Thioselonocarboxylic Ester, Selenetane, and Dihydrodiselenine Complexes Prepared from Pentacarbonyl(selenobenzaldehyde)tungsten with π-Donor-Substituted Alkynes

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Pentacarbonyltungsten-coordinated selenobenzaldehyde, $[(CO)_5W\{Se=C(Ph)H\}]$ (**1**), reacts with *t*Bu−C≡C−SMe (**2**) by insertion of the C≡C into the Se=C bond to form in a highly regio- and stereoselective manner the α,β-unsaturated thioselonocarboxylic ester complex (Z)(C=C)-$[(CO)_5W\{\eta^1$-Se=C(SMe)C(*t*Bu)=C(Ph)H}] (**3**). The thioselonocarboxylic ester ligand is cleaved intact from the metal by treatment of **3** with $[NEt_4]Br$. Three complexes are formed in the reaction of **1** with Me−C≡C−SMe (**5**): the thioselonocarboxylic ester complex $[(CO)_5W\{\eta^1$-Se=C(SMe)C(Me)=C(Ph)H}] (**6**) as a mixture of the (*E*) and (Z)(C=C) isomers, a selenetane complex (**7**) and a dihydrodiselenine complex (**8**). The product distribution depends on the ratio **1**:**5** and on the solvent. The reaction of **1** with the bis(organylthio)alkynes RS−C≡C−SR (**9**) [R = Me (**a**), *i*Pr (**b**), 2,6-$C_6H_3Me_2$ (**c**)] yields mixtures of the (*E*) and (Z)(C=C) isomers of the α,β-unsaturated α-organylthio thioselonocarboxylic ester complexes $[(CO)_5W\{\eta^1$-Se=C(SR)C(SR)=C(Ph)H}] (**10a−c**). In contrast, the reaction of **1** with *tert*-butoxyethyne, H−C≡C−O*t*Bu (**11**), affords a bis(pentacarbonyltungsten) 5,6-dihydro-1,2-diselenine complex (**12**). Compound **12** is probably formed by consecutive reaction of **1** with **11** to give the selonocarboxylic ester complex $[(CO)_5W\{\eta^1$-Se=C(O*t*Bu)C(H)=C(Ph)H}] which then further reacts as a heterodiene by highly regioselective [4 + 2] cycloaddition with the Se=C bond of a second molecule of **1** to give **12**. In the reaction of **1** with **5** and **9a** the isomer with a *trans* arrangement of C(=Se)SMe and Ph is the kinetically controlled reaction product [(*E*)-**6** and (Z)-**10a**, respectively]. The formation of (*E*)-**6** and (Z)-**10a** is followed by isomerization until an (*E*)/(Z) equilibrium is reached. Complexes **3** and **7** were characterized by X-ray structural analyses.

Thio- and selenoaldehydes not stabilized by either very bulky groups or by mesomeric effects of heteroatoms such as nitrogen or sulfur are unstable and immediately oligomerize[1]. This considerably restricts their potential use in organic synthesis. Until now, there is only one isolable selenoaldehyde known that is not stabilized by the mesomeric effect of heteroatoms: 2,4,6-tri-*tert*-butylselenobenzaldehyde[2].

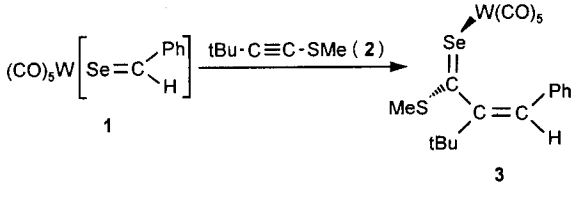
Some problems connected with the high reactivity of thio- and selenoaldehydes can be circumvented by using their complexes. In recent years, we have been able to show that $(CO)_5M$-coordinated thio- and selenoaldehydes (M = Cr, W) are conveniently accessible C=S and C=Se building blocks for the synthesis of thia- and selenaheterocycles[3]. In addition, the reactions of $(CO)_5W[S=C(Aryl)H]$ with π-donor-substituted alkynes, R′−C≡C−XR (XR = NR_2, OR, SR, SeR), offer access to a variety of α,β-unsaturated thiono-, selenothiono-, dithiocarboxylic ester, and thioamide complexes[4−9]. Similarly, the reaction of $(CO)_5W$-[Se=C(Aryl)H] with ynamines gives α,β-unsaturated selenoamides[5−9].

In this paper we report on the reactions of $(CO)_5W[Se=C(Ph)H]$ (**1**) with alkylthio- and alkoxyalkynes affording thioselonocarboxylic ester complexes and on the formation of four- and six-membered selenacycles.

Results and Discussion

The selenobenzaldehyde complex **1** slowly reacted at −30°C with a ca. 4-fold excess of 1-methylthio-3,3-dimethyl-1-butyne (**2**) in dichloromethane by formal insertion of the C≡C bond into the Se=C bond. For completion the reaction required ca. two days. After chromatography and crystallization from pentane/CH_2Cl_2 the red crystalline thioselonocarboxylic ester complex **3** was obtained in moderate yield (Scheme 1).

Scheme 1



The reaction very likely proceeds by sequential cycloaddition of the C≡C bond of the alkyne to the Se=C bond of **1** to form a 2*H*-selenete complex and electrocyclic ring

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opening to the final product **3**. Since it has neither been possible to isolate nor to spectroscopically detect the 2*H*-selenete complex, ring opening must be rapid compared to cycloaddition. 2*H*-Selenete formation, however, is plausible on the basis of observations made in the system $(CO)_5W[Se{=}C(Ph)H]$/bis(*tert*-butylthio)ethyne where the corresponding 2*H*-selenete complex was isolated and fully characterized[10]. An analogous pathway has already been proposed for the reactions of π-donor-substituted alkynes with $(CO)_5W[S{=}C(Aryl)H]$[4] and of $(CO)_5W[Se{=}C(Aryl)Ph]$ with ynamines[11].

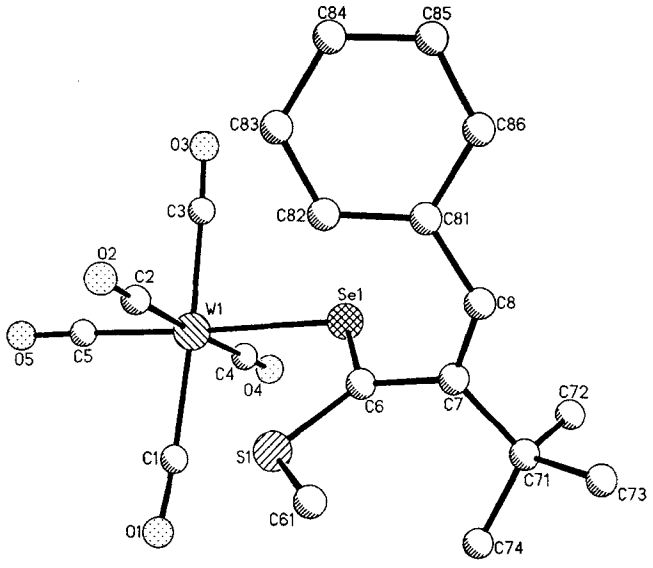
The reaction of **1** with **2** is highly regio- and stereoselective. Only one isomer is formed. From the ν(CO) absorptions in the IR spectra it follows that the thioselonoester ligand is η^1-bonded to tungsten. In contrast, the starting complex **1** is present in solution as a rapidly equilibrating mixture of the η^2 isomer and the η^1 isomers with the η^2 isomer dominating[12]. However, in pentacarbonyltungsten selenoamide complexes exclusive η^1 coordination was observed[5–9]. The η^1 coordination mode in **3** could also be deduced from the resonance of the selenocarbonyl carbon atom in the ^{13}C-NMR spectra at low field (δ = 241.9). The *C*=Se resonance for an η^2-coordination mode is to be expected at a much higher field (e.g. δ = 73.99 for **1** at −80°C in CD_2Cl_2). Low-field resonances for the *C*=Se atom are also characteristic of noncoordinated thioselonoesters $Se{=}C(SR)CH_2R'$ (R = Et, Pr, *t*Bu; R′ = H, Ph)[13].

