Synthesis of the First 2*H*-Selenete Complexes, Decomplexation and Dimerization to Dihydro-1,2-diselenine

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Pentacarbonyltungsten-coordinated selenobenzaldehydes, $(CO)_5W[Se{=}C(C_6H_4R\text{-}p)H]$ (R = OMe, H, CF_3), react with $Bu^tS{-}C{\equiv}C{-}SBu^t$ by addition of the C≡C to the Se=C bond to give 2*H*-selenete complexes; treatment of the selenete complex (R=H) with NEt_4Br affords the uncoordinated 2*H*-selenete and a 3,4-dihydro-1,2-diselenine.

The activation barrier for electrocyclic ring opening of cyclobutene significantly decreases when a CH_2 group is replaced by oxygen or sulfur.[1] The experimentally determined barrier for cyclobutene (**1a**, X = CH_2) is 32.9 kcal mol^{-1} (1 cal = 4.184 J),[2] while for oxete **1b** it is 24.1 ± 1.5 kcal mol^{-1}.[3] Calculated barriers agree reasonably well with the experimental data. Calculations indicate that the barrier for thiete **1c** to thioacrolein ring opening is similar to that for oxete to acrolein. All ring opening reactions are exothermic but the exothermicity drastically decreases on going from **1b** to **1c** [$\Delta\Delta H$ = −11.4 (**1a**),[4] *ca.* −35 (**1b**)[1] and 7.9–12.4 kcal mol^{-1} (**1c**)[1]]. On the basis of these results, one would expect the selenium analogues of **1a–c** to be an isolable species. The 2*H*-thiete **1c**[5] and several derivatives[6] have been synthesized and characterized, however, isolation of 2*H*-selenetes has not been reported until now.

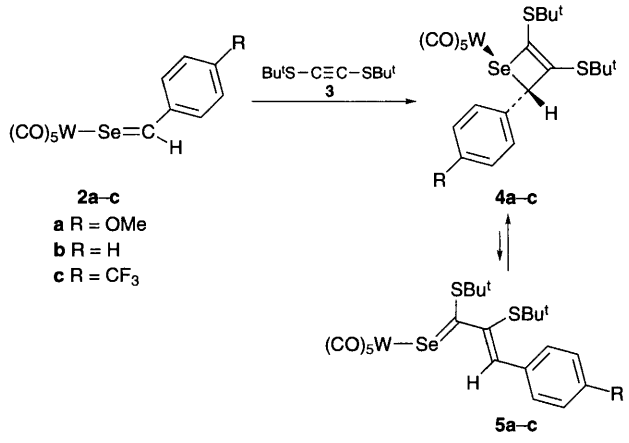
Pentacarbonylchromium- and -tungsten-coordinated selenetes have been postulated several times as intermediates in the reaction of selenobenzaldehyde and selenoketone complexes with π-donor-substituted alkynes to yield coordinated 1-selenabutadiene derivatives.[7,8] So far, attempts to isolate or spectroscopically detect these species have failed. The intermediate formation of a benzoselenete has also been proposed in the photolysis of diazobenzoselenophen-2-one to give a dibenzodiselenocine derivative.[9] We now report on the isolation of the first selenete complexes including the characterization of one example by X-ray structural analysis, the decomplexation to afford uncoordinated selenetes and the ring opening and subsequent dimerization by [4 + 2] cycloaddition to form a 3,4-dihydro-1,2-diselenine.

The selenobenzaldehyde complexes **2a–c** react with a *ca.* 2.5-fold excess of bis(*tert*-butylthio)ethyne **3** in dichloromethane at −50 to −10 °C within 3 to 6 h by cycloaddition to form 1 : 1 adducts. After column chromatography on flash silica gel and recrystallization from dichloromethane–pentane the novel 2*H*-selenete complexes **4a–c** are obtained in crystalline form in 53 (**4a**), 72 (**4b**) and 80% yield (**4c**), respectively (Scheme 1).†

The complexes are surprisingly stable. They melt without decomposition, and when solutions of **4a–c** were kept at room temperature for a week there was no noticable decomposition. The ^1H and ^{13}C NMR spectra show that the Bu^t groups are nonequivalent. Low-field resonances (^{13}C NMR: δ > 210; ^{77}Se NMR: δ > 1000) characteristic for selenocarbonyl groups are absent in the ^{13}C and ^{77}Se NMR spectra. The structure of **4b** was additionally established by X-ray structural analysis (Fig. 1)‡. The C_3Se ring is almost planar [torsion angle Se–C(6)–C(7)–C(8) −5.4(5)°, C(6)–C(7)–C(8)–Se 5.1(4)°] and is coordinated to tungsten *via* the selenium atom and not *via* the C=C bond. Both bulky groups [$(CO)_5W$ and Ph] are *trans*. Due to ring strain and the small bond angle C(6)–Se–C(8) [68.9(2)°] both Se–C distances are rather long as compared to Se–C(sp^3) and Se–C(sp^2) bond lengths in other Se–C compounds.[10]

