systems is currently under investigation.

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Registry No. 1c, 15975-93-6; **7a**, 622-29-7; **7b**, 17972-15-5; **7c**, 17972-13-3; **8a**, 97879-05-5; **8b**, 97879-06-6; **8c**, 97879-07-7; **9a**, 97879-03-3; **9b**, 97889-72-0; **9c**, 97879-04-4; **12**, 88034-35-9.

Supplementary Material Available: Full details of the X-ray structure determination (27 pages). Ordering information is given on any current masthead page.

Silicon-Containing Carbene Complexes. 5.[1] (Ethylthio)(triphenylsilyl)ketene by Thermal Decomposition of $(CO)_5WC(SEt)SiPh_3$[†]

Hannelore Hörnig, Elke Walther, and Ulrich Schubert*

Institut für Anorganische Chemie der Universität
Am Hubland, D-8700 Würzburg, Germany

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Summary: Thermal decomposition of the carbene complex $(CO)_5WC(SEt)SiPh_3$ yields (ethylthio)(triphenylsilyl)ketene and a complex, in which the ketene is S-coordinated to a $W(CO)_5$ moiety. The structure of $EtS(Ph_3Si)C{=}C{=}O$ has been determined by X-ray diffraction.

We have recently shown[3-5] that the products obtained by thermolysis of ethoxysilylcarbene complexes $(CO)_5MC(OEt)SiPh_3$[6] (M = Cr, Mo, W) are totally different to those obtained from the corresponding alkyl- or arylalkoxycarbene complexes $(CO)_5MC(OR)R'$.[7] Depending on the metal and on the solvent, ethyl triphenylsilyl ketone,[4,5] ethyltriphenylsilane,[5] and ethylene and triphenylsilane[3-5] are formed in varying portions but with nearly quantitative combined yields.

The corresponding thiocarbene complex $(CO)_5WC(SEt)SiPh_3$ (**1**)[8] is prepared in 96% yield by reaction of $(CO)_5WC(OEt)SiPh_3$ with neat ethanethiol. Strict adherance to the reaction conditions (30 min at 0 °C) and monitoring of the progress of the reaction by IR is essential, since increasing amounts of $(CO)_5WS(H)Et$[9] are formed with increasing temperature and time.

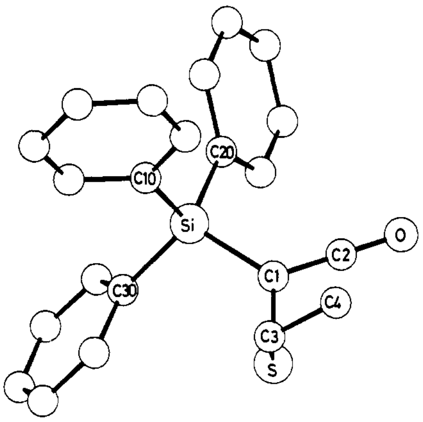
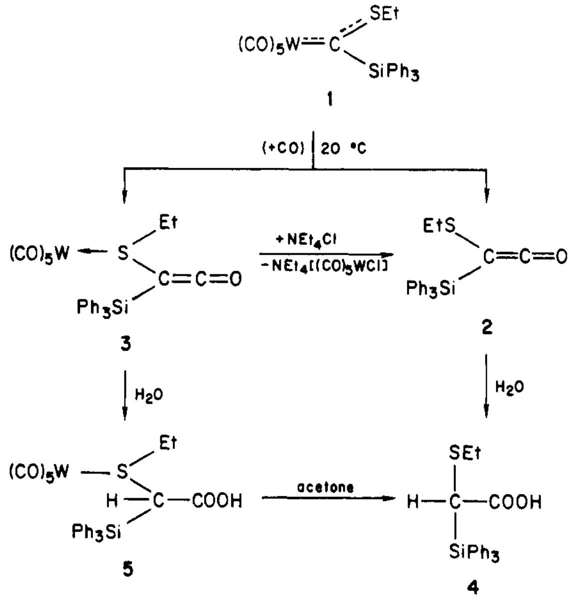


Figure 1. ORTEP diagram of **2**. Hydrogen atoms have been omitted. Important bond lengths (pm) and angles (deg) are as follows: Si–C1 = 184.9 (6), Si–C10 = 184.9 (6), Si–C20 = 186.7 (6), Si–C30 = 185.5 (6), C1–S = 177.7 (6), S–C3 = 176.2 (10), C1–C2 = 130.8 (10), C2–O = 116.1 (10); C1–C2–O = 179.4 (8), C2–C1–S = 112.2 (5), C2–C1–Si = 122.7 (5), S–C1–Si = 125.0 (4), C1–S–C3 = 104.5 (4).