A comparison of the C(Ph)*H* resonance of **3** with that of the related thiocarbonyl complexes $(CO)_5W[S{=}C(XR)C(R'){=}C(Ph)H]$ (X = NR, O, S, Se)[4] and selenoamide complexes $(CO)_5W[Se{=}C(NR_2)C(R'){=}C(Ph)H]$[5–9] revealed that C(=Se)SMe and Ph are mutually *cis*-configured [(*Z*) configuration with respect to the C=C bond]. In contrast, an (*E*) arrangement was observed in all *kinetically* controlled products of the insertion of aminoalkynes into the X=C bond of thio- and selenoaldehyde complexes[4–9].

The ^1H-NMR spectrum is temperature-dependent. At room temperature only one set of singlets for the C(Ph)*H*, SCH_3, and $C(CH_3)_3$ hydrogen atoms is observed. When solutions of **3** in $CDCl_3$ are cooled to −35°C these resonances are split into two sets of singlets (intensity ratio ca. 9:1). Analogously, at −10°C the ^{77}Se-NMR spectrum shows a weak resonance at δ = 1148 in addition to a strong signal at δ = 1091. Two processes can account for the splitting of signals: (a) interconversion of two rotamers (which differ by the orientation with respect to the central C–C single bond) and (b) (*E*)/(*Z*)(C=C) isomerization. The free energy of activation $\Delta G^{\neq}$ for (*E*)/(*Z*) isomerization in $(CO)_5W[S{=}C(NEt_2)C(NEt_2){=}C(Ph)H]$ is 102 kJ/mol (at 40°C in CD_3COCD_3)[8]. Although $\Delta G^{\neq}$ for the corresponding selenoamide complex is lower, the barrier for **3** is expected to be at least 100 kJ/mol. Therefore, rapid (*E*)/(*Z*)(C=C) isomerization can be excluded and **3** is presumably present in solution at low temperature in two rotameric forms.

The η^1(Se) coordination of the thioselonocarboxylic ester and the rather unusual (*Z*) orientation were also confirmed by the results of an X-ray diffraction study of **3** (Figure 1).

Figure 1. Structure of complex **3** in the crystal[a]



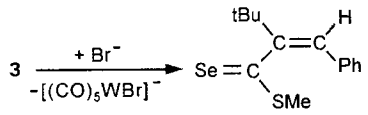
[a] Selected bond lengths [Å] and angles [°] (standard deviations in parentheses): W(1)–C(4) 2.033(8), W(1)–C(5) 1.980(7), W(1)–Se(1) 2.639(1), Se(1)–C(6) 1.813(7), C(6)–S(1) 1.703(7), C(6)–C(7) 1.488(9), C(7)–C(8) 1.344(10), C(7)–C(71) 1.545(10), C(8)–C(81) 1.456(11); W(1)–Se(1)–C(6) 112.5(2), Se(1)–C(6)–S(1) 119.7(4), Se(1)–C(6)–C(7) 117.0(5), C(6)–C(7)–C(8) 120.8(6), C(7)–C(8)–C(81) 131.6(6); C(1)–W(1)–Se(1)–C(6) −43.9(3), W(1)–Se(1)–C(6)–C(7) −176.0(5), Se(1)–C(6)–C(7)–C(8) 82.1(8), Se(1)–C(6)–S(1)–C(61) −172.8(4), C(6)–C(7)–C(8)–C(81) 2.7(12)

The two planes formed by the atoms Se(1), C(6), S(1), C(7) and C(6), C(7), C(71), C(8), C(81) are almost orthogonal [torsion angle Se(1)–C(6)–C(7)–C(8) 82.1(8)°] due to repulsive steric interaction between the SMe and CMe_3 substituent. A torsion angle between 80° and 90° was observed in all pentacarbonyl complexes $(CO)_5M-[Y{=}C(XR)C(R'){=}C(R^1)R^2]$ (XR = NR_2, OR, SR, SeR; Y = S, Se) carrying a bulky group R′. This arrangement prevents π-interaction between the C=C and the X=C bond[5–8,15]. As a consequence the central $C(sp^2)–C(sp^2)$ bond in **3** [C(6)–C(7): 1.488(9) Å] is rather long. A similar distance was observed for selenoamide complexes[5–7] and for the uncoordinated selenoamide $Se{=}C(NEt_2){=}C(Ph)H$[5,6]. The bond length also agrees well with that characteristic of the C–C single bond in unconjugated C=C–C=O systems[14]. However, for (*Z*)-$(CO)_5W[Se{=}C(SPh)CPh{=}C(OEt)Ph]$ a shorter C(6)–C(7) distance [1.39(3) Å] was reported[15]. In contrast to **3**, the C=C and the S=C plane in $(CO)_5W-[S{=}C(OEt)C(H){=}C(Ph)H]$ are coplanar and the C(6)–C(7) distance is 1.44(1) Å[4].

Treatment of a solution of **3** in dichloromethane with an excess of tetraethylammonium bromide gave rise to W–Se dissociation and formation of the uncoordinated thioselonocarboxylic ester **4** (Scheme 2).

Compound **4** is the first acyclic α,β-unsaturated thioselonocarboxylic ester to be isolated and characterized. A dimerization was not observed. Only recently, the first saturated thioselonocarboxylic esters were synthesized[13]. De-

Scheme 2

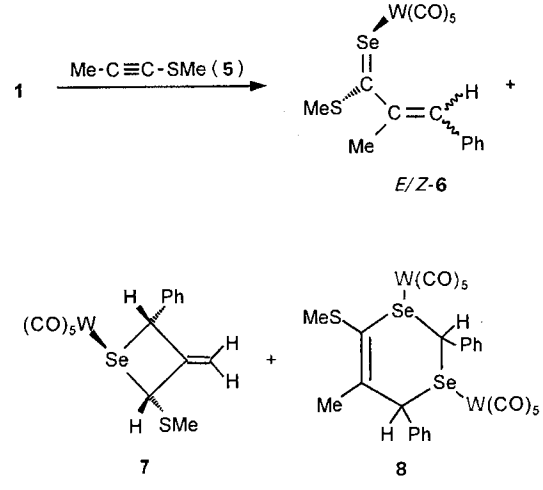


4

complexation proceeded with retention of the (*Z*) configuration as could be deduced from the NMR spectra. Significant low-field shifts were observed only for the ^{1}H signal of the SCH_3 group ($\Delta\delta$ = 0.35) and the ^{77}Se resonance ($\Delta\delta$ = 512). The influence of decoordination on the position of all other resonances is very small.

The reaction of **1** with a ca. 8-fold excess of 1-methylthio-1-propyne (**5**) proceeded faster than that with **2**, probably due to steric factors. Three complexes (**6**–**8**) were isolated from the reaction mixture (Scheme 3). It was not possible to separate the major products **6** and **7** chromatographically.