In contrast to the reactions of **2a–c** with bis(*tert*-butylthio)ethyne, those of **2a–c** with RS–C≡C–SR (R = Me, Pr^i, 2,6-$C_6H_3Me_2$) did not afford isolable (or spectroscopically detectable) 2*H*-selenete complexes but rather thioselonocarboxylic ester complexes analogous to **5a–c** (Scheme 1).[8]

Crystalline compounds **4a–c** are yellow (**4b**) or yellow–green (**4a** and **4c**), however, solutions in pentane or dichloromethane are blue to violet. Thioselonocarboxylic ester complexes are known to be blue or violet.[8] Therefore, it is reasonable to presume that the complexes **4a–c** are present in solution as a rapidly equilibrating mixture of 2*H*-selenete (**4a–c**) and thio-



Scheme 1

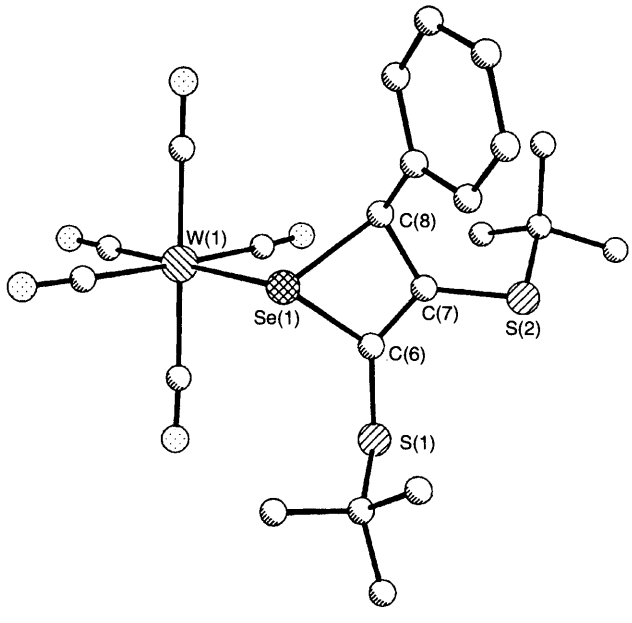


Fig. 1 Molecular structure of **4b** Selected distances (Å) and angles (°): W(1)–Se(1) 2.627(1), Se(1)–C(6) 1.953(5), Se(1)–C(8) 2.061(5), C(6)–C(7) 1.330(8), C(7)–C(8) 1.516(7), C(6)–S(1) 1.733(6), C(7)–S(2) 1.742(6); W(1)–Se(1)–C(6) 109.4(2), W(1)–Se(1)–C(8) 111.2(2), C(6)–Se(1)–C(8) 68.9(2), Se(1)–C(6)–C(7) 97.6(4), C(6)–C(7)–C(8) 105.7(5), Se(1)–C(8)–C(7) 87.5(3); torsion angles W(1)–Se(1)–C(6)–C(7) 110.1(3), Se(1)–C(6)–C(7)–C(8) −5.4(5), S(1)–C(6)–C(7)–S(2) −15.9(9)

1a X = CH_2
1b X = O
1c X = S

selonocarboxylic ester complexes (**5a–c**, Scheme 1). Assuming that the extinction coefficient of the low-energy absorption of **5a–c** at *ca.* 550 nm is the same as that of isolable thioselonocarboxylic ester complexes,[8] the fraction of **5a–c** in the equilibrium is estimated to be *ca.* 6–10%. Similar equilibria between a cyclic and an open structure are known for 2*H*-thietes–α,β-unsaturated dithio esters.[11] Retro-cycloaddition for **4a–c** can be excluded since the selenobenzaldehyde complexes **2a–c** react in solution at room temperature within a few hours to form binuclear selenobenzaldehyde bridged complexes.[12] The complexes **4a–c** are, however, stable in solution for at least one week.

