Thietane and Selenetane Complexes by Thermal Cycloaddition of Vinyl Ethers to Transition-Metal-Coordinated Thio- and Selenoaldehydes – Crystal Structure of Pentacarbonyl(7-phenyl-2-oxa-8-thiabicyclo[4.2.0]octane-*S*)tungsten(0)☆

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Pentacarbonyl(thiobenzaldehyde)tungsten und pentacarbonyl(selenobenzaldehyde)tungsten (**1a** and **1b**) undergo a thermal [2 + 2] cycloaddition with several vinyl ethers to give highly substituted transition metal-coordinated thietanes and selenetanes. The addition is highly regio- and stereospecific. The products undergo acid-catalyzed rearrangements, which lead to thermodynamically more stable diastereomers of the thietanes and selenetanes. The stereochemistry of both addition and rearrangement was established by reaction of deuterium-labeled vinyl ethers and by reaction of the *cis* and *trans* isomers of ethyl propenyl ether. The crystal structure of the bicyclic addition product of **1a** and 3,4-dihydro-2*H*-pyran is reported.

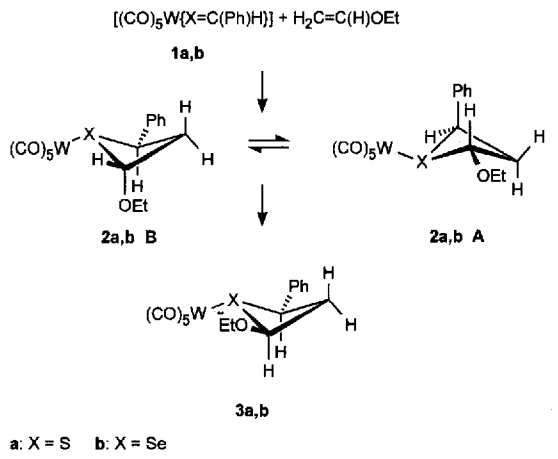
Thio- and selenoaldehydes not stabilized by either bulky substituents or by conjugation with heteroatoms like nitrogen or sulfur are unstable and immediately oligomerize[1a–f]. The high reactivity considerably restricts the use of thio- and selenoaldehydes as building blocks in organic synthesis. Until now, only inter-[2a–e] or intramolecular[3a,b] [4 + 2] cycloadditions with conjugated dienes and ene reactions are known. In these reactions the heteroaldehydes are generated in situ. One way to circumvent the problems connected with the high reactivity of thio- and selenocarbonyl compounds is to use their transition metal complexes[4]. In the past decade, we successfully employed pentacarbonyl(thiobenzaldehyde)tungsten complexes[5] in cycloaddition reactions with electron-rich alkynes[6a–c] and dienes[7a–d] and observed a similar reactivity pattern for the analogous selenobenzaldehyde complexes[8a–d]. Recently, cationic thiobenzaldehyde complexes of ruthenium, $[(\eta^5\text{-}C_5H_5)(P\text{-}P)Ru\{S{=}C(C_6H_4R)H\}]^+$ (P-P = dppe, dppm, dmpe; R = H, Cl, OMe), were also used as starting compounds in cycloaddition reactions with cyclopentadiene and 2,3-dimethylbutadiene[9a,b].

We now report on (a) the reactions of thiobenzaldehyde and selenobenzaldehyde complexes with vinyl ethers, (b) a study of the isomerization of the kinetically controlled reaction product containing a four-membered heterocycle to its more stable isomer and (c) an X-ray structural analysis of a thietane tungsten complex. A preliminary account of part of this work as well as a kinetical investigation of the cycloaddition reaction have appeared[10,11].

Results and Discussion

When a solution of pentacarbonyl(thiobenzaldehyde)-tungsten (**1a**)[5] in dichloromethane was treated with an excess of ethyl vinyl ether, the dark violet solution turned red-brown within several hours. Since **1a** slowly decomposes in solution at ambient temperature, the reaction had to be carried out at −30 °C. Column chromatography of the reaction products on silica gel afforded the thietane complex **3a** (Scheme 1) as a yellow oil.

Scheme 1



The structure of **3a** was established by spectroscopic means. According to the IR spectrum of the yellow oil the pentacarbonyl tungsten fragment is still present in the isolated compound. The elemental analysis and the mass spectrum both indicated a 1:1 adduct of **1a** and the vinyl ether. The multiplicity of the proton resonances in the ^{1}H-NMR spectrum led to the conclusion that the product contains a ring system formed by cycloaddition of the C=C bond of the ethyl vinyl ether to the S=C bond of **1a**. Double resonance experiments and the results of an analogous synthesis

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carried out with the monodeuterated compound [(CO)$_5$W{S=C(Ph)D}] ([D]-**1a**) established the regiochemistry. Finally, the stereochemistry (Ph and OEt substituents mutually *cis*) could be assigned on the basis of the H,H coupling constants (Table 1). In addition, from these spectra a regiospecific cycloaddition of the ethyl vinyl ether to the S=C bond could be deduced.

