

Thietane and Selenetane Complexes by Thermal Cycloaddition of Vinyl Ethers to Transition Metal Coordinated Thio- and Seleno-aldehydes

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Pentacarbonyl tungsten coordinated thio- and seleno-benzaldehydes react with vinyl ethers by regiospecific addition of the C=C to the X=C bond of the heteroaldehydes to form thietane and selenetane complexes, respectively.

Thio- and seleno-aldehydes not stabilized by either very bulky substituents or by mesomeric effect of heteroatoms such as nitrogen or sulfur are unstable and immediately oligomerize.^{1,2} This considerably restricts their potential use in organic synthesis. Therefore, until now only inter-^{3,4} or intra-molecular [4 + 2] cycloadditions^{3,5,6} with conjugated dienes (trapping of the intermediates) and ene reactions^{3,6,7} are known. In addition, the reactions of the isolable 2,4,6-tri-*tert*-butylthiobenzaldehyde with Grignard and organolithium reagents have also been studied.⁸

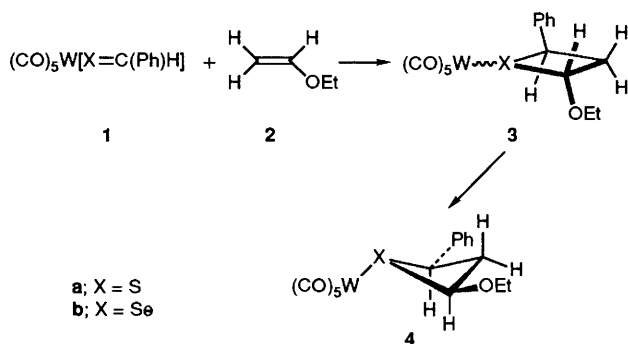
The problems connected with the high reactivity of the heteroaldehydes can be circumvented by using their complexes. Heteroaldehydes stabilized by coordination to a (CO)₅W or (CO)₅Cr fragment are conveniently accessible building blocks. They readily react with (i) electron-rich alkynes by regiospecific [2 + 2] cycloaddition and subsequent stereospecific electrocyclic ring-opening to give heteroacrylic acid derivatives⁹ and (ii) with conjugated dienes by [4 + 2] cycloaddition to form six-membered heterocycles.¹⁰ The coordination to the (CO)₅M fragment strongly influences the stereoselectivity of the Diels–Alder reaction.¹¹ We now report the first thermal [2 + 2] cycloaddition of vinyl ethers to metal-coordinated thio- and seleno-aldehydes. The reactions proceed regiospecifically and stereoselectively to give thietane and selenetane complexes, respectively.

The heteroaldehyde complexes **1a** and **b** react with ethyl vinyl ether **2** even at –20 °C within several hours to form 1 : 1 adducts. The progress of the reaction can be followed easily by IR spectroscopy or by monitoring the colour change of the solution from deep-red to orange. After column chromatography on silica gel the thietane and selenetane complexes **4a**

and **b**,[†] respectively, are obtained as yellow oils in more than 80% yield. The addition of **2** to the X=C bond of **1** is regiospecific. In the resulting heterocycles the H(EtO)C-group of **2** is bonded to the heteroatom X. According to the ¹H NMR spectra, which are in the range from –95 to 20 °C independent of the temperature, both substituents (OEt and Ph) are mutually *cis* thus minimizing steric interaction with the bulky pentacarbonylmetal fragment on X.

The initial reaction products, however, are the isomeric complexes **3a**, **a'** and **3b**, **b'**,[†] respectively, as can be shown by the NMR spectra of the crude reaction mixture. At room temperature **3a** and **a'** rapidly interconvert [$\Delta G^\ddagger = 44$ kJ mol⁻¹ (at –30 °C)]. The interconversion for **3b**, **b'** is slow on the NMR time scale even at room temperature [$\Delta G^\ddagger > 58$ kJ mol⁻¹]. In both isomers, **3** and **3'**, the substituents OEt and Ph occupy mutual *trans* positions. The reaction rate for the addition of **2** to **1a**, which initially gives the sterically more demanding '*trans*' complexes, is only slightly solvent depen-

[†] Selected ¹H NMR data: **4a** δ (CDCl₃) 3.17 (ddd, *J* 13.1, 10.1 and 7.7 Hz, 1 H, CH₂), 3.43 (ddd, *J* 13.1, 8.1 and 6.9 Hz, 1 H, CH₂), 4.47 [dd, *J* 10.1 and 8.1 Hz, C(Ph)*H*] and 5.37 [dd, *J* 7.6 and 6.9 Hz, C(OEt)*H*]; **4b**: δ (CDCl₃, –10 °C) 3.54 (ddd, *J* 13.9, 11.1 and 8.5 Hz, 1 H, CH₂), 3.95 (ddd, *J* 13.9, 7.9 and 6.6 Hz, 1 H, CH₂), 4.65 [dd, *J* 11.1 and 7.8 Hz, C(Ph)*H*] and 5.57 [dd, *J* 8.4 and 6.5 Hz, C(OEt)*H*]; **3a/a'** (CDCl₃, –90 °C): **3a**: δ 4.75 [dd, *J* 9.9 and 3.6 Hz, C(Ph)*H*] and 6.06 [dd, *J* 7.1 and 6.9 Hz, C(OEt)*H*]; **3a'**: δ 5.40 [dd, *J* 8.5 and 8.4 Hz, C(Ph)*H*] and 5.50 [dd, *J* 6.7 and 2.7 Hz, C(OEt)*H*]; **3b/b'** (CDCl₃, –30 °C): **3b**: δ 4.60 [dd, *J* 10.0 and 3.6 Hz, C(Ph)*H*] and 5.93 [dd, *J* 7.6 and 7.0 Hz, C(OEt)*H*]; **3b'**: δ 5.19 [dd, *J* 6.7 and 2.7 Hz, C(OEt)*H*] and 5.63 [dd, *J* 9.4 and 9.1 Hz, C(Ph)*H*].