The decomplexation of the 2*H*-selenete ligand of **4b** was achieved with NEt_4Br in dichloromethane (4 °C, 35 h). Chromatography of the reaction mixture gave 35% of 2*H*-selenete **6** and 48% of the 3,4-dihydro-1,2-diselenine **7** (Scheme 2). Most spectroscopic data of the 2*H*-selenete ligand are only marginally influenced by decomplexation. Exceptions are the low-field shift of the ^{77}Se resonance ($\Delta\delta$ > 80 ppm) and the high-field shifts of both selenium-bound ring carbon atoms ($\Delta\delta$ *ca.* 13 ppm).

In $CDCl_3$ at room temperature, 2*H*-selenete **6** slowly (half-life *ca.* 7 d) 'dimerizes' to form **7**.† The structure of **7** was established by spectroscopic means and by an X-ray structural analysis (Fig. 2)‡. Formation of **7** presumably proceeds by ring opening of **6** to form the α,β-unsaturated thioselonocarboxylic ester **8** which then serves both as a 4π selenadiene (C=C–C=Se) and as a 2π dienophile (Se=C) in a 'head-to-head' Diels–Alder reaction to form **7**. Since it has not been possible to detect **8**, [4 + 2] cycloaddition is faster than ring opening of **6**. Ring opening and cycloaddition are highly regio- and stereo-selective. Formation of isomers of **7** could not be observed. In contrast, *cis/trans* isomeric mixtures of 3,4-dihydro-1,2-diselenines have been obtained by an analogous dimerization of α,β-unsaturated selenoaldehydes and selenoketones which were generated *in situ* by selenation of the corresponding carbonyl derivatives with bis(dimethylaluminium) selenide.[13]

These results demonstrate that 2*H*-selenetes are stabilized by coordination to a $(CO)_5W$ fragment and that by reaction of transition metal-coordinated selenoaldehydes with suitable substrates selenacycles are accessible which are either unknown or difficult to prepare by other methods. Until now, 2*H*-selenetes were unknown and 3,4-dihydro-1,2-diselenines were very rare. Only recently have the first monocyclic 3,4-dihydro-1,2-diselenines been prepared.[13]

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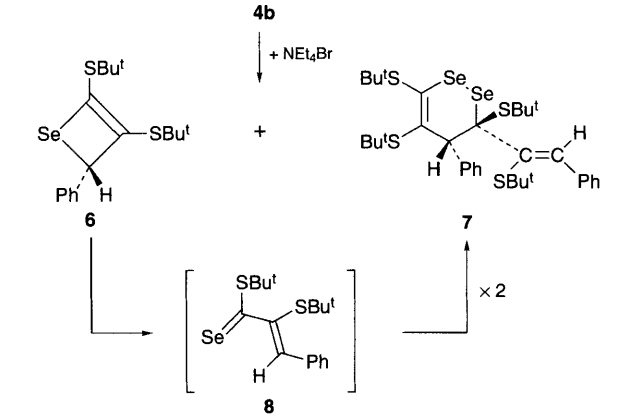

Scheme 2

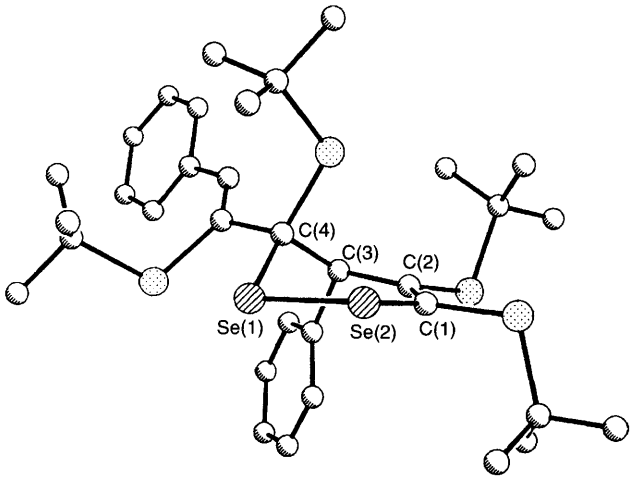

Fig. 2 Molecular structure of **7** Selected distances (Å) and angles (°): Se(1)–Se(2) 2.337(2), Se(1)–C(4) 1.985(9), Se(2)–C(1) 1.90(1), C(1)–C(2) 1.35(2), C(2)–C(3) 1.54(1), C(3)–C(4) 1.57(1), C(1)–S(1) 1.77(1), C(2)–S(2) 1.77(1); Se(1)–Se(2)–C(1) 102.0(3), Se(2)–C(1)–C(2) 128.9(7), C(1)–C(2)–C(3) 126.5(9), C(2)–C(3)–C(4) 118.6(9), C(3)–C(4)–Se(1) 109.6(6); torsion angles C(4)–Se(1)–Se(2)–C(1) −39.1(5), Se(1)–Se(2)–C(1)–C(2) 17.5(11), Se(2)–Se(1)–C(4)–C(3) 64.0(7)