Scheme 3



E/*Z*-**6**

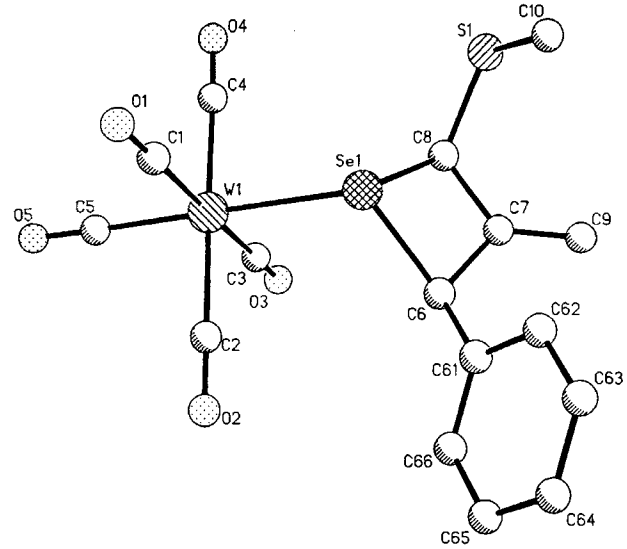
7 8

The product distribution depends on the solvent and on the ratio of the reacting complexes **5** to **1**. When the reaction was performed in dichloromethane using an 8.2-fold excess of **5**, complexes **6** and **7** together (isolated yield: 39%; **7**/**6** ca. 3:1) constituted the major products. However, when only a 1.7-fold excess of **5** and trichloromethane as the solvent were employed, complex **8** (43%) constituted the major product (ratio **7**/**6** ca. 1:1.7). Compound **8** is labile and decomposes already at −30°C in solution within a few hours.

After chromatography thioselonocarboxylic ester complex **6** was present in solution as a mixture of the (*E*)- and (*Z*)-configurational isomers. The ratio (*E*)-**6** / (*Z*)-**6** was ca. 2:1 as determined by integration of the C(Ph)*H* resonances. In the ^{1}H-NMR spectrum of the crude reaction mixture signals due to (*Z*)-**6** are absent. Therefore, initially (*E*)-**6** [C(=Se) and Ph *trans*] was formed which subsequently isomerized (presumably acid-catalyzed) to the (*E*)/(*Z*) mixture of the thioselonocarboxylic ester complex **6**. The same arrangement was observed in all kinetically controlled products of the insertion of π-donor-substituted alkynes into the X=C bond of thio- and selenoaldehyde complexes[8]. Complex **3** constitutes an exception which was obtained exclusively as the (*Z*) isomer. However, cycloaddition of **2** to **1** to form **3** [presumably (*E*)-**3**] is very slow. Therefore, the subsequent (*E*) → (*Z*) isomerization is probably faster, accellerated by repulsive steric interaction of the phenyl with the bulky *tert*-butyl substituent in the (*E*) isomer (Ph and *t*Bu *cis*). Similar to the ^{1}H-NMR spectrum of (*Z*)-**3**, that of (*Z*)-**6** [but not that of (*E*)-**6**] is temperature-dependent between −35°C and 25°C which indicates that at low temperature two rotamers of (*Z*)-**6** but only one isomer of (*E*)-**6** are present in solution.

The structure of **7** was deduced from its NMR spectra [^{1}H: singlets at δ = 2.37, 4.88, 5.23, 5.66, and 5.85 (relative intensity 5:1:1:1:1); ^{13}C: signals for the C(sp^3) ring atoms at δ = 58.0, 62.2 and the $=CH_2$ carbon atom at δ = 113.5]. In one case it was possible to obtain several crystals of **7** from the mixture of **6** and **7**. Therefore, the structure of **7** was additionally confirmed by an X-ray analysis. Compound **7** is the first selenetane derivative to be characterized by an X-ray analysis (Figure 2).

Figure 2. Structure of complex **7** in the crystal[a]

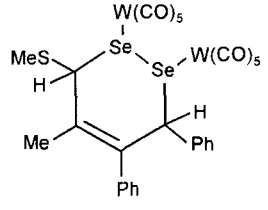


[a] Selected bond lengths [Å] and angles [°] (standard deviations in parentheses): W(1)–C(4) 2.051(7), W(1)–C(5) 1.989(9), W(1)–Se(1) 2.634(1), Se(1)–C(6) 2.032(7), Se(1)–C(8) 2.041(6), C(6)–C(7) 1.512(8), C(7)–C(8) 1.484(11), C(6)–C(61) 1.483(10), C(7)–C(9) 1.315(11), C(8)–S(1) 1.758(7); W(1)–Se(1)–C(6) 110.6(2), Se(1)–C(8)–S(1) 120.0(4), Se(1)–C(6)–C(7) 88.7(4), C(6)–C(7)–C(8) 104.0(6), Se(1)–C(8)–C(7) 89.1(4), C(6)–Se(1)–C(8) 70.9(3); Se(1)–C(6)–C(7)–C(8) −23.6(5), C(7)–C(6)–C(61)–C(62) 41.4(10)

The selenium atom is pyramidally coordinated, the sum of bond angles at Se(1) is 292.7°. The selenetane ring is puckered. The torsion angle Se(1)–C(6)–C(7)–C(8) [−23.6(5)°] compares well with the analogous angle in the uncoordinated thietanes *cis*- and *trans*-S–CPh_2–C(Cl)H–C(Cl)H (*cis* −21.3°[16], *trans* −22.6°[17]) and SeC_3H_6 (150.5 ± 1°, determined by microwave spectroscopy[18]). Due to the larger radius of Se the C(6)–X–C(8) angle in **7** [70.9(3)°] is smaller than that in

these thietanes (*cis* 79.3°, *trans* 76.6°). The substituents at C(6) and C(8) are in equatorial positions, the $(CO)_5W$ fragment occupies an axial position, thus avoiding unfavorable steric interaction of the bulky $(CO)_5W$ group with the Ph as well as with the SMe substituent. The W–Se [2.634(1) Å] distance is slightly shorter than that in **3** [2.639(1) Å].

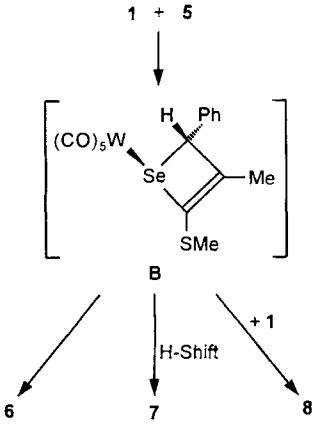
According to the mass spectrum compound **8** consists of two molecules of **1** and one molecule of the alkyne **5**. From the IR spectrum it follows that both pentacarbonyltungsten fragments are bound to selenium atoms. The coordination of one $(CO)_5W$ fragment to the C=C bond can be excluded since ν(CO) absorptions at higher energy are to be expected for a η^2 coordination. The ^{1}H-NMR spectrum of **8** shows, in addition to the signals for the aromatic hydrogen atoms, singlets at δ = 1.74, 2.19, 5.27, and 5.93 (relative intensity: 3:3:1:1). The ^{13}C-NMR spectrum shows signals for two CH_3 carbon atoms (δ = 19.4 and 28.0) and two CH carbon atoms in the aliphatic region (δ = 54.4 and 68.7) and four signals each for CH and for non-hydrogen carrying carbon atoms in the aromatic/olefinic region. Two resonances each for the *cis*- and *trans*-CO substituents indicate that the $(CO)_5W$ fragments are inequivalent. On the basis of these spectroscopic data the most probable structure for **8** is that shown in Scheme 3. However, alternative structures (e.g. 3,6-dihydro-1,2-diselenine complex **A** or a tautomer of **8**) cannot be completely ruled out.