dent $[k(\text{pentane}) : k(\text{toluene}) : k(\text{CH}_2\text{Cl}_2) = 1 : 1.8 : 2.4]$. When *cis*- $[\text{2H}_1]$ **2** is employed instead of **2**, the *cis* arrangement of D and OEt is preserved in $[\text{2H}_1]$ **3a, a'** (Ph and D being *trans*). Conversely, the reaction of **1a** with *trans*- $[\text{2H}_1]$ **2** gives $[\text{2H}_1]$ **3a, a'** with OEt and D *trans* and Ph and D *cis*. Therefore, diradical or dipolar intermediates involving rotation around the (EtO)C–CH₂ bond can be excluded. The results can be explained by a nonsynchronous concerted $[2\pi_s + 2\pi_a]$ process or by a $[2 + 2 + 2]$ process (additionally involving the lone electron pair at the heteroatom X).

At room temperature in CDCl₃ the complexes **3** isomerize completely within several hours to form **4**. The rearrangement is acid-catalysed and very likely proceeds by protonation of OEt, subsequent elimination of EtOH, and readdition of EtO[−]–EtOH. In agreement with such a sequence an exchange (i) of OC₂H₅ for OC₂D₅ in C₂D₅OD–CF₃CO₂D and (ii) of OC₂H₅ for OCH₃ in CH₃OH/CF₃CO₂H is observed.

Apart from **2** other vinyl ethers, e.g. butyl vinyl ether and 1- and 2-substituted vinyl ethers [e.g. 2-methoxypropene, α -methoxystyrene, *cis*- and *trans*-H(Me)C=C(OEt)H] also add to the X=C bond of **1** to form the corresponding thietane and selenetane complexes in high yield.

The reactivity of thietane complexes has recently attracted considerable interest.¹² Until now, thietane and selenetane complexes were prepared by ligand substitution reactions. However, only a few methods for the preparation of selenetanes are available. Apart from selenetane itself, only 3-mono- and 3,3-di-substituted selenetanes are known. Therefore, the reaction of metal-coordinated thio- and selenoaldehydes with electron-rich alkenes considerably extends the accessible substitution pattern of thietane and selenetane

ligands and offers a convenient route for the synthesis of their complexes.

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References

- 1 See e.g. P. D. Magnus, in *Comprehensive Organic Chemistry*, ed. D. N. Jones, Pergamon Press, Oxford, 1979, p. 489; K. A. Jensen and A. Kjaer, in *The Chemistry of Organic Selenium and Tellurium Compounds*, ed. S. Patai and Z. Rappoport, Wiley, Chichester, 1986, p. 1.
- 2 Stable thioaldehydes: R. Okazaki, A. Ishii, N. Fukuda, H. Oyama and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, 1982, 1187; E. Vedejs, D. A. Perry and R. G. Wilde, *J. Am. Chem. Soc.*, 1986, **108**, 2985; R. Okazaki, A. Ishii and N. Inamoto, *J. Am. Chem. Soc.*, 1987, **109**, 279; W. Ando, T. Ohtaki, T. Suzuki and Y. Kabe, *J. Am. Chem. Soc.*, 1991, **113**, 7782. There is only one selenoaldehyde known that is not stabilized by the mesomeric effect of heteroatoms: R. Okazaki, N. Kumon and N. Inamoto, *J. Am. Chem. Soc.*, 1989, **111**, 5949.
- 3 J. E. Baldwin and R. C. G. Lopez, *Tetrahedron*, 1983, **39**, 1487.
- 4 E.g. G. W. Kirby and A. W. Lochead, *J. Chem. Soc., Chem. Commun.*, 1983, 1325; G. W. Kirby and A. N. Trethewey, *J. Chem. Soc., Chem. Commun.*, 1986, 1152; E. Vedejs, J. S. Stults and R. G. Wilde, *J. Am. Chem. Soc.*, 1988, **110**, 5452; P. T. Meinke and G. A. Krafft, *J. Am. Chem. Soc.*, 1988, **110**, 8671.
- 5 M. Segi, M. Takahashi, T. Nakajima, S. Suga, S. Murai and N. Sonoda, *Tetrahedron Lett.*, 1988, 6965.
- 6 E. Vedejs, T. H. Eberlein and R. G. Wilde, *J. Org. Chem.*, 1988, **53**, 2220.
- 7 S. S.-M. Choi and G. W. Kirby, *J. Chem. Soc., Chem. Commun.*, 1988, 177; S. S.-M. Choi, G. W. Kirby and M. P. Mahajan, *J. Chem. Soc., Chem. Commun.*, 1990, 138.
- 8 R. Okazaki, N. Fukuda, H. Oyama and N. Inamoto, *Chem. Lett.*, 1984, 101.
- 9 E.g. H. Fischer, A. Tirilomis, U. Gerbing, B. Huber and G. Müller, *J. Chem. Soc., Chem. Commun.*, 1987, 559.
- 10 H. Fischer, U. Gerbing, J. Riede and R. Benn, *Angew. Chem.*, 1986, **98**, 80; *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 78.
- 11 H. Fischer, K. Treier, U. Gerbing and J. Hofmann, *J. Chem. Soc., Chem. Commun.*, 1989, 667.
- 12 See, e.g. R. D. Adams, J. A. Belinski and J. Schierlmann, *J. Am. Chem. Soc.*, 1991, **113**, 9004 and references cited therein.