Footnotes

† *Selected data* for **4a**: mp 78 °C; IR (pentane) ν(CO)/cm^{-1} 2072w, 1984vw, 1944vs, 1936sh; ^1H NMR ($CDCl_3$, 238 K) δ 1.34, 1.51 (s, CCH_3), 3.86 (s, OCH_3), 5.58 [s, C(Aryl)*H*]; ^{13}C NMR ($CDCl_3$, 238 K) δ 31.1, 31.8 (CCH_3), 49.5, 49.9 (CCH_3), 55.4 (OCH_3), 64.8 (C-2), 142.6, 143.6 (C-3, C-4), 196.8 (J_{WC} 127 Hz, *cis*-CO), 200.6 (*trans*-CO). For **4b**: mp 86 °C; IR (pentane) ν(CO)/cm^{-1} 2073w, 1985vw, 1945vs, 1938sh; ^1H NMR ($CDCl_3$, 238 K) δ 1.34, 1.52 (s, CH_3), 5.55 [s, C(Aryl*H*]; ^{13}C NMR ($CDCl_3$, 238 K) δ 31.1, 31.7 (CH_3), 49.6, 49.9 (CCH_3), 63.9 (C-2), 142.4, 143.9 (C-3, C-4), 196.6 (J_{WC} 128 Hz, *cis*-CO), 200.5 (*trans*-CO); ^{77}Se NMR ($CDCl_3$, 263 K) δ 745. For **4c**: mp 105 °C; IR (pentane) ν(CO)/cm^{-1} 2074w, 1985vw, 1947vs; ^1H NMR ($CDCl_3$, 238 K) δ 1.35, 1.52 (s, CH_3), 5.53 [s, C(Aryl)*H*]; ^{13}C NMR ($CDCl_3$, 238 K) δ 31.2, 31.8 (CH_3), 49.9, 50.2 (CCH_3), 61.9 (C-2), 123.6 (J_{FC} 272 Hz, CF_3), 142.1, 145.2 (C-3, C-4), 196.5 (J_{WC} 128 Hz, *cis*-CO), 200.2 (*trans*-CO); ^{77}Se NMR ($CDCl_3$, 263 K) δ 762. For **6**: orange oil; ^1H NMR ($CDCl_3$, 223 K) δ 1.35, 1.52 (s, CH_3), 5.52 [s, C(Ph)*H*], 7.35 (m, Ph); ^{13}C NMR ($CDCl_3$, 223 K) δ 31.2, 31.6 (CH_3), 48.3, 49.7 (CCH_3), 50.8 (C-2), 127.9, 128.2, 128.8 (Ph), 130.8, 136.8, 143.5 (C-3, C-4, *i*-Ph); ^{77}Se NMR ($CDCl_3$, 243 K) δ 833. For **7**: mp 134 °C; ^1H NMR ($CDCl_3$, 263 K) δ 0.81, 1.42, 1.47, 1.58 (s, CH_3), 4.52 [s, C(Ph)*H*], 8.29 [s, =C(Ph)*H*]; ^{13}C NMR ($CDCl_3$, 238 K) δ 31.7, 32.0, 32.2 (CH_3), 50.0, 50.2, 50.9, 53.5 (CCH_3), 67.6 (C-4), 70.6 (C-3).

‡ *Crystal data* for **4b**: $C_{22}H_{24}O_5S_2SeW$, M = 695.3, monoclinic, space group $P2_1/c$, a = 13.847(5), b = 10.083(4), c = 18.184(7) Å, β = 94.15(3)°, V = 2532(2) Å^3, D_c = 1.824 g cm^{-3}, Z = 4. 4896 Unique reflections were collected, of which 4280 were observed with $F > 2.0\sigma(F)$ (ω-scan). $R(R_w)$ = 0.038 (0.037). For **7**: $C_{34}H_{48}S_4Se_2$, M = 742.9, monoclinic, space group $P2_1/c$, a = 10.586(3), b = 16.432(3), c = 21.216(5) Å, β = 100.93(2)°, V = 3623(2) Å^3, D_c = 1.362 g cm^{-3}, Z = 4. 5494 Unique reflections were collected, of which 3035 were observed with $F > 3.0\sigma(F)$ (Wyckoff-scan). $R(R_w)$ = 0.076 (0.052). For both structural analyses Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator, on a Siemens R3m/V diffractometer was used. Solution and refinement by SHELXTL PLUS. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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