A

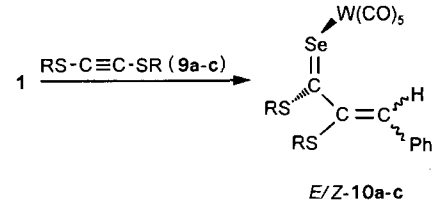
All complexes (**6**–**8**) are formally derived from the 2*H*-selenete complex **B** which results from regiospecific cycloaddition of **5** to **1**: complex **6** by electrocyclic ring opening, complex **7** by a 1,3-H-shift and compound **8** by cycloaddition of the Se=C–C=C fragment of **6** to the Se=C bond of **1** (Scheme 4).

Scheme 4



Selenoaldehyde complex **1** reacts with the bis(alkylthio)alkynes **9a**–**c** in a similar manner as with **2**. After chromatography the red-violet α,β-unsaturated α-alkylthio thioselenocarboxylic ester complexes **10a**–**c** were obtained as mixtures of the (*E*) and (*Z*) isomers with respect to the C=C bond [(*E*)/(*Z*) = 1:1 (**10a**), 1:1.4 (**10b**), 1.7:1 (**10c**)] (Scheme 5). The structural assignment [η^1 coordination, (*E*) and (*Z*) configuration] was based on the IR, ^{1}H-, ^{13}C-, and ^{77}Se-NMR spectra.

Scheme 5



E/Z-**10a-c**

9,10: R = Me (**a**), iPr (**b**), 2,6-$C_6H_3Me_2$ (**c**)

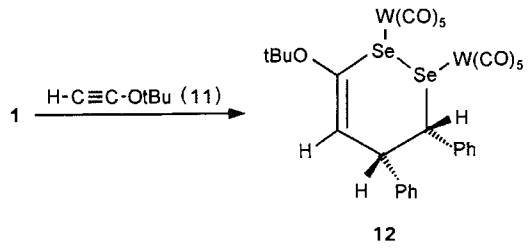
Monitoring of the reaction of **1** with **9a** in $CDCl_3$ at −53°C revealed that (*Z*)-**10a** was the kinetically controlled reaction product. Subsequent fast isomerization gave rise to the formation of a (*E*)/(*Z*) (1:1) isomeric mixture. The ratio did not change further within one day even at room temperature. Preferential formation of the (*Z*) isomer in the reactions of **1** with **9b** and **9c**, respectively, could not be established. The (*E*)/(*Z*) isomeric ratio in the crude reaction mixtures was already that of the samples after purification by chromatography. The ratio did not change when solutions of **10b** and **10c** in $CDCl_3$ were kept at room temperature for 11 days. Presumably, (*E*)/(*Z*) isomerization of **10b**, **c** is faster than their formation from **1** and **9b**, **c**. Compared to the analogous dithiocarboxylic ester complexes[4], (*E*)/(*Z*) isomerization of **10a**–**c** is significantly faster.

Between −70°C and 25°C the ^{1}H-NMR spectra of **10a** and **10b** are temperature-dependent. At low temperature both isomers of **10a**, **b** are present in solution as two rotamers which rapidly interconvert at room temperature. From the coalescence of the C(Ph)*H* resonances the free energy of activation $\Delta G^{\neq}$ for the interconversion (presumably rotation around the central C–C single bond) of (*E*)-**10a** and (*E*)-**10b** was calculated to be $\Delta G^{\neq}$ = 52 ± 3 kJ/mol (at −25°C) and 54 ± 2 kJ/mol (at −35°C), respectively. The barrier for interconversion of the corresponding dithiocarboxylic ester complex (*E*)-$(CO)_5W$[S=C(SMe)C(SMe)=C(Ph)H] is similar ($\Delta G^{\neq}$ = 55 ± 1 kJ/mol)[4]. For (*Z*)-**10a**, **b** $\Delta G^{\neq}$ is smaller, the coalescence temperature is ca. −65°C for (*Z*)-**10a** and lower than −70°C for (*Z*)-**10b**.

The reaction of **1** with a 3.4-fold excess of the terminal alkyne **11** in dichloromethane proceeded fast even at −50°C. After chromatography the dark red, crystalline adduct **12** was obtained in 36% yield (Scheme 6). Compound **12** which consists of two molecules of **1** and one molecule of **11** is thermolabile and readily decomposes in solution

($CDCl_3$ at room temperature or acetone even at low temperature) within a few hours to yet unidentified products.

Scheme 6



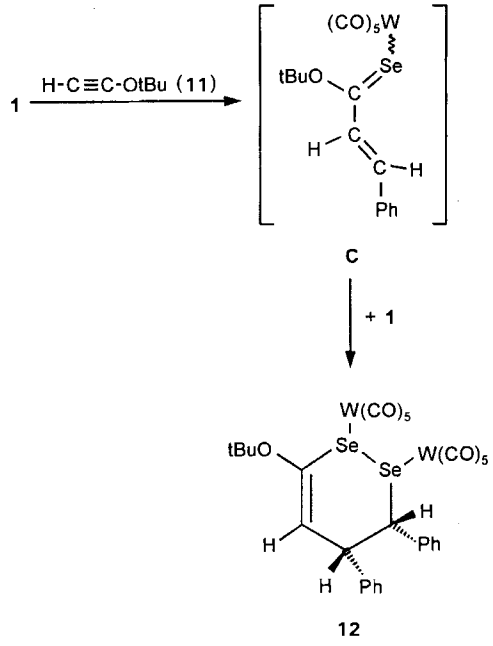
12

The ^{1}H-NMR spectrum of **12** shows at −35°C, in addition to resonances in the aromatic region, a singlet at δ = 1.61, two doublets at δ = 5.46 (J = 3.1 Hz) and 5.71 (J = 7.1 Hz), and a doublet of a doublet at δ = 4.11 (J = 7.0 and 3.4 Hz). The ^{13}C-NMR spectrum exhibits four signals in the aliphatic region [δ = 29.9, 86.1 (*t*BuO), 55.0, 80.3], 11 signals in the aromatic/olefinic region and resonances for two inequivalent $(CO)_5W$ fragments. Low-field signals at δ > 205 characteristic of selenocarbonyl carbons are absent. These spectroscopic data are consistent with the structure shown in Scheme 6. The proposed connectivity of the atoms was confirmed by an X-ray structural analysis of **12**. However, due to the poor quality of the crystals and the large standard deviation of the bond lengths and angles a discussion of the structure in detail is not feasible.

Weak absorptions in the IR spectrum at higher energy in addition to the ν(CO) pattern expected for η^1-coordinated organylseleno complexes and two weak resonances in the ^{13}C-NMR spectrum (δ = 197.6 and 204.1) for another $(CO)_5W$ fragment indicate that in solution another isomer of **12** is present in low concentration. Position and intensity ratio of the additional ν(CO) absorptions are similar to those of olefin complexes. Presumably, in the second isomer one $(CO)_5W$ fragment is η^1-bonded to a selenium atom and the other one η^2-coordinated to the C=C bond of the diselenine ligand.