Table 1. Selected ^{1}H-NMR data of complexes ($CDCl_3$, 297 K); δ values, coupling constants [Hz] in parentheses

R', R	C(OR*)*H* (^3J, ^3J)	C(Ph)*H* (^3J, ^3J)	C(R)*R'* (^2J, ^3J, ^3J)	C(*R*)R' (^2J, ^3J, ^3J)
2a	dd, 5.40 - 5.45	dd, 4.90 - 4.96	ddd, 3.44 - 3.51	ddd, 3.28 - 3.40
H, H[a]	(6.7, 5.5)	(6.9, 8.8)	(13.7, 6.7, 6.9)	(13.7, 5.2, 9.3)
3a	dd, 5.34 - 5.40	dd, 4.43 - 4.50	ddd, 3.38 - 3.49	ddd, 3.11..3.23
H, H	(6.9, 7.6)	(8.1, 10.1)	(13.1, 6.9, 8.1)	(13.1, 7.7, 10.1)
trans-[D]-**3a**	d, 5.66	d, 4.74		
H, D[b]	(6.7, -)	(7.9, -)		
cis-[D]-**3a**	d, 5.66	d, 4.73		
D, H[b]	(-, 8.2)	(-, 10.4)		
cis-Me-**3a**	d, 5.25 - 5.28	d, 4.42 - 4.46	m, 3.72 - 3.94	d, 0.81 - 0.83
Me, H	(-, 8.2)	(-, 10.1)		(- , 7.0, -)
trans-Me-**3a**	d, 5.48 - 5.51	d, 4.65 - 4.69	d, 0.92 - 0.95	m, 3.75..3.89
H, Me	(7.0, -)	(8.5, -)	(- , 7.4, -)	
2b	see Table 2			
3b	dd, 5.54 - 5.60	dd, 4.62 - 4.69	ddd, 3.89 - 4.00	ddd, 3.50 - 3.59
H, H	(6.6, 8.3)	(7.8, 11.1)	(13.9, 6.9, 7.9)	(13.9, 8.4, 11.1)

[a] Averaged spectrum of the two conformers A and B, see Table 2. – [b] In [D_6]acetone. – Data for Ph, OR' etc. see Experimental.

However, a comparison of the ^{1}H-NMR spectrum of **3a** with that of the crude reaction mixture excluded **3a** to be the initially formed reaction product. The first product exhibits a similar spectrum, however, all resonances appear at slightly lower field, except for the signal of C(Ph)*H* which is observed at considerably lower field (Δδ = 0.47). From these observations it follows that the initially formed product (**2a**) only differs from **3a** with respect to its configuration at the carbon atom bearing the hydrogen atom and the phenyl group (**2a** in Scheme 1:Ph and OEt substituents in *trans position*). The coupling constants observed for **2a** supported this assignment.

In contrast to the ^{1}H-NMR spectrum of **3a** which is temperature-independent in the range from −95 to 20°C that of **2a** is strongly temperature-dependent. When the temperature of a solution of **2a** is lowered, the signals for C(OEt)*H* and C(Ph)*H* are broadened and are finally split into two sets of resonances (Table 2). Therefore, **2a** is present in solution as two conformers (**2a**, **A** and **2a**, **B**) which rapidly interconvert. The interconversion very likely proceeds by pyramidal inversion on sulfur *and* ring inversion (Scheme 1).

The two conformers differ by the relative arrangement of the Ph and the OEt substituent. In **2a**, **A** the phenyl group occupies an axial and the OEt group an equatorial position. Conversely, in **2a**, **B** the Ph substituent is in the equatorial and the OEt group in the axial position. The bulky (CO)$_5$W substituent presumably occupies an equatorial position in both conformers. From the coalescence temperature (−44°C) and Δν [214.4 Hz for C(OEt)*H* and C(Ph)*H* at −93°C] the barrier to interconversion of the conformers was calculated to be $\Delta G^{\neq}$ = 44 kJ/mol. The activation barrier compares well with those reported for the inversion of thietane and selenetane rings coordinated to platinum or palladium[12].

Table 2. Low-temperature ^{1}H-NMR data for ring conformers A and B; δ values, coupling constants [Hz] in parentheses

	C(OEt)*H* (^3J, ^3J)	C(Ph)*H* (^3J, ^3J)	Solvent, Temp. [K]
2a, A	dd, 6.06 (6.9, 7.1)	dd, 4.75 (3.6, 9.9)	[D_6]acetone, 180
cis-[D]-**2a, A**	d, 6.05 (6.9, –)	d, 4.72 (3.7, –)	[D_6]acetone, 180
trans-[D]-**2a, A**	d, 6.05 (–, 7.0)	d, 4.73 (–, 9.9)	[D_6]acetone, 180
2a, B	dd, 5.50 (6.7, 2.7)	dd, 5.40 (8.5, 8.4)	[D_6]acetone, 180
cis-[D]-**2a, B**	d, 5.52 (7.2, –)	d, 5.38 (7.7, –)	[D_6]acetone, 180
trans-[D]-**2a, B**	d, 5.52 (–, 2.7)	d, 5.38 (–, 8.8)	[D_6]acetone, 180
2b, A	dd, 5.91 - 5.96 (7.6, 7.7)	dd, 4.57 - 4.62 (10.0, 3.6)	$CDCl_3$, 242
2b, B	dd, 5.17 - 5.21 (6.7, 2.7)	dd, 5.60 - 5.67 (9.4, 9.1)	$CDCl_3$, 242

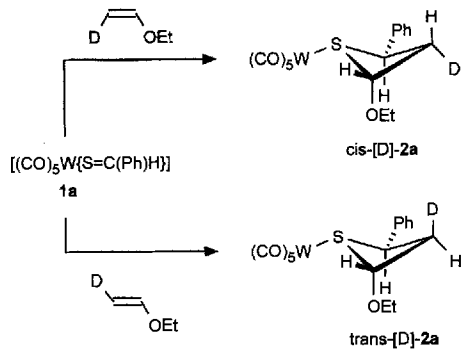
The reaction of the selenobenzaldehyde complex **1b** with an excess of ethyl vinyl ether gave the selenetane complex **3b** after column chromatography (Scheme 1). Compound **3b** was isolated as an orange oil.

The structure of **3b** corresponds to that of the thietane complex **3a**, the IR and NMR spectra of both complexes are similar. Analogously to the reaction of **1a** with ethyl vinyl ether, the stereoisomer that was finally isolated (**3b**) is not the initial cycloaddition product. The ^{1}H-NMR spectra of the crude reaction mixture indicated that isomer **2b** (Scheme 1) is initially formed. At −30°C two distinct sets of signals for C(OEt)*H* and C(Ph)*H* each were observed in agreement with the presence of two conformers of **2b** (Table 2). When the solution was warmed to room temperature, the signals broadened. However, it was not possible to determine the coalescence temperature for the equilibration of the two ring conformers since **2b** decomposed above room temperature. Therefore, the inversion barrier could only be estimated to be higher than 60 kJ/mol (T_c > 293 K). This agrees well with reported data for inversion on selenium[12].

