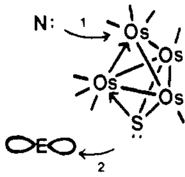
Scheme I



1

linear terminal carbonyl ligands. There is a triply bridging sulfido ligand linked to the triosmium group Os(1), Os(2), and Os(3) and a quadruply bridging phenylvinylidene on the opposite side of the rhombus from the sulfido ligand. The vinylidene hydrogen atom H(14) was characterized by direct observation in a difference Fourier synthesis and by its ^1H NMR signal at δ 6.703. Carbon atom C(13) is bonded to all four metal atoms while C(14) is bonded only to Os(4). The C(13)–C(14) distance of 1.446 (16) Å is indicative of partial multiple bonding. Similarly, coordinated vinylidene ligands have been observed in other cluster complexes; in fact, the formation of vinylidene ligands by 1,2-hydrogen shifts is a characteristic feature of the reactivity terminal acetylene ligands.[10]

Compound **3a** has been formulated as $Os_4(CO)_{12}[\mu_4\text{-}\eta^3\text{-}SC(Ph)CH]$ and an ORTEP diagram of its molecular structure is shown in Figure 2.[11] The molecule consists of a butterfly tetrahedral cluster of four osmium atoms. The five osmium–osmium bonding distances are normal and range from 2.7640 (7) to 2.8490 (7) Å. Each metal atom has three linear terminal carbonyl ligands.[12] The most unusual ligand is the thiolato ligand SC(Ph)═CH, which to our knowledge has an unprecedented form. It was apparently formed by the formation of a carbon–sulfur bond between the phenyl-substituted carbon atom of the acetylene and the sulfido ligand. The C(14)–S bond length 1.817 (11) Å is characteristic of a carbon–sulfur single bond. The sulfur atom bridges metal atoms Os(3) and Os(4) while the acetylenic portion (C(13) and C(14)) is coordinated in a σ, π fashion to Os(1) and Os(2). The C(13)–C(14) separation at 1.400 (15) Å indicates that considerable multiple-bond character is still present. The hydrogen atom on C(13) was observed in a difference Fourier synthesis, and its very low-field ^1H NMR shift (δ 9.406) is characteristic of coordinated terminal acetylenes.[13] The formation of carbon–sulfur bonds is quite unusual but has been observed previously in metal complexes containing sulfido[14] and thiolato[15] ligands.

We believe it is significant that **2a** and **3a** can not be interconverted.[6] In fact, this observation strongly suggests that they were formed by different mechanisms. The structure of **1** could be viewed as a triangular cluster of three $Os(CO)_3$ groups bridged by a "capping" $Os(CO)_3$ group and a triply bridging sulfido ligand.[5] The electron-deficient character of $Os(CO)_3$ "capping" groups was recognized several years ago.[16] These sites permit nucleophilic ligand additions through the cleavage of a metal–metal bond, path 1; see Scheme I. This could be the first step in the formation of compound **2a**. The greater yield of the product **3b** for the more electron-deficient acetylene $MeO_2CC{\equiv}CH$ suggests a nucleophilic character of the cluster, path 2. Thus, a reaction proximate to the electron-rich sulfido ligand might be favored, and this could lead to the formation of products **3a** and **3b**.

Acknowledgment. This work was supported by the Division of Basic Energy Science of the U.S. Department of Energy under Contract DE-FG09-84ER 13296.

Registry No. **1**, 82080-90-8; **2a**, 97919-65-8; **3a**, 97919-66-9; **3b**, 97919-67-0; $MeO_2CC{\equiv}CH$, 922-67-8; $PhC{\equiv}CH$, 536-74-3.

Supplementary Material Available: Tables of structure factor amplitudes, final fractional atomic coordinates and thermal parameters, interatomic distances, and selected bond angles for compounds **2a** and **3a** (33 pages). Ordering information is given on any current masthead page.

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(10) (a) Bruce, M. I. *Adv. Organomet. Chem.* **1983**, *22*, 60. (b) Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *J. Chem. Soc., Chem. Commun.* **1981**, 476. (c) Roland, E.; Vahrenkamp, H. *J. Mol. Catal.* **1983**, *21*, 233.

(11) Black crystals of **3a** were grown by slow evaporation of hexane solvent at 0 °C. Crystals of **3a** belong to the monoclinic crystal system, space group $P2_1/c$, with a = 8.923 (1) Å, b = 10.315 (1) Å, c = 27.868 (6) Å, β = 97.09 (1)°, Z = 4, and ρ_{calcd} = 3.21 g/cm^3. The structure was solved by a combination of direct methods (MULTAN) and difference Fourier techniques. Full-matrix least-squares refinement on 2770 reflections ($F^2 \geq 3.0\sigma(F^2)$) yielded the final residuals R_F = 0.033 and R_{wF} = 0.034.

(12) Selected interatomic distances (Å) and angles (deg) are as follows: Os(1)–Os(2) = 2.7840 (7), Os(1)–Os(3) = 2.8490 (7), Os(1)–Os(4) = 2.8442 (7), Os(2)–Os(3) = 2.8132 (7), Os(3)–Os(4) = 2.7640 (7), Os(3)–S = 2.391 (3), Os(4)–S = 2.370 (3), Os(1)–C(13) = 2.124 (11), Os(2)–C(13) = 2.198 (12), Os(2)–C(14) = 2.366 (11), C(14)–S = 1.817 (11), C(13)–C(14) = 1.400 (15); Os(2)–Os(1)–Os(4) = 103.75 (2), Os(2)–Os(3)–Os(4) = 105.10 (2), Os(3)–S–Os(4) = 70.98 (9), Os(3)–S–C(14) = 100.7 (4), Os(4)–S–C(14) = 109.7 (4), S–C(14)–C(13) = 116.3 (7), Os(2)–C(14)–S = 102.0 (5).