The formation of **12** is easily rationalized by assuming the sequence shown in Scheme 7. A regiospecific cycloaddition of **11** to the Se=C bond of **1** to give a selenete complex (related to **B** in Scheme 4) is followed by stereoselective electrocyclic ring opening to form the *E* isomer of selonocarboxylic ester complex **C**. These reaction steps proceed analogously to those of the reactions of **1** with **5** and **9**. Subsequent fast regio- and stereoselective Diels-Alder reaction of **C** as a 4π selenadiene with **1** as a dienophile finally affords complex **12**. The observed *cis* arrangement of the phenyl substituents in **12** is very likely the result of minimizing steric interaction in the transition structure of the [4 + 2] cycloaddition.

Scheme 7



12

5,6-Dihydro-1,2-diselenines are very rare. Only recently the first monocyclic 5,6-dihydro-1,2-diselenines were prepared by dimerization of α,β-unsaturated selenoaldehydes which were generated in situ by selenation of cinnamoyl derivatives with bis(dimethylaluminium) selenide[19].

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Experimental

All manipulations were carried out under either nitrogen or argon by using conventional Schlenk techniques. Solvents were dried by refluxing over sodium/benzophenone ketyl, CaH_2, or $LiAlH_4$ and were freshly distilled prior to use. The silica gel used for chromatography (Baker, silica gel for flash chromatography) was nitrogen-saturated. Flash chromatography was performed at an N_2 pressure of 1.3 bar. The yields refer to analytically pure compounds and were not optimized. The complex **1**[20], and the alkynes **2**[21], **5**[22], **9a**[22], **9b**, **c**[23], and **11**[24] were prepared according to literature procedures, alkyne **2c** was purchased from Merck and was used without further purification. – IR: FT-IR spectrophotometer, Fa. Bio-Rad and Perkin-Elmer IR spectrophotometer 983 G. – ^{1}H NMR and ^{13}C NMR: Bruker WM 250, Bruker AC 250, Jeol 400. Unless specifically mentioned $CDCl_3$ was used as the solvent. Chemical shifts are reported relative to TMS (^{1}H NMR) or relative to the solvent signal (^{13}C NMR). – UV-Vis: Hewlett-Packard diode array spectrophotometer 8452A. – MS: Finnigan MAT 312, modified for EI (70 eV) or FAB-MS (matrix: NBOH).

Pentacarbonyl[S-methyl (Z)-2-tert-butyl-3-phenylthioselono-2-propenoate]tungsten (**3**): A solution of 480 mg (0.97 mmol) of **1** and 0.5 ml (3.5 mmol) of **2** in 3 ml of dichloromethane is stirred for 51 h at −30°C and then chromatographed at −40°C. A red-violet band is eluted with pentane/CH_2Cl_2 (10:1). The solvents are removed in vacuo at −10°C and the residue is crystallized from

pentane/CH_2Cl_2 (10:1). Red crystals. Yield 310 mg (0.50 mmol; 52% based on **1**), m.p. 110°C. – IR (pentane): ν(CO) = 2068 cm^{-1} w, 1948 vs, 1935 s. – ^1H NMR (298 K): δ = 1.33 [s, 9H, $C(CH_3)_3$], 2.26 (br s, 3H, SCH_3), 6.49 [br s, 1H, C(Ph)*H*], 7.24–7.42 (m, 5H, Ph). – ^1H NMR (238 K): δ = 1.33 + 1.37 [9:1, $C(CH_3)_3$)], 2.26 + 2.35 (10:1, SCH_3), 6.46 + 6.62 (9:1, SCH_3), 7.24–7.42 (Ph). – ^{13}C NMR (270 K): δ = 25.0 (SCH_3), 30.4 [$C(CH_3)_3$], 36.2 [$C(CH_3)_3$], 123.0, 128.2, 128.6, 128.9, 134.4, 154.8 (Ph, C_α, C_β), 197.3 (*cis*-CO, J_{WC} = 127.0 Hz), 202.0 (*trans*-CO), 241.9 [*C*(Se)SCH_3]. – ^{77}Se-NMR (263 K): δ = 1148, 1091. – VIS (CH_2Cl_2): λ_{max} (lg ε) = 516 nm (3.929). – MS (FAB, based on ^{80}Se and ^{184}W), *m/z* (%): 622 (78) $[M]^+$, 566 (14) $[M - 2\ CO]^+$, 538 (13) $[M - 3\ CO]^+$, 510 (14) $[M - 4\ CO]^+$, 482 (74) $[M - 5\ CO]^+$, 218 (55) $[M - W(CO)_5 - Se]^+$, 217 (100) $[M - W(CO)_5 - Se - H]^+$, 203 (19) $[M - W(CO)_5 - Se - CH_3]^+$, 171 (41) $[M - W(CO)_5 - Se - S - CH_3]^+$. – $C_{19}H_{18}O_5SSeW$ (621.2): calcd. C 36.74, H 2.92; found C 36.46, H 2.91.

S-Methyl (Z)-2-tert-butyl-3-phenylthioselono-2-propenoate (**4**): A solution of 280 mg (0.45 mmol) of **3** and 290 mg (1.4 mmol) of NEt_4Br in 3 ml of CH_2Cl_2 is stirred at 4°C for 4 d and then chromatographed at −30°C. With pentane/CH_2Cl_2 (ratio decreasing from 10:1 to 6:1) a slightly violet band is eluted which contains **4**. Removal of the solvents affords **4** as a slightly violet oil. Yield 100 mg (0.34 mmol; 76% based on **3**). – ^1H NMR (238 K): δ = 1.35 [s, 9H, $C(CH_3)_3$], 2.61 (s, 3H, SCH_3), 6.46 [s, 1H, C(Ph)*H*], 7.22–7.28 (m, 3H, Ph), 7.42–7.45 (m, 2H, Ph). – ^{13}C NMR (238 K): δ = 25.1 (SCH_3), 30.6 [$C(CH_3)_3$], 35.5 [$C(CH_3)_3$], 122.0, 127.0, 128.0, 128.8, 135.9, 161.6 (C_6H_5, C_α, C_β), 240.2 (C=Se). – ^{77}Se NMR (263 K): δ = 1660. – MS (EI, based on ^{80}Se), *m/z* (%): 298 (100) $[M]^+$, 283 (55) $[M - CH_3]^+$, 251 (22) $[M - SCH_3]^+$, 217 (46) $[M - Se - H]^+$, 195 (41) $[M - SCH_3 - C_4H_8]^+$, 170 (53) $[M - Se - SCH_3 - H]^+$, 161 (33) $[M - Se - C_4H_9]^+$, 115 (70) $[M - Se - SCH_3 - C_4H_8]^+$, 91 (27) $[C_7H_7]^+$, 57 (69) $[C_4H_9]^+$.