Since the cycloadditions of ethyl vinyl ether to **1a**, **b** proceed not only highly regioselectively but also highly stereoselectively, we also performed the reactions of **1a** with the two isomeric β-monodeuterated ethyl vinyl ethers *cis*- and *trans*-EtO(H)C=C(D)H. The ^{1}H-NMR spectra of the reaction mixtures clearly indicated the formation of a single diastereomer for each of the vinyl ethers. From an analysis of the coupling constants it followed that the geometry of the vinyl ether is retained in the initially formed product **2a**, i.e. the reaction of **1a** with *trans*-EtO(H)C=C(D)H yielded the thietane ring with the ethoxy and the deuterium substituents in *trans* position (*trans*-[D]-**2a**), *cis*-EtOCH=C(D)H gave the product with OEt and D mutually *cis* (*cis*-[D]-**2a**, Scheme 2).

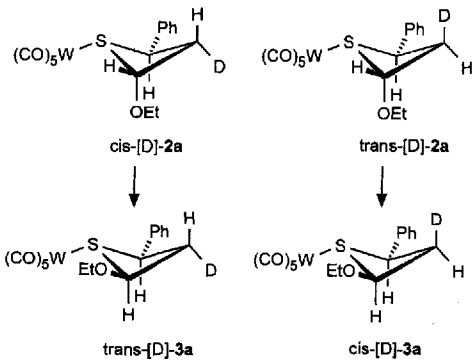
The use of deuterium-labeled vinyl ether not only allowed us to establish the stereochemistry of the addition step but also provided information on the subsequent conversion of **2a** to **3a**. Both *trans*- and *cis*-[D]-**2a**, rearranged as described in Scheme 3. The ^{1}H-NMR spectra (positions of the resonances and coupling constants) of the products formed by rearrangement of *trans*- and *cis*-[D]-**2a**, respectively, ruled out an epimerization on *C*(Ph)H. The mutual

Scheme 2



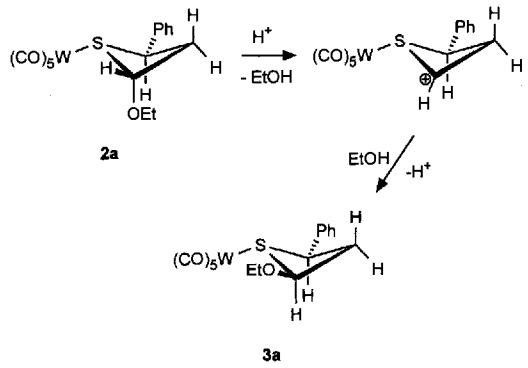
positions of D and Ph in the initially formed complex [D]-**2a** remained unchanged during isomerization to [D]-**3a** (Scheme 3, *trans*- and *cis*-[D]-**2a** also consist of two conformers each, only one of both is shown).

Scheme 3



It is noteworthy that a scrambling of the deuterium labels was *not* observed. Scrambling of the labels would indicate the formation of a cation analogous to **II** (vide infra). Therefore, the intermediate formation of such a cation can be excluded. The high stereoselectivity of the rearrangement of **2a** to **3a** also excluded any mechanism involving ring opening. In addition, a ring closure of any ring-opened intermediate to reform a strained four-membered ring is very unlikely. The fact that chromatography of **2a** on silica gel yielded the rearrangement product **3a** indicated that the isomerization **2a** → **3a** might be acid-catalyzed. Therefore the influence of acids on **2a** was investigated. When a small amount of trifluoroacetic acid was added to a solution containing both **2a** and **3a**, the rearrangement of **2a** to **3a** was complete within a few seconds as established by the ^{1}H-NMR spectrum of the solution. Obviously, there is a rapid epimerization at *C*(OEt)H. Most likely the epimerization proceeds by (a) protonation at C(*O*Et)H, (b) elimination of EtOH and formation of a carbenium ion, (c) readdition of EtOH and (e) subsequent deprotonation yielding the thermodynamically more favorable product **3a**. The rearrangement of the phenyl and alkoxy group in **3a** (mutually *cis*) and that of the bulky pentacarbonyltungsten fragment (*trans* to both Ph and OEt) minimizes steric repulsion (Scheme 4).

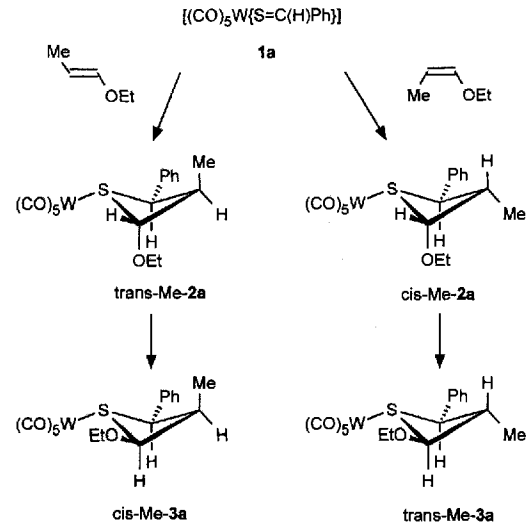
Scheme 4



The mechanistic proposal for the rearrangement was additionally supported by the results of the reactions of **2a** with trifluoroacetic acid/methanol or [D_6]ethanol. In either case, free ethanol could be detected by ^{1}H-NMR spectroscopy and the substitution of a MeO or a C_2D_5O group for C_2H_5O was observed.