Scheme I



1 slowly decomposes at 20 °C both in the solid state and in pentane solution, yielding (ethylthio)(triphenylsilyl)ketene (**2**)[10] and a metal complex, **3**[11] in which the ketene is coordinated to a $(CO)_5W$ fragment (Scheme I). No products of the type obtained by thermolysis of $(CO)_5WC(\mathit{OEt})SiPh_3$ are observed. The total yield of **2** + **3** can be considerably increased, if carbon monoxide is bubbled through a solution of **1** in pentane at 20 °C. Under these conditions **3** is the main product. However, **3** is rather labile and slowly decomposes by cleavage of **2** from the metal. More quantitatively, **2** can be obtained from **3** (or from a mixture containing both **2** and **3**) by reaction with NEt_4Cl in CH_2Cl_2 and subsequent separation from NEt_4 $[(CO)_5WCl]$ (Scheme I).

The small difference in the ν(CCO) frequencies and the somewhat different ^1H NMR chemical shifts of the ethyl groups of **2**[10] and **3**[11] prove that in **3** the sulfur atom of the

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[†] Dedicated to Prof. Max Schmidt on the occasion of his 60th birthday.

(1) Parts 1–4: ref. 2–4 and 18.

(2) Schubert, U.; Wiener, M.; Köhler, F. H. *Chem. Ber.* **1979**, *112*, 708.

(3) Schubert, U.; Hörnig, H.; Erdmann, K.-U.; Weiss, K. *J Chem. Soc., Chem. Commun.* **1984**, 13.

(4) Schubert, U.; Hörnig, H. *J. Organomet. Chem.* **1984**, *273*, C11.

(5) Hörnig, H. *Dissertation*, Univ. Würzburg, 1985.

(6) Fischer, E. O.; Hollfelder, H.; Friedrich, P.; Kreissl, F. R.; Huttner, G. *Chem. Ber.* **1977**, *110*, 3467.

(7) Dötz, K. H. In "*Transition Metal Carbene Complexes*"; Verlag Chemie: Weinhein, 1983.

(8) **Data**: mp 84 °C dec; ^1H NMR (acetone-d_6) δ 7.64 (m, 15 H), 3.88 (q, 2 H), 1.68 (t, 3 H); IR (pentane) ν(CO) 2062 (m), 1989 (w), 1953 (s), 1947 (vs), 1940 (sh) sm^{-1}. Anal. Calcd for $C_{26}H_{20}O_5SSiW$: C, 47.56; H, 3.05. Found: C, 47.69; H, 3.13. We found that the reaction of $(CO)_5WC(OEt)SiPh_3$ with EtSH to give **1** is catalyzed by unknown impurities within the EtSH. This kind of catalysis has been observed for a related reaction: see: Fischer, E. O.; Kreis, G.; Kreissel, F. R.; Kreiter, C. G.; Müller, J. *Chem. Ber.* **1973**, *106*, 3910.

(9) **Data**: green crystals; mp 95 °C; ^1H NMR (acetone-d_6) δ 3.30 (q, 2 H), 1.60 (t, 3 H), 1.20 (s, 1 H); IR (pentane) ν(CO) 2030 (m), 1983 (m), 1968 (vs), 1962 (s), 1952 (sh) cm^{-1}.

(10) **2**: mp 75 °C; ^1H NMR (chloroform-d_1) δ 7.53 (m, 15 H), 2.20 (q, 2 H), 1.10 (t, 3 H); IR (pentane) ν(CCO) 2093 cm^{-1}. Anal. Calcd for $C_{22}H_{20}OSSi$: C, 73.29; H, 5.59. Found: C, 73.09; H, 5.67.

(11) **3**: ^1H NMR (chloroform-d_1) δ 7.57 (m, 15 H), 2.57 (q, 2 H), 1.20 (t, 3 H); IR (pentane) ν(CO) 2103 (s), 2072 (m), 1984 (w), 1944 (vs), 1936 (s) cm^{-1}.

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ketene ligand is bonded to the metal.