Pentacarbonyl[S-methyl (Z)-2-methyl-3-phenylthioselono-2-propenoate]tungsten (**6**), *selenetane complex* 7 *and 1,3-diselenacyclohexene complex* **8**: A solution of 350 mg (0.71 mmol) of **1** and 0.5 ml (5.8 mmol) of **5** in 3 ml of CH_2Cl_2 is stirred at −60°C for 60 min. The color of the solution turns from blue to red. The solution is chromatographed at −35°C. With pentane/CH_2Cl_2 (ratio decreasing from 10:1 to 5:1) first a red-violet band containing **6** and **7** (ratio ca. 3:1) is eluted. The succeeding yellow-brown band contains **8** (ca. 5–15%) which is the major product when the reaction is performed in $CHCl_3$ and only a slight excess of **5** is used (vide supra). Removal of the solvents of the red-violet eluate at −10°C in vacuo affords a mixture (ca. 3:1) of **6** and **7** as a violet oil. Only once it was possible to obtain several red crystals of **7** by crystallization from pentane/dichloromethane (5:1) at −30°C. Therefore, the spectral data refer to mixtures of **6** [(*E*)/(*Z*) = 2:1] and **7**. Combined yield of **6** and **7** 160 mg (0.28 mmol; 39% based on **1**). – IR (pentane): **6**: ν(CO) = 2070 cm^{-1} w, 1985 vw, 1947 vs, 1936 s; **7**: ν(CO) = 2073 cm^{-1} w, 1984 vw, 1945 vs, 1937 s. – ^1H NMR (298 K): (*E*)-**6**: δ = 2.38 (d, *J* = 1.3 Hz, 3H, CH_3), 2.74 (s, 3H, SCH_3), 6.86 [br s, 1H, C(Ph)*H*], 7.15–7.48 (m, 5H, Ph); (*Z*)-**6**: δ = 2.23 (d, *J* = 1.5 Hz, 3H, CH_3), 2.52 (br s, 3H, SCH_3), 6.46 (q, *J* = 1.3 Hz, 1H, C(Ph)*H*) [2 broad signals at 238 K: 6.40 and 6.54], 7.15–7.48 (m, 5H, Ph), **7**: δ = 2.37 (s, 1H, SCH_3), 4.88 (s, 1H, CH_2), 5.23 (s, 1H, CH_2), 5.66 [s, 1H, C(Ph)*H*], 5.85 [s, 1H, C(SCH_3)*H*], 7.38–7.51 (m, 5H, Ph). – ^{13}C NMR (JMODXH) (263 K): (*E*)-**6**/(*Z*)-**6**: δ = 13.8, 19.5 (Me), 197.3, 197.6 (J_{WC} = 128.6 Hz) (*cis*-CO), 201.7 (*trans*-CO), 241.5 [*C*(Se)SMe]; **7**: δ = 58.0, 62.2 [*C*(Ph)H, *C*(SMe)H], 113.5 (CH_2), 197.0 (*cis*-CO), 199.9 (*trans*-CO); (*E*)-**6**/(*Z*)-**6**/**7**: δ = 24.2, 24.8, 26.0 (SMe), 16 signals between 125.8 and 148.8 [Ph, C_α (**6**), C_β (**6**), C-3 (**7**)]. – MS (FAB, based on ^{80}Se and ^{184}W), *m/z* (%): 580 (16) $[M]^+$, 496 (8) $[M - 3\ CO]^+$, 468 (12) $[M - 4\ CO]^+$, 440 (25) $[M - 5\ CO]^+$, 425 (11) $[M - 5\ CO - Me]^+$, 209 (14) $[M - W(CO)_5 - S - Me]^+$, 176 (12) $[M - W(CO)_5 - Se]^+$, 161 (15) $[M - W(CO)_5 - Se - Me]^+$, 129 (100) $[M - W(CO)_5 - Se - S - Me]^+$. – $C_{16}H_{12}O_5SSeW$ (579.2): calcd. C 33.18, H 2.09; found C 32.79, H 2.40.

At −75°C, 86 µl (0.99 mmol) of **5** is added to a solution of 280 mg (0.57 mmol) of **1** in 5.4 ml of $CHCl_3$. The solution is warmed to −35°C within 150 min. during which the color of the solution changes from blue to yellow-brown. The solution is then chromatographed at −35°C with pentane/dichloromethane (ratio decreasing from 10:1 to 5:1). First the red-violet band containing **6** and **7** (ratio ca. 1.7:1; 13–26% yield) is eluted and then the succeeding yellow-brown band containing **8**. The solvents of the yellow-brown solution are removed in vacuo at −30°C to afford **8** as a yellow-brown oil. Yield 130 mg (0.12 mmol; 43% based on **1**). – IR (pentane): ν(CO) = 2074 cm^{-1} w, 1986 vw, 1949 vs, 1940 sh. – ^1H NMR (238 K): δ = 1.74 (s, 3H, CH_3), 2.19 (s, 3H, SCH_3), 5.27 [s, 1H, C(Ph)*H*], 5.93 [s, 1H, C(Ph)*H*], 7.21–7.50 (m, 10H, Ph). – ^{13}C NMR (JMODXH) (238 K): δ = 19.4 (CH_3), 28.0 (SCH_3), 54.4 [*C*(Ph)H], 68.7 [*C*(Ph)H], 127.5, 128.7, 129.5, 130.3 [*o*-, *m*-, *p*-C_{Ph}], 133.4, 135.6, 140.8, 148.5 (*C*SCH_3, *C*CH_3, *i*-C_{Ph}), 196.5 (J_{WC} = 130.1 Hz), 195.9 (J_{WC} = 128.7 Hz) (*cis*-CO), 200.0, 198.8 (*trans*-CO). – MS (FAB, based on ^{80}Se and ^{184}W), *m/z* (%): 1072 (2) $[M]^+$, 1046 (4) $[M - CO]^+$, 934 (5) $[M - 5\ CO]^+$, 878 (9) $[M - 7\ CO]^+$, 850 (3) $[M - 8\ CO]^+$, 747 (4) $[M - 10\ CO - SMe]^+$, 666 (5) $[M - W(CO)_5 - 3\ CO]^+$, 638 (12) $[M - W(CO)_5 - 4\ CO]^+$, 610 (6) $[M - W(CO)_5 - 5\ CO]^+$, 580 (63) $[M - (CO)_5W[Se=C(Ph)H]]^+$, 524 (27) $[M - (CO)_5W[Se=C(Ph)H] - 2\ CO]^+$, 496 (22) $[M - (CO)_5W[Se=C(Ph)H] - 3\ CO]^+$, 468 (26) $[M - (CO)_5W[Se=C(Ph)H] - 4\ CO]^+$, 440 (83) $[M - (CO)_5W-[Se=C(Ph)H] - 5\ CO]^+$, 345 (34) $[M - Se - 2\ W(CO)_5 - H]^+$, 218 (95) $[M - 2\ Se - 2\ W(CO)_5 - SMe - H]^+$, 175 (100) $[M - (CO)_5W[Se=C(Ph)H] - W(CO)_5 - H]^+$. – $C_{28}H_{18}O_{10}SSe_2W_2$ (1072.1): calcd. C 31.37, H 1.69; found C 31.06, H 2.06.