The reactions of the thiobenzaldehyde complex **1a** with *cis*- and *trans*-ethyl propenyl ether afforded *cis*-Me-**2a** and *trans*-Me-**2a** as the kinetically controlled reaction products, respectively (Scheme 5).

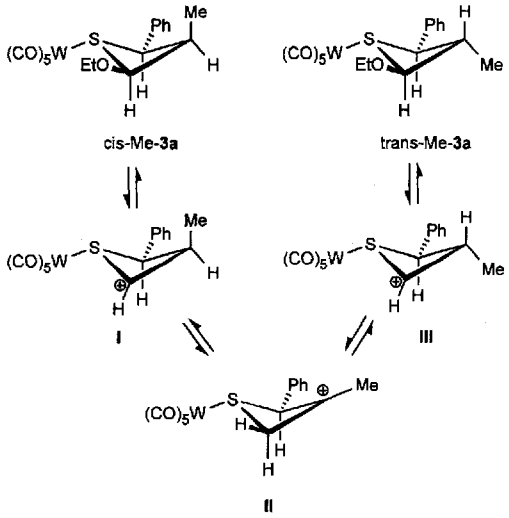
Scheme 5



Since it was not possible to obtain isomerically pure samples of *cis*- and *trans*-ethyl propenyl ether, both thietane complexes were contaminated by small amounts of the other diastereomer. Analogously to the reactions of **1a** with β-monodeuterated ethyl vinyl ether, the *cis* and *trans* arrangement of the substituents at the C=C bond is retained in the initial products. The formation of *cis*- and *trans*-Me-**2a** is followed by isomerization (acid-catalyzed) to *trans*-Me-**3a** and *cis*-Me-**3a** as the thermodynamically controlled reaction products. Note that during isomerization the mutual arrangement of Ph and Me remains unchanged while that of Me and OEt is inversed. The rearrangement is faster than that of **2a**.

When a solution of *cis*-Me-**3a** in $CDCl_3$ was kept at room temperature for several hours, a second isomerization was detected. The intensity of the signals of *cis*-Me-**3a** slowly decreased and peaks due to *trans*-Me-**3a** appeared, grew in intensity and finally an equilibrium was obtained (Scheme 6). The ratio *cis*-/*trans*-Me-**3a** in the equilibrium was nearly 1:1. The same equilibrium mixture was obtained when solutions of *trans*-Me-**3a** in $CDCl_3$ were kept at room temperature. This rearrangement (epimerization on *C*(Me)H) may be explained by the reaction sequence shown in Scheme 6.

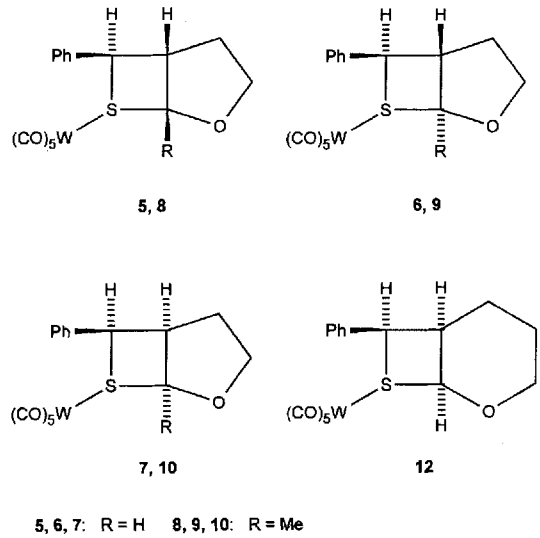
Scheme 6



Protonation of the OEt substituent at *C*(OEt)H in *cis*-Me-**3a** and EtOH elimination gives the carbenium ion **I** which is stabilized by interaction with the lone pair at sulfur. 1,2-H shift affords the tertiary carbenium ion **II** which is stabilized by interaction of the Me substituent with the carbenium center. 1,2-Migration of hydrogen gives either **I** or **III**, subsequent EtOH addition and deprotonation finally yield *cis*-Me-**3a** or *trans*-Me-**3a**. Thus, the configurational stability at *C*(H)Me is lost. Although a 1,2-H shift from *C*(Ph)H to the carbenium carbon in **II** would give rise to the formation of the most stable carbenium ion (stabilized by interaction of the carbenium center with the Ph substituent and the sulfur lone pair) products derived from such a carbenium ion have not been ovserved so far. This is presumably due to a high kinetic barrier since formation of such a benzyl cation requires the phenyl group to rotate into or nearly into the plane of the carbenium center. Besides, EtOH addition to the benzyl cation and subsequent deprotonation would give a sterically very crowded 4,4-disubstituted thietane complex. Very likely, such a thietane complex would readily eliminate "OEt^-" again and reform the benzyl cation. This assumption is supported by the observation that the sterically less congested thietane complex formed by cycloaddition of $H_2C{=}C(OMe)Me$ to **1a** is unstable and decomposes during column chromatography even at −40°C. For **2a** and [D]-**2a** a 1,2-hydrogen shift comparable to **I** → **II** and **III** → **II** is expected to be unfavorable since the resulting secondary carbenium ion is considerably higher in energy than the initially formed heteroatom-stabilized cation. Consequently, an epimerization at *C*(D)H in *cis*- and *trans*-[D]-**3a** was not observed.