Ketene **2** can be isolated by column chromatography on silica. If adsorbed water has not been removed from the silica (by heating under vacuum) prior to use, water adds to both the coordinated and the uncoordinated ketene and both acid **4**[12] and its metal complex **5**[13] are obtained. **4** is readily cleaved from the metal by heating an acetone solution of **5** (Scheme I).

Though the hitherto unknown ketene **2** is thermally stable, it is extremely reactive toward moisture. It is a very interesting compound for organic reactions, because of the different properties of the substituents at the ketene carbon. Owing to the workup procedure (including treatment of the reaction mixture with NEt_4Cl) the isolated yield of **2** is rather low (12%). However, since we could not detect other silicon-containing products from the thermolysis of **1**, we believe that the actual yield of **2** + **3** is much higher. For instance, the isolated yield of acid **4** is 32%, if a mixture of **2** + **3** is chromatographed on (undried) silica and the resulting mixture of **4** + **5** is treated with acetone as described above. Use of ketene **2** for syntheses therefore should proceed without isolation of **2**.

The structure of **2** is shown in Figure 1.[14] The dihedral angle between the planes O, C1, C2, S, Si and C1, S, C3 is 86°. This conformation excludes conjugation between the sulfur lone pairs and the C=C bond and rather suggests hyperconjugation between the C—S and C=C bonds.[15] The latter view is also supported by the S–C1 (sp^2) distance, which is as long as S–C3 (sp^3). Similar C–S bond lengths are found in thio enol ethers, e.g., 174.8 pm in $CH_2{=}CHSMe$[16] and 176.4 (2)–177.1 (2) pm in *cis*- and *trans*-Ph(MeS)C=C(SMe)Ph.[17] Interestingly, the C1—Si distance in **2** (184.9 (6) pm) is distinctly shorter than the C(carbene)—Si distance in $(CO)_5M{=}C(OEt)SiPh_3$ (M = Cr, 200 (2)pm; M = Mo, 194 (2) pm)[6] and other silylcarbene complexes.[18]

Carbonylation of carbene ligands to yield ketenes or ketene complexes is probably an important step in catalytic reactions. Formation of these compounds has occasionally been observed in stoichiometric reactions of carbene complexes (e.g., ref. 19 and 20). For $(CO)_5M{=}CPh_2$ (M = Cr, W) an intramolecular carbene–CO coupling has been proven.[18] In the case of **1** attack of CO (intra- or intermolecularly) to the carbene carbon is obviously facilitated by the SEt substituent, because the corresponding ethoxy-substituted complex $(CO)_5W{=}C(OEt)SiPh_3$ only yields the corresponding ketene $EtO(Ph_3Si)C{=}C{=}O$ at a CO pressure of about 50 atm.[3]

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fond der Chemischen Industrie for financial support.

Registry No. **1**, 98014-95-0; **2**, 98014-97-2; **3**, 98014-96-1; **4**, 98014-98-3; **5**, 98049-99-1.

Supplementary Material Available: Listings of final atomic parameters, bond lengths and angles, and observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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[12] **4**: mp 180 °C; ^{1}H NMR (chloroform-d_1) δ 10.73 (s, 1 H), 7.53 (m, 15 H), 3.80 (3, 1 H), 2.70 (q, 2 H), 1.2 (t, 3 H); IR (methylene chloride) ν(CO) 1691 cm^{-1}. Anal. Calcd for $C_{22}H_{22}O_2SSi$: C, 69.80; H, 5.86. Found: C, 70.00; H, 5.96.

[13] **5**: ^{1}H NMR (acetone-d_6) δ 10.8 (s, 1 H, 7.6 (m, 15 H), 4.5 (s, 1 H), 3.1 (q, 2 H), 1.0 (t, 3 H); IR (pentane) ν(CO) 2072 (m), 1982 (w), 1943 (vs), 1930 (sh), 1695 (w) cm^{-1}.

[14] Crystals obtained by cooling a pentane solution of **2**: triclinic, space group $P\bar{1}$,a = 975.7 (6) pm, b = 1015.2 (6) pm, c = 1052.3 (5) pm, α = 83.77 (4)°, β = 79.28 (4)°, γ = 76.11 (4)°; $V = 992 \times 10^6$ pm^3; Z = 2, d(calcd) = 1.21 g cm^{-3}; Mo Kα (λ = 71.069 pm). A total of 2874 independent reflections (ω scan, $2° \leq 2\theta \leq 49°$) were reduced to structure factors by correction for Lorentz and polarization effects. Solution of the structure by MULTAN. Anisotropic refinement for all atoms by full-matrix least squares (fixed hydrogen parameters, isotropic B) resulted in $R = 0.087$ and $R_w = 0.090$ ($1/w = \sigma(F)^2$) for 2291 structure factors with $F_o \geq 4\sigma\ (F_o)$.