Pentacarbonyl[S-methyl (Z)-2-methylthio-3-phenylthioselono-2-propenoate]tungsten (**10a**): A solution of 120 mg (0.24 mmol) of **1** and 0.2 ml (1.99 mmol) of **9a** in 3 ml of CH_2Cl_2 is stirred for 2 h at −50°C and then chromatographed at −40°C. With pentane/CH_2Cl_2 (ratio decreasing from 10:1 to 5:1) the red-violet band is eluted. Removal of the solvents in vacuo at −10°C affords a (*E*)/(*Z*) mixture (ratio ca. 1:1) of **10a** as a red-violet sticky oil. The mixture of the configurational isomers cannot be separated by chromatography. Combined yield of both isomers 90 mg (0.15 mmol; 63% based on **1**). – IR (pentane): ν(CO) = 2069 cm^{-1} w, 1950 vs, 1937 s. – ^1H NMR (298 K): (*Z*)-**10a**: δ = 2.32 (s, 3H, SCH_3), 2.77 (s, 3H, SCH_3), 6.96 [s, 1H, C(Ph)*H*], 7.24–7.43 (m, 3H, Ph), 7.75–7.79 (m, 2H, Ph); (*E*)-**10a**: δ = 2.43 (s, 3H, SCH_3), 2.58 (br s, 3H, SCH_3), 6.59 [s, 1H, C(Ph)*H*], 7.24–7.43 (m, 5H, Ph). – ^{13}C NMR (238 K): (*Z*)-**10a**/(*E*)-**10a**: δ = 15.7, 15.9 (SCH_3), 23.9, 24.7, 25.1 (SCH_3), 14 signals between 124.7 and 143.0 (Ph, C_α, C_β), 197.0 (J_{WC} = 127.8 Hz), 197.2 (J_{WC} = 127.9 Hz) (*cis*-CO), 201.9 (J_{WC} = 158.6), 202.1 (J_{WC} = 158.4 Hz) (*trans*-CO), 231.0, 232.3, 232.8 (C=S). – ^{77}Se NMR (263 K): (*Z*)-**10a**/(*E*)-**10a**: δ = 1162, 1167. – VIS (CH_2Cl_2): λ_{max} (lg ε) = 534 nm (3.918). – MS (FAB, based on ^{80}Se and ^{184}W), *m/z* (%): 612 (3) $[M]^+$, 584 (51) $[M - CO]^+$, 528 (26) $[M - 3\ CO]^+$, 472 (26) $[M - 5\ CO]^+$, 457 (16) $[M - 5\ CO - Me]^+$, 207 (15) $[M - W(CO)_5 - Se - H]^+$, 161 (100) $[M - W(CO)_5 - Se - SMe]^+$, 146 (16) $[M - W(CO)_5 - Se - SMe - Me]^+$, 115 (34) $[C_9H_7]^+$, 91 (34) $[C_7H_7]^+$, 77 (38) $[C_6H_5]^+$. – $C_{16}H_{12}O_5S_2SeW$ (611.2): calcd. C 31.44, H 1.98; found C 31.29, H 2.51.

Pentacarbonyl[S-isopropyl (Z)-2-isopropylthio-3-phenylthioselono-2-propenoate]tungsten (**10b**): A solution of 220 mg (0.45 mmol) of **1** and 0.3 ml (1.6 mmol) of **9b** in 3 ml of CH_2Cl_2 is stirred. The temp. of the solution is allowed to increase within 3 h from −52°C to −42°C. The solution is chromatographed at −75°C and the violet band eluted with pentane/CH_2Cl_2 (10:1). Removal of the solvents in vacuo at −30°C affords a (*E*)/(*Z*) mixture (ratio ca. 1:1.4) of **10b** as a red-violet sticky oil. The mixture of the configurational isomers cannot be separated by chromatography. Combined yield of both isomers 190 mg (0.29 mmol; 64% based on **1**). − IR (pentane): ν(CO) = 2067 cm^{-1} w, 1949 vs, 1935 s. − ^1H NMR (298 K): (*Z*)-**10b**: δ = 4.23 [sept, *J* = 6.8 Hz, 1H, C(S)C(CH$_3$)$_2$*H*], 7.17 [s, 1H, C(Ph)*H*], 7.37−7.42 (m, 3H, Ph), 7.86−7.89 (m, 2H, Ph); (*E*)-**10b**: δ = 4.00 [sept, *J* = 6.9 Hz, 1H, C(S)C(CH$_3$)$_2$*H*], 6.89 [s, 1H, C(Ph)*H*], 7.29−7.32 (m, 3H, Ph), 7.37−7.42 (m, 2H, Ph); (*Z*)-**10b**/(*E*)-**10b**: δ = 1.31−1.49 (m, 24H, CH$_3$), 3.31 [m, 2H, SC(CH$_3$)$_2$*H*]. − ^{13}C NMR (238 K): (*Z*)-**10b**/(*E*)-**10b**: δ = 19.9, 21.0, 21.4, 21.8, 22.1, 22.2, 22.4, 23.5, 23.7, 23.9 (CH$_3$), 36.9, 38.0, 38.7 (SCH), 45.3, 46.3, 47.1 [C(Se)S*C*], 14 signals between 128.5 and 143.0 (Ph, C_α, C_β), 197.3 (J_{WC} = 128.1 Hz), 197.6 (J_{WC} = 128.2 Hz) (*cis*-CO), 202.2, 202.3 (*trans*-CO), 231.1, 232.5, 233.4 (*C*=Se). − ^{77}Se NMR (263 K): (*Z*)-**10b**/(*E*)-**10b**: δ = 1123. − VIS (CH_2Cl_2): λ_{max} (lg ε) = 540 nm (3.957). − MS (FAB, based on ^{80}Se and ^{184}W), *m/z* (%): 668 (2) $[M]^+$, 640 (58) $[M - CO]^+$, 584 (18) $[M - 3\ CO]^+$, 528 (29) $[M - 5\ CO]^+$, 485 (24) $[M - 5\ CO - C_3H_7]^+$, 443 (37) $[M - 5\ CO - 2\ C_3H_7 + H]^+$, 221 (15) $[M - W(CO)_5 - Se - C_3H_7]^+$, 189 (55) $[M - W(CO)_5 - Se - S - C_3H_7]^+$, 147 (100) $[M - W(CO)_5 - Se - S - 2\ C_3H_7 - H]^+$, 115 (98) $[C_9H_7]^+$, 91 (25) $[C_7H_7]^+$, 77 (17) $[C_6H_5]^+$. − $C_{20}H_{20}O_5S_2SeW$ (667.3): calcd. C 36.00, H 3.02; found C 36.13, H 3.11.