1a also reacts with cyclic vinyl ethers such as 2,3-dihydrofuran (**4**) and 4,5-dihydro-2-methylfuran (**Me-4**) though at very different rates. The reaction of **1a** with an excess of **4** required several hours for completion. In contrast, that of **1a** with stoichiometric amounts of **Me-4** at −30°C was complete within seconds even when more dilute solutions in dichloromethane were employed. The isolation of the products from the reaction of **1a** with **4** was complicated by polymeric **4**. However, the ^{1}H-NMR spectrum of the crude reaction mixture clearly indicated the presence of two diastereomers in a ratio of 1:0.7. The ratio was neither influenced by chromatography on silica gel nor by addition of trifluoroacetic acid. We therefore concluded that rearrangement had already occurred. Two pairs of diastereomers are conceivable: (a) **5** and **6** or (b) **5** and **7** (Scheme 7). By analogy with the reactions of **1a** with non-cyclic vinyl ethers, **5** is assumed to be the inital product. In **5** the phenyl group and the substituents at *C*(OR)H and C(Ph)H*C*H are mutually *trans*.

Scheme 7



Complex **6** is derived from **5** by the rearrangement shown in Scheme 4. Compound **7** is derived from **5** by the rearrangement sequence summarized in Scheme 6. For several reasons formation of the diastereomeric pair **5/7** is more likely than that of **5/6**. Steric arguments render formation of **6** by protonation and ring opening very unfavorable. In addition, both diastereomers exhibit the same ^3J coupling constant C(OR)*H*/C(Ph)HC(*H*) (5.81 Hz). Finally, irradiation of the C(Ph)HC(*H*) signal affected both C(OR)*H* signals to a similar extent which is to be expected for diastereomers **5** and **7**, but not for isomer **6**.

The products obtained by treatment of **1a** with **Me-4** were assigned structures **8** and **10** on the basis of the ^3J coupling constants C(OR)*H*/C(Ph)HC(*H*) which are equal to those of **5** and **7**. The initial isomeric ratio of ca. 1:1 (after chromatography) slowly changed to 5:1 as monitored by ^{1}H-NMR spectroscopy. However, on the basis of the

NMR data it was not possible to unambiguously establish whether **8** or **10** is the major diastereomer.

Substitution of a methyl group in 2-position of 4,5-dihydrofuran for hydrogen (**4** → **Me-4**) considerably accelerates the rate of cycloaddition to **1a**. A similar increase in reaction rate was observed when ethyl vinyl ether was replaced by isopropenyl methyl ether, $H_2C{=}C(OMe)Me$. Isopropenyl methyl ether reacts approximately 200 times faster with **1a** than ethyl vinyl ether[11]. Obviously, the rate strongly depends on the nucleophilicity of the olefinic C_β atom of the vinyl ether.

Ring enlargement of the cyclic vinyl ether by one CH_2 unit [2,3-dihydrofuran → 3,4-dihydro-2*H*-pyran (**11**)] decreases the rate. The reaction of **1a** with **11** in neat **11** at −30°C took about two weeks for completion. The ^{1}H-NMR spectrum of the crude reaction mixture indicated the formation of a single product which is identical with the isolated complex (**12**). After chromatography, compound **12** was obtained as a yellow powder. In contrast, all other thietane complexes were isolated as highly viscous oils. In general, it was not possible to obtain these oils without traces of the corresponding solvent. Efforts to completely remove the solvent in vacuo at room temperature led to slow decomposition of the compounds.

However, slow diffusion of pentane into a solution of **12** in dichloromethane gave crystals which were suitable for X-ray diffraction analysis. The structure of **12** is shown in Figure 1. The phenyl group and the anellated pyran ring occupy *cis* positions at the thietane ring. In contrast, the initial product of cycloaddition of *cis*-ethyl propenyl ether to **1a** exhibits a *trans* geometry both for Ph/OEt and Ph/Me (Scheme 5). Two possible interpretations may account for the difference. The selectivity of cycloaddition of **11** to *cis*-ethyl propenyl ether could have been inversed or **12** is not the initially formed complex but, more likely, already the product of rearrangement (compare **2a** → **3a**, Schemes 5 and 6) which requires that rearrangement is faster than or at least equal in rate to the cycloaddition. Note that the cycloaddition of **11** to **1a** is very slow. In the case of the adducts of dihydrofurans the analogous rearrangement leads to mixtures of diastereomers (**5/7** and **8/10**).

Until now only very few thietanes and thietane complexes have been characterized by X-ray structural analyses. So far structural data for only two pentacarbonyl-thietane complexes, pentacarbonyl(2,2,4,4-tetramethyl-3-thietanone)-chromium(0)[13] (**13**) and pentacarbonyl(thietane)-tungsten(0)[14] (**14**), have been reported. Bond lengths of **13** and **14** slightly differ. The S−C(Ph)H bond (1.915 Å) in **12** is longer than the S−CMe_2 bonds in **13** (average 1.884 Å) and the S−CPh_2 bonds in *trans*- and *cis*-2,2-diphenyl-3,4-dichlorothietane (1.871 Å and 1.889 Å, respectively)[15a,b]. S−C bond lengths are remarkably short in the unsubstituted thietane ligand of **14** [1.75(1) Å and 1.80(1) Å]. Usually, the S−C distances of coordinated thietanes vary between 1.801 Å and 1.838 Å. The W−S bond lengths of **12** and **14** differ only slightly [2.516(2) Å and 2.540(3) Å] and obviously do not depend on the steric demand of the thietane ligands. The thietane ring is puckered. The puckering angle (angle between the planes S1,C6,C11 and C6,C7,C11) is 143.7°.

The sum of angles at sulfur, which might be regarded as an indicator for π-bonding contributions, is insensitive to variation of the metal ligand fragment. It is remarkable, that this angle is approximately the same in many different structures. For **12**, this angle is 303° compared to 300° in $[ReCl(CO)_4L]$[16], 305° in $[\{Re(CO)_4L\}_2]$[16], 306° in $[Re_2(CO)_9L]$[16], 307° in $[\{Mn(CO)_3(\mu\text{-}Cl)L\}_2]$[17] (L = 3,3-dimethylthietane), 308° in $[Os_3(CO)_{11}(SC_3H_6)]$[18a,b] and 310° in $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(SC_3H_6)]$[19]. It is therefore unlikely that the coordinated thietane acts as a strong π-donor.

