positions, Ph and $(\text{CO})_5\text{W}$ being mutually *trans*.

The reaction of **1b** with SeCN^- is slower, the only isolable product (ca. 15%) being the 1,2-diselenolane **3b** (Ph being equatorial and OEt axial). Presumably the initial product is **2b**, the diselenolane ligand of which is displaced by excess of SeCN^- . The selenium atom of the selenocyanate specifically inserts into an Se-C bond of the coordinated selenetane; only the 1,2-diselenolane can be detected.

From the reaction of tellurocyanate with **1a** and **1b** two isomeric pentacarbonyl tungsten complexes, **4a/a'** and **4b/b'**,[†]

respectively, are isolated containing novel thia- and selenatellurolane as ligands. In both isomers the phenyl group occupies an equatorial and the ethoxy group an axial position. These compounds are not stable and quickly decompose at room temperature by loss of tellurium.

The starting complexes **1b** and **c** are prepared from the selenobenzaldehyde complex **5** and the corresponding vinyl ethers in excess.⁷ When these reactions are performed with only 1.5 equiv. of the vinyl ethers and under a CO pressure of 50 bar at -40°C , in addition to selenetane complexes considerable amounts of diselenolane complexes are formed



Scheme 1

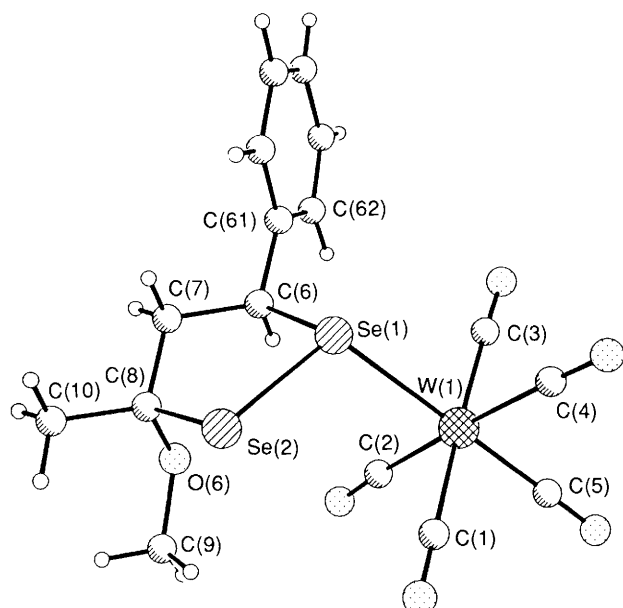
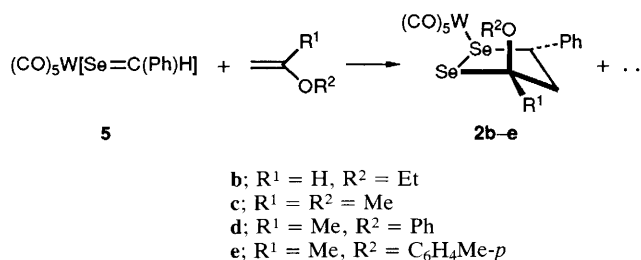


Fig. 1 Molecular structure of **2c**. Important distances (Å) and angles ($^\circ$) are: W-Se(1) 2.648(1), Se(1)-Se(2) 2.367(1), Se(1)-C(6) 1.999(5), C(6)-C(7) 1.514(9), C(7)-C(8) 1.504(8), Se(2)-C(8) 2.021(6); W-Se(1)-Se(2) 110.4(1), W-Se(1)-C(6) 107.0(1), C(6)-Se(1)-Se(2) 92.7(2), Se(1)-Se(2)-C(8) 92.1(2), Se(1)-C(6)-C(7) 107.9(3), C(6)-C(7)-C(8) 114.7(4), C(7)-C(8)-Se(2) 105.3(4); torsional angle C(6)-Se(1)-Se(2)-C(8) 5.5° .

[†] Selected ^1H NMR data (in CDCl_3): **2b**: δ 5.83 [dd, J 13.3 and 2.9 Hz, C(Ph)H], 6.07 [dd, J 1.9 and 1.4 Hz, C(OEt)H]; **3b**: δ 5.44 [dd, J 13.1 and 3.2 Hz, C(Ph)H], 6.05 [dd, J 3.0 and 1.6 Hz, C(OEt)H]; **2c**: δ 5.62 [dd, J 13.0 and 3.2 Hz, C(Ph)H]; **3c**: 5.41 [dd, J 12.8 and 3.7 Hz, C(Ph)H]; **4a**: δ 5.04 [dd, J 13.0 and 2.7 Hz, C(Ph)H], 6.90 [dd, J 3.0 and <1 Hz, C(OEt)H]; **4a'**: δ 5.04 [dd, J 13.0 and 2.7 Hz, C(Ph)H], 7.04 [dd, J 2.1 and <1 Hz, C(OEt)H]; **4b**: δ 5.45 [dd, J 12.9 and 2.5 Hz, C(Ph)H], 6.76 [dd, J 3.3 and 1.2 Hz, C(OEt)H]; **4b'**: δ 5.53 [dd, J 13.4 and 2.9 Hz, C(Ph)H], 6.89 [dd, J 3 and 1 Hz, C(OEt)H]; **2d**: 5.73 [dd, J 12.9 and 3.5 Hz, C(Ph)H]; **2e**: 5.73 [dd, J 13.1 and 3.4 Hz, C(Ph)H].

[‡] Crystal data for **2c**: $\text{C}_{16}\text{H}_{14}\text{O}_6\text{Se}_2\text{W}$, M = triclinic, space group $\bar{P}1$, a = 9.828(4), b = 9.949(4), c = 10.226(4) Å, α = 79.59(3), β = 74.30(3), γ = 82.34(3)°, U = 942.9(6) Å³, D_c = 2.268 g cm⁻³, Z = 2. 3713 Unique reflections were recorded, of which 3702 were 'observed' with $I > 3.0\sigma(I)$ (ω -scan) using Mo-K α radiation (λ = 0.71073 Å), graphite monochromator, on a Siemens R3 diffractometer. Solution by SHELXTL PLUS. R (R_w) = 0.037 (0.027). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 2

in yields ranging from 8 to 45% (Scheme 2). We assume that the first step involves the addition of the vinyl ethers to the Se=C-bond of **5** to give selenetane complexes **1**⁷ which then insert 'Se' to afford **2b-e**.[†] Thus in these reactions **5** is the source of both selenium atoms of **2b-e**. Since formation of **1** is slow at -40°C , much longer reaction times (11–25 h) are required compared to the synthesis of **2b,c** from **1b,c** and selenocyanate (Scheme 1). Only one isomer of **2b** is observed; however, a mixture of two isomers is obtained for **2c-e** both containing the phenyl group in equatorial position. The two forms probably differ either in the relative orientation of R^1 and OR^2 or in the coordination of the diselenolane to the pentacarbonyl tungsten fragment.⁸

Until now, the ring-expansion of selenetanes by chalcogen atoms is unknown although the formation of a 1,2-thiaselenolane from a thietane and grey selenium in the presence of traces of KCN has been observed at high temperature

(160–180 $^\circ\text{C}$, 16 h).⁹ Our results indicate that coordination to a pentacarbonylmetal fragment strongly promotes the insertion of a chalcogen atom into the X–C bond of four-membered chalcogeno heterocycles. Furthermore, ring-expansion of these transition metal coordinated heterocycles offers a route to hitherto unknown dichalcogenolanes.

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