[15] Müller, C.; Schäfer, W.; Schweig, A.; Thon, N. *J. Am. Chem. Soc.* **1976**, *98*, 5440.

[16] Samdal, S.; Seip, H. M. *Acta Chem. Scand.* **1971**, *25*, 1903.

[17] Adiwidjaja, G.; Kistenbrugger, L.; Voss, J. *J. Chem. Res., Synop.* **1981**, 88; *J. Chem. Res., Minipr.* **1981**, 1227.

[18] Schubert, U.; Ackerman, K.; Rustemeyer, P. *J. Organomet. Chem.* **1982**, *231*, 323.

[19] Dorrer, B.; Fischer, E. O. *Chem. Ber.* **1974**, *107*, 2683. Mitsudo, T.; Sasaki, T.; Watanabe, Y.; Takegami, Y.; Nishigaki, S.; Nakatsu, K.; *J. Chem. Soc., Chem. Commun.* **1978**, 252. Herrmann, W. A.; Plank, J. *Angew. Chem.* **1978**, *90*, 555; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 525. Klimes, J.; Weiss, E. *Angew. Chem.* **1982**, *94*, 207; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 205.

[20] Fischer, H. *Angew. Chem.* **1983**, *95*, 913; *Angew. Chem.*, Int. *Ed. Engl.* **1983**, *22*, 874.

Two-Dimensional ^{119}Sn NMR Exchange Spectroscopy as a Tool for the Elucidation of the Dynamic Stereochemistry of Tin Compounds

Chantal Wynants,[1a] **Georges Van Binst,**[1a]
Clemenz Mügge,[1b] **Klaus Jurkschat,**[1b]
Alfred Tzschach,[1b] **Henri Pepermans,**[1c,d]
Marcel Gielen,[1c] **and Rudolph Willem***[1c]

Eenheid Organische Chemie en Instrumentele Eenheid and
Dienst voor Algemene en Organische Scheikunde
Vrije Universiteit Brussel, B-1050 Brussel, Belgium
and Department of Chemistry, Martin-Luther University
Halle/S, German Democratic Republic

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Summary: The first ^{119}Sn 2D NOESY NMR spectrum allows to demonstrate unambiguously that the ditin compound $CH_2[(C_6H_5)Sn(SCH_2CH_2)_2NCH_3]_2$ isomerizes at the tin center in an uncorrelated way. The advantages of 2D NMR over traditional 1D NMR line-shape analysis are shortly emphasized.

This report describes the first two-dimensional (2D) ^{119}Sn NMR (exchange spectroscopy, EXSY) spectrum. It illustrates the power of this method in the elucidation of the dynamic stereochemistry of tin compounds. The model system examined for this purpose is a compound exhibiting two five-coordinate tin centers, $CH_2[(C_6H_5)Sn(SCH_2CH_2)_2NCH_3]_2$, hereafter compound **1**. Its synthesis, molecular structure, and solution stereochemistry were discussed recently.[2] The static stereochemistry in solution was unambiguously established from NMR data.[2] Among these the 1D ^{119}Sn NMR spectrum of **1**, at room temperature in $CDCl_3$, exhibits four signals in the approximate ratio 0.9:1:1:0.2. This was interpreted by assigning the first and the last signals to the C_{2v} isomers aa and ae, respectively, in which the two tin atoms are homotopic, while the two central, equally intense signals were

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[1] (a) Eenheid Organische Chemie en Instrumentele Eenheid, Fakulteit Wetenschappen, Vrije Universiteit Brussel. (b) Department of Chemistry, Martin-Luther University, Weinberg 16, 4020 Halle/S, GDR. (c) Dienst voor Algemene en Organische Scheikunde, Fakulteit Toegepaste Wetenschappen, Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussel, Belgium. (d) Aspirant at the Belgian "Nationaal Fonds voor Wetenschappelijk Onderzoek (NFWO)".

[2] Willem, R.; Gielen, M.; Meunier-Piret, J.; Van Meersche, M.; Jurkschat, K.; Tzschach, A. *J. Organomet. Chem.* **1984**, *277*, 335.

0276-7333/85/2304-1906$01.50/0