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Experimental

General: All operations were carried out under nitrogen or argon by using conventional Schlenk techniques. Solvents were dried by refluxing over sodium/benzophenone ketyl, $LiAlH_4$ or CaH_2 and were freshly distilled prior to use. The silica gel used for chromatography (J. T. Baker Corp., silica gel for flash chromatography) was argon- or nitrogen-saturated. The yields refer to analytically pure compounds (whenever available) and were not optimized. The complexes **1a**, **b**, [D]-**1a**[5], *cis*- and *trans*-ethyl β-deuteriovinyl ether[20] were prepared according to literature procedures. Ethyl propenyl ether was purchased from Fluka as a mixture of the *cis* and *trans* isomer which were separated by repeated distillation with a Spaltrohr® column (Fischer Labor- und Verfahrenstechnik Corp.) until an isomeric purity of about 95% each was obtained. Contents were verified by gas chromatography (Carlo Erba Instruments GC 6000). − IR: FT-IR spectrophotometer Bio-Rad Corp. − ^{1}H NMR and ^{13}C NMR: Bruker WM 250, Bruker AC 250, Jeol FX 90. − MS: Varian MAT 512 (FAB). Chemical shifts are reported relative to TMS.

Pentacarbonyl(4-ethoxy-2-phenylthietane)tungsten(0) (**3a**): 2.5 ml (27 mmol) of ethyl vinyl ether was added to a dark violet solution of 400 mg (0.9 mmol) of **1a** in 6 ml of CH_2Cl_2 at −30°C. After 6 h reaction was complete as indicated by the red-brown color of the reaction mixture and the IR spectrum. The solvent was removed in vacuo and the residue was chromatographed at −40°C on silica gel. First with pentane/CH_2Cl_2 (5:1), a red band was eluted with contained $[\{W(CO)_5\}_2\{\mu\text{-}\eta^1{:}\eta^2\text{-}S{=}C(Ph)H\}]$, a decomposition product of **1a**[21]. The second, yellow band which was eluted with pentane/CH_2Cl_2 (ratio decreasing from 2:1 to 1:1) contained the cycloaddition product. Removal of the solvent in vacuo gave a mixture of **2a** and **3a** as a yellow oil. Addition of a drop of trifluoroacetic acid completed the conversion of **2a** into **3a** within seconds. The acid was removed in vacuo. Yellow oil. Yield: 370 mg (80% based on **1a**). − IR (pentane): $\tilde{\nu}$(CO) = 2075 cm^{-1}m, 1986 w, 1947 vs, 1942 vs, 1936 s. − ^{1}H NMR ($CDCl_3$; see Table 1): δ = 1.33 (t, ^3J = 7.0 Hz, 3H, CH_2CH_3), 3.57−3.64, 3.75−3.81 (2 dq, ^2J = 9.1 Hz, ^3J = 7.0 Hz, 2H, OCH_2), 7.33−7.48 (m, 5H, PH). − ^{13}C NMR ($CDCl_3$, 238 K): δ = 14.7 (CH_2CH_3), 43.5 [*C*(H)Ph], 50.5 (CH_2), 66.7 (CH_2CH_3), 89.6 [*C*(OEt)H], 127.9, 128.7, 128.9, 138.2 (Ph), 196.5 (*cis*-CO), 200.8 (*trans*-CO). − MS (FAB, NBOH), *m/z* (%): 518 (9) [M^+], 462 (3), 434 (5), 378 (4) [$M^+ - n$ CO; n = 2, 3, 5], 446 (30) [M^+ − CO − CH_3CHO], 193 (6) [M^+ − $(CO)_5WH$], 161 (100) [M^+ − $(CO)_5WSH$]. − $C_{16}H_{14}O_6SW$ (518.2): calcd. C 37.08 H 2.72; found C 37.36 H 2.76.

Pentacarbonyl(3-ethoxy-2-phenylselenetane)tungsten(0) (**3b**): At −40°C 2.6 ml (27 mmol) of ethyl vinyl ether was added to a solu-

tion of 440 mg (0.9 mmol) of **1b** in 5 ml of CH_2Cl_2. Within ca. 4–5 h the color of the solution changed from dark blue to red-brown. The solvent was removed in vacuo and the residue was chromatographed at −40 °C on silica gel. With pentane/CH_2Cl_2 (5:1) a red band was eluted [{$W(CO)_5$}$_2${μ-η^1:η^2-Se=C(Ph)H}], a decomposition product of **1b**[21], then with pentane/CH_2Cl_2 (ratio decreasing from 2:1 → 1:1) a light orange band. The solvent of the orange fraction was removed in vacuo to give a mixture of **2b** and **3b** as an orange oil. To complete the conversion of **2b** into **3b** a drop of trifluoroacetic acid was added. The acid was removed in vacuo to afford pure **3b** as an orange oil. Yield: 400 mg (80% based on **1b**). – IR (pentane): ν̃(CO) = 2072 cm^{-1} m, 1981 w, 1940 vs, 1933 s. – ^{1}H NMR ($CDCl_3$; see Table 1): δ = 1.33–1.39 (t, ^3J = 6.9 Hz, 3H, CH_2CH_3), 3.60–3.68 (dq, ^2J = 9.6 Hz, ^3J = 6.9 Hz, 2H, OCH_2), 7.32–7.56 (m, 5H, Ph). – ^{13}C NMR ($CDCl_3$, 238 K): δ = 14.5 (CH_2CH_3), 40.9 [*C*(H)Ph], 44.9 (CH_2), 66.9 (CH_2CH_3), 83.1 [*C*(OEt)H], 127.7, 128.7, 129.1, 139.4 (Ph), 197.2 (*cis*-CO), 200.5 (*trans*-CO). – MS (FAB, NBOH): *m/z* (%): 566 (15) [M$^+$], 538 (9) [M$^+$ – CO], 494 (37) [M$^+$ – CO – CH_3CHO], 482 (19) [M$^+$ – 3 CO], 438 (38) [M$^+$ – 3 CO – CH_3CHO], 242 (100) [M$^+$ – $(CO)_5W$]. – $C_{16}H_{14}O_6SeW$ (565.1): calcd. C 34.00 H 2.49; found C 33.77 H 2.47.