Pentacarbonyl[S-(2,6-dimethylphenyl) (Z)-2-(2,6-dimethylphenylthio)-3-phenylthioselono-2-propenoate]tungsten (**10c**): A solution of 100 mg (0.20 mmol) of **1** and 66 mg (0.22 mmol) of **9c** in 3 ml of CH_2Cl_2 is warmed from −42°C to −9°C within 4 h 45 min and then chromatographed with pentane/CH_2Cl_2 (ratio decreasing from 10:1 to 5:1) at −35°C. The violet band containing **10c** is collected. The solvents are removed in vacuo and the residue is crystallized from pentane. A mixture of configurational isomers of (*E*)-**10c** and (*Z*)-**10c** (ratio 1.7:1) is obtained as violet needles. Combined yield of both isomers 60 mg (0.08 mmol; 40% based on **1**). m.p. 142°C (dec.). − IR (pentane): ν(CO) = 2068 cm^{-1} w, 1947 vs, 1932 s. − ^1H NMR (238 K): (*E*)-**10c**: δ = 1.90 (s, br, 3H, CH$_3$), 2.02 (s, br, 3H, CH$_3$), 2.65 (br s, 6H, CH$_3$), 6.63 [s, 1H, C(Ph)*H*]; (*Z*)-**10c**: δ = 2.21 (br s; 6H, CH$_3$), 2.47 (br s; 6H, CH$_3$); (*E*)-**10c**/(*Z*)-**10c**: δ = 7.05−7.85 [m, 21H, Aryl and C(Ph)*H* of (*Z*)-**10c**], 8.07−8.09 (m, 2H, Aryl). − ^{13}C NMR (238 K): (*E*)-**10c**/(*Z*)-**10c**: δ = 14.3, 20.0, 20.2, 20.4, 21.4, 22.6, 23.2 (CH$_3$), 27 signals between 128.4 and 145.7 (Ph, Aryl, C_α, C_β), 197.4, 197.8 (*cis*-CO), 201.9, 202.1 (*trans*-CO), 229.9, 230.4 (C=Se). − Vis (CH_2Cl_2): λ_{max} (lg ε) = 538 nm (4.000). − MS (FAB, based on ^{80}Se and ^{184}W); *m/z* (%): 792 (4) $[M]^+$, 765 (29) $[M - CO]^+$, 736 (4) $[M - 2\ CO]^+$, 708 (20) $[M - 3\ CO]^+$, 680 (33) $[M - 4\ CO]^+$, 652 (27) $[M - 5\ CO]^+$, 571 (5) $[M - 3\ CO - SC_8H_9]^+$, 543 (16) $[M - 4\ CO - SC_8H_9]^+$, 515 (16) $[M - 5\ CO - SC_8H_9]^+$, 388 (8) $[M - W(CO)_5 - Se]^+$, 283 (23) $[M - W(CO)_5 - Se - C_8H_9]^+$, 251 (100) $[M - W(CO)_5 - Se - S - C_8H_9]^+$, 137 (51) $[SC_8H_9]^+$, 115 (87) $[C_9H_7]^+$, 105 (90) $[C_8H_9]^+$, 91 (95) $[C_7H_7]^+$. − $C_{30}H_{24}O_5S_2SeW$ (791.5): calcd. C 45.53, H 3.06; found C 45.39, H 3.26.

1,2-Diselenacyclohexene(bispentacarbonyltungsten) Complex **12**: A solution of 0.5 g (1.0 mmol) of **1** and 4.0 ml (3.4 mmol) of **11** in 3 ml of dichloromethane is stirred at −50°C for 5 min. The color of the solution changes from blue to red. The solution is chromatographed at −40°C. The red main band is eluted with pentane/dichloromethane (ratio decreasing from 100:1 to 10:1). The solvents are removed in vacuo at −10°C and the red oily residue crystallized at −30°C from pentane/dichloromethane (1:1). Red-black needles. Yield 190 mg (0.18 mmol; 36% based on **1**), m.p. 78°C (dec.). − IR (pentane): ν(CO) = 2105 cm^{-1} w, 2082 w, 2068 m, 2041 vw, 2020 w, 1994 m, 1985 w, 1960 s, 1943 vs, 1938 sh. − ^1H NMR (238 K): δ = 1.61 (s, 9H, OC_4H_9), 4.11 (dd, *J* = 3.5 Hz, 7.0 Hz, 1H, 4-H), 5.46 (d, *J* = 3.3 Hz, 1H, 5-H), 5.71 (d, *J* = 7.0 Hz, 1H, 3-H), 6.75−6.78 (m, 2H, Ph), 6.98 (br s, 2H, Ph), 7.26−7.42 (m, 6H, Ph). − ^{13}C NMR (238 K): δ = 27.9 [OC(*C*H$_3$)$_3$], 55.0 (C-4), 80.3 (C-3), 86.1 [O*C*(CH$_3$)$_3$], 125.7, 127.8, 128.0, 128.4, 128.8, 128.9, 129.0, 129.8 (C-5, *o*-, *m*-, *p*-C_{Ph}), 134.4, 138.1, 144.4 (C-6, *i*-C_{Ph}), 196.4 (J_{WC} = 128.2 Hz, *cis*-CO), 196.5 (J_{WC} = 128.8 Hz, *cis*-CO), 197.6, 198.7, 199.0, 204.1 (*trans*-CO). − VIS (CH_2Cl_2): λ_{max} (lg ε) = 486 nm (3.775). − MS (FAB, based on ^{80}Se and ^{184}W), *m/z* (%): 946 (0.4) $[M - 5\ CO]^+$, 834 (1) $[M - 9\ CO]^+$, 564 (2) $[M - (CO)_5W[Se{=}C(Ph)H] - CO]^+$, 536 (4) $[M - (CO)_5W[Se{=}C(Ph)H] - 2\ CO]^+$, 301 (5) $[M - 2\ W(CO)_5 - Se - C_4H_9]^+$, 221 (100) $[M - 2\ W(CO)_5 - 2\ Se - C_4H_9]^+$. − $C_{30}H_{22}O_{11}Se_2W_2$ (1084.1): calcd. C 33.24, H 2.05; found C 32.64, H 2.02. Compound **12** could not be obtained free from solvent.

X-ray Structural Analyses of **3** *and* **6**: **3**: $C_{19}H_{18}O_5SSeW$, molecular mass 621.2, crystal size 0.1 × 0.1 × 0.1 mm (obtained from pentane/CH_2Cl_2, 10:1); monoclinic, $P2_1/n$, *a* = 11.688(3), *b* = 10.926(4), *c* = 16.893(4) Å, β = 95.88(2)°, *V* = 2146(1) Å^3, *Z* = 4, $d_{calcd.}$ = 1.923 g cm^{-3}; μ(Mo-K_α) = 7.14 mm^{-1}, *F*(000) = 1184; Wyckoff-scan, 2Θ range 4.0−54.0°, scan rate 2.0−29.3° min^{-1} in ω; Δω = 0.70°, temp. 227 K, 5169 reflections collected, 4680 independent reflections, 3548 reflections with $F > 3.0\sigma(F)$; min./max. transmission 0.3599/0.4559, 244 refined parameters; *R* = 0.041, R_w = 0.040. Largest difference peak (hole): +0.78 e Å^{-3} (−0.94 e Å^{-3}). − **7**: $C_{16}H_{12}O_5SSeW$, molecular mass 579.1, crystal size 0.3 × 0.3 × 0.3 mm (obtained from pentane/CH_2Cl_2, 5:1); monoclinic, $P2_1/n$, *a* = 11.475(2), *b* = 14.698(3), *c* = 11.726(4) Å, β = 109.38(1)°, *V* = 1866(1) Å^3, *Z* = 4, $d_{calcd.}$ = 2.062 g cm^{-3}; μ(Mo-K_α) = 8.21 mm^{-1}, *F*(000) = 1088; ω-scan, 2Θ range 4.0−52.0°, scan rate 2.0−29.3° min^{-1} in ω; Δω = 1.80°, temp. 193 K, 3975 reflections collected, 3630 independent reflections, 2897 reflections with $F > 4.0\sigma(F)$; min./max. transmission 0.742/0.972, 217 refined parameters; *R* = 0.033, R_w = 0.037. Largest difference peak (hole): +0.98 e Å^{-3} (−1.30 e Å^{-3}). − The measurements were made with a crystal mounted in a glass capillary on a Siemens R3m/V diffractometer (graphite monochromator, Mo-K_α radiation, λ = 0.71073 Å). A semi-empirical absorption correction (based on 10 reflections) was carried out. The structures were solved by Patterson methods using the SHELXTL PLUS (VMS) program package. The positions of the hydrogen atoms were calculated by assuming ideal geometry (d_{C-H} = 0.96 Å) and their coordinates were refined together with the attached C atoms as "riding model". The positions of all other atoms were refined anisotropically by the full-matrix least-squares method. Complete lists of atom coordinates and thermal parameters have been deposited[25].

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