Pentacarbonyl(4-ethoxy-cis-3-methyl-2-phenylthietane)-tungsten(0) (*cis*-Me-**3a**): 1.4 ml (13 mmol) of *trans*-ethyl propenyl ether was added at −30 °C to a dark violet solution of 590 mg (1.3 mmol) of **1a** in 4 ml of CH_2Cl_2. After 3 h the solvent was removed in vacuo and the residue was chromatographed as described for **3a**, *cis*-Me-**3a** was obtained as a yellow-brown oil which did not contain any detectable amounts of *trans*-Me-**3a**. Yield: 480 mg (83% based on **1a**). – IR (pentane): ν̃ = (CO) = 2073 cm^{-1} m, 1985 w, 1945 vs, 1942 vs, 1935 s. – ^{1}H NMR ($CDCl_3$; see Table 1): δ = 1.35 (t, ^3J = 7.0 Hz, 3H, CH_2CH_3), 3.41–3.82 (2 dq, ^2J = 9.5 Hz, ^3J = 7.0 Hz, 2H, OCH_2), 7.37–7.42 (m, 5H, Ph). – $C_{17}H_{16}O_6SW$ (532.2). Correct elemental analyses and mass spectra could not be obtained due to the instability of the complex.

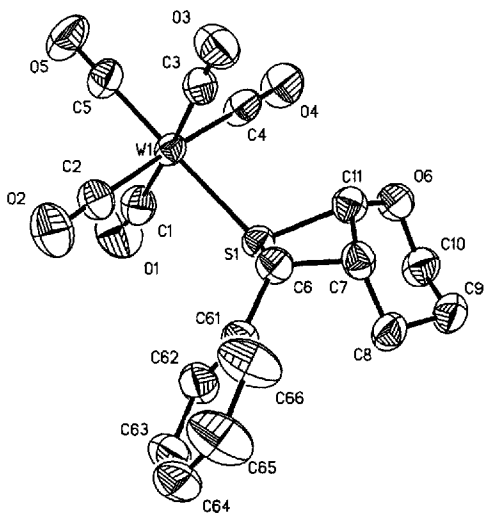
Pentacarbonyl(4-ethoxy-trans-3-methyl-2-phenylthietane)-tungsten(0) (*trans*-Me-**3a**): 1.3 ml (12 mmol) of *cis*-ethyl propenyl ether was added at −30 °C to a solution of 210 mg (0.47 mmol) of **1a** in 4 ml of CH_2Cl_2. After 6 h the reaction was complete. Chromatography as described for **3a** gave *trans*-Me-**3a** as yellow-brown oil which did not contain any detectable amounts of *cis*-Me-**3a**. Yield: 160 mg (78% based on **1a**). – IR (pentane): ν̃(CO) = 2073 cm^{-1} m, 1985 w, 1945 vs, 1941 vs, 1935 s. – ^{1}H NMr ($CDCl_3$; see Table 1): δ = 1.34 (t, ^3J = 7.0 Hz, 3H, CH_2CH_3), 3.63–3.88 (2 dq, ^2J = 9.4 Hz, ^3J = 7.0 Hz, 2H, OCH_2), 7.28–7.40 (m, 5H, Ph). – $C_{17}H_{16}O_6SW$ (532.2). Correct elemental analyses and mass spectra could not be obtained due to the instability of the complex.

Pentacarbonyl-(6-phenyl-2-oxa-7-thiabicyclo[3.2.0]heptane)-tungsten(0) (**5/7**): 1.5 ml (13 mmol) of 2,3-dihydrofuran was added at −20 °C to a solution of 730 mg (1.6 mmol) of **1a** in 30 ml of CH_2Cl_2. After 3 h the reaction was complete. Chromatography as described for **3a** gave a yellow residue which contained polyfuran as an impurity. The residue was extracted with acetone at −10 °C. Removal of the acetone in vacuo gave a mixture of **5** and **7** as a green oil. Yield: 100 mg (10% based on **1a**). The ratio of the two diastereomers was 1:0.7. – IR (pentane): ν̃(CO) = 2075 cm^{-1} m, 1984 w, 1948 vs, 1941 vs, 1931 vs. – ^{1}H NMR ($CDCl_3$): δ = 1.69–2.07 (m, 2H, OCH_2CH_2), 4.10–4.25 [m, 1H, C(Ph)HCH], 4.10–4.25, 4.44–4.67 (2 m, 2H, OCH_2), 4.45, 4.86 [2 d, ^3J = 6.4, 8.9 Hz, 1H, C(Ph)H], 5.79, 5.87 [2 d, ^3J = 5.8, 5.8 Hz, 1H C(OR)H], 7.26–7.54 (m, 5H, Ph). – $C_{16}H_{12}O_6SW$ (516.2): calcd. for $C_{16}H_{12}O_6SW$ · 2/3 acetone: C 38.96, H 2.91; found C 38.66, H 3.17.

Pentacarbonyl(1-methyl-6-phenyl-2-oxa-7-thiabicyclo[3.2.0]-heptane)tungsten(0) (**8/10**): 100 ml (95 mg, 1.1 mmol) of 2-methyl-4,5-dihydrofuran was added at −30 °C to a solution of 500 mg (1.1 mmol) of **1a** in 4 ml of CH_2Cl_2. After 15 min the reaction was complete. Chromatography as described for **3a** gave a mixture of **8/10** as a yellow-brown oil. Yield: 370 mg (63% based on **1a**). Immediately after chromatography the ratio of the two diastereomers was ca. 1:1. However, it slowly changed to 5:1. – IR (pentane): ν̃(CO) = 2075 cm^{-1} m, 1983 m, 1949 vs, 1940 vs, 1931 vs. – ^{1}H NMR ($CDCl_3$): δ = 1.84, 2.02 (2 s, 3H, CH_3), 2.01 (m, 2H, OCH_2CH_2), 3.66, 3.78 [2 m, 1H, C(Ph)HCH], 4.19–4.34, 4.45–4.63 (2 m, 2H, OCH_2), 4.26, 4.67 [2 d, ^3J = 6.9, 6.4 Hz, 1H, C(Ph)H], 7.32–7.46 (m, 5H, Ph). – ^{13}C NMR ($CDCl_3$, 273 K): δ = 25.7 (OCH_2CH_2), 28.4, 31.2 (CH_3), 48.0, 48.8 (OCH_2), 58.2, 59.3 [C(Ph)H], 70.1, 70.7 [C(Ph)HCH], 100.5, 106.0 [*C*(OR)H], 127.3, 127.5, 127.9, 128.5, 128.9, 129.0, 134.6, 138.8 (Ph), 196.3, 196.4 (*cis*-CO), 200.1, 200.6 (*trans*-CO). – $C_{17}H_{14}O_6SW$ (530.2): calcd. for $C_{17}H_{14}O_6SW$ × 0.2 CH_2Cl_2: C 37.76, H 2.65; found C 37.66, H 2.93.

Pentacarbonyl(7-phenyl-2-oxa-8-thiabicyclo[4.2.0]octane)-tungsten(0) (**12**): A solution of 300 mg (0.67 mmol) of **1a** in 5 ml of 3,4-dihydro-2*H*-pyran was kept for 14 days at −30 °C. Then excess pyran was removed in vacuo and the residue was chromatographed as described for **3a**. After removal of the solvent in vacuo **12** was obtained as a yellow powder. Yield: 180 mg (53% based on **1a**). – IR (pentane): ν̃(CO) = 2074 cm^{-1}, m; 1983, m; 1950, vs; 1941, vs; 1931, vs. – ^{1}H NMR ($CDCl_3$): δ = 1.44–1.90 [m, 4H, OCH_2CH_2, C(Ph)HCHCH_2], 3.42 [m, 1H, C(Ph)HCH], 3.72–3.96 (m, 2H, OCH_2), 4.63 [d, ^3J = 7.0 Hz, 1H, C(Ph)H], 5.91 [d, ^3J = 6.1 Hz, 1H, C(OR)H], 7.17–7.43 (m, 5H, Ph). – ^{13}C NMR ($CDCl_3$, 273 K): δ = 20.2 [C(Ph)HCHCH_2], 22.8 (OCH_2CH_2), 29.3 [C(Ph)CH], 47.8 [*C*(Ph)H], 64.2 (OCH_2), 88.1 [*C*(OR)H], 127.0, 127.7, 128.7, 129.0, 133.7 (Ph), 196.5 (*cis*-CO), 200.1 (*trans*-CO). – $C_{17}H_{14}O_6SW$ (530.2): calcd. for $C_{17}H_{14}O_6SW$ × 0.2 pentane: C 39.70, H 3.04; found C 39.39, H 3.21.

Figure 1. Molecular structure of **12** (Hydrogen atoms are omitted for clarity)[a]



[a] Selected bond lengths [Å] and angles [°]: W(1)–S(1) 2.516(2), S(1)–C(6) 1.853(6), S(1)–C(11) 1.915(6), C(6)–C(7) 1.558(8), C(7)–C(11) 1.532(9); W(1)–S(1)–C(6) 115.4(2), C(6)–S(1)–C(11) 73.6(2), W(1)–S(1)–C(11) 113.6(3), S(1)–C(6)–C(7) 91.0(3), C(6)–C(7)–C(11) 93.8(5), S(1)–C(11)–C(7) 89.5(4).

X-ray Structural Analysis of **12**: $C_{17}H_{14}O_6SW \cdot 0.5\ CH_2Cl_2$, (572.7), crystal size 0.3 × 0.3 × 0.3 mm (obtained by slow diffusion of pentane into a solution of **12** in CH_2Cl_2); triclinic crystal system; space group $P\bar{1}$; a = 8.882(5), b = 10.848(6), c = 12.241(6) Å; α = 65.14(4), β = 81.32(4), γ = 82.92(4)°; V = 1055.5(10) Å^3; Z = 2, $d_{calcd.}$ = 1.802 g cm^{-3}; μ (Mo-K_α) = 5.84 mm^{-1}; $F(000)$ = 550. Wyckoff scan; 2Θ range 4–54°; scan speed variable 2.0–29.3° min^{-1} in ω. 4608 independent reflections with 4099 [$F > 3\sigma(F)$]. A semi-empirical absorption correction using 10 reflections was applied. Data were collected at −25°C of the crystal mounted in a glass capillary on a Siemens R3m/V diffractometer (graphite monochromator, Mo-K_α radiation, λ = 0.71073 Å). The structure was solved (Patterson methods) and refined by using the SHELXTL PLUS (VMS) program package. 233 parameters refined, R = 0.038, R_w = 0.047. Largest difference peak(hole) +1.43 eÅ^{-3} (−1.05 eÅ^{-3}). The positions of hydrogen atoms were calculated by assuming ideal geometry (d_{C-H} 0.96 Å) and their coordinations were refined together with the attached C atoms as a "riding model". The positions of all other atoms, except that of the solvent, were refined anisotropically by full-matrix least-squares methods. Complete lists of atomic coordinates and thermal parameters were deposited[22].

☆ Dedicated to Professor *Max Herberhold* on the occasion of his 60th birthday.

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[22] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405248 the names of the authors, and the journal citation.

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