(13) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203.

(14) (a) Giolando, D. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 6455. (b) McKenna, M.; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. C.; DuBois, M. R. *J. Am. Chem. Soc.* **1983**, *105*, 5329. (c) Halbert, T. R.; Pan, W. H.; Stiefel, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 5476.

(15) Davidson, J. L.; Shiralian, M.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1979**, 30.

(16) John, G. R.; Johnson, B. F. J.; Lewis, J. *J. Organomet. Chem.* **1979**, *181*, 143.

Application of Pentacarbonylchromium Carbenes in β-Lactam Synthesis: Preparation and X-ray Crystallographic Study of (1-Methyl-4-phenyl-3(*E*)-(phenylmethylene)-azetidinylidene)pentacarbonylchromium

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Received May 31, 1985

Summary: The reaction of the tetramethylammonium salt of (1-hydroxyethylidene)pentacarbonylchromium (**1c**) with toluene-4-sulfonyl chloride and *N*-benzylidenemethylamine (**7a**) gave the title azetidine complex **8a** (25%), whose structure was confirmed by a crystal structure determination. Subsequent oxidation with pyridine *N*-oxide gave 1-methyl-4-(phenylmethylene)-2-azetidinone **9a** (96%). These reactions were extended to *N*-(3-methylbenzylidene)methylamine and *N*-(4-methylbenzylidene)methylamine.

In 1974 Fischer reported an intriguing observation on the dehydration of (1-hydroxyethylidene)pentacarbonylchromium (**1a**). Thus reaction of **1a** with dicyclohexylcarbodiimide (**2**) in dichloromethane solution gave the iminoazetidinylidene complex **4** (47%).[1] It is possible but by no means certain that **4** was produced via the formal [2 + 2] cycloaddition[2] reaction between excess **2** and the

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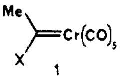
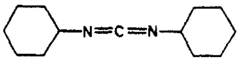
(1) Weiss, K.; Fischer, E. O.; Müller, J. *Chem. Ber.* **1974**, *107*, 3548.

reactive intermediate **3**. Since the $C{=}Cr(CO)_5$ substituent can readily be converted by oxidation into a carbonyl substituent,[3] we sought to exploit this chemistry for β-lactam synthesis. Recently Hegedus has developed some very elegant β-lactam methodology using carbene complexes. For example, the photolysis of **1b** in the presence of **5** gave **6**.[4] This photochemical protocol is clearly mechanistically very distinct from the application of the ketene surrogate[5] **3** in β-lactam construction.



1

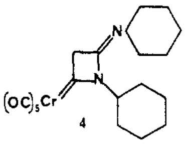
a X = OH
b X = OMe
c X = O⁻Me₄N⁺



2

$CH_2{=}C{=}Cr(CO)_5$

3



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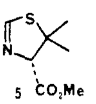

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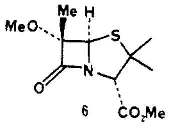
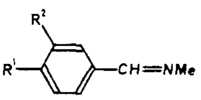


6



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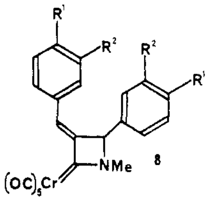
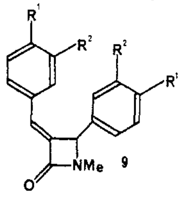


8

a R¹ = R² = H
b R¹ = H, R² = Me
c R¹ = Me, R² = H



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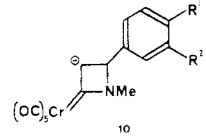

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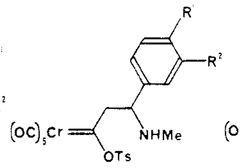

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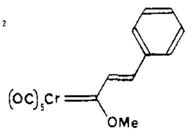

12

In dichloromethane, **1c** was reacted sequentially with toluene-4-sulfonyl chloride (1.0 equiv) and imine **7a** (4 equiv) at 20 °C. After 9 h evaporation and chromatography on silica gave an orange crystalline solid ($C_{22}H_{15}CrNO_5$, 25%): mp 163 °C; IR (CH_2Cl_2) 1920 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.35 (s, 3 H), 6.08 (s, 1 H), 7.0–7.4 (m, 11 H); UV λ_1 408 nm (ϵ 3300), λ_2 290 (11400) (CH_2Cl_2). An X-ray crystallographic study established the structure as the azetidinylidene complex **8a**. Crystal data: crystals of **8a** ($C_{22}H_{15}CrNO_5$), $M = 425.36$, were obtained from diethyl ether–hexane; $a = 9.034$ (2) Å, b ; 22.649 (4) Å, $c = 10.067$ (1) Å, $\beta = 95.10$ (1)°, $V = 2051.7$ (11) Å^3, space group $P2_1/c$ (no. 14, C_{2h}^5), $Z = 4$, $D_{calcd} = 1.377$ g cm^{-3}. A total of 4702 independent reflections ($\theta \leq 27.5°$) were measured on a diffractometer using Mo Kα radiation, and of these 1999 had $I \geq 3\sigma(I)$ and were classed as observed. The structure was solved by direct methods and refined anisotropically to $R = 0.035$. Both the short C-6 carbon to nitrogen (1.340 (4) Å) and long C-6 carbon to chromium bonds (2.034 (3) Å) confirm the importance of considerable electron donation from nitrogen to chromium in the four-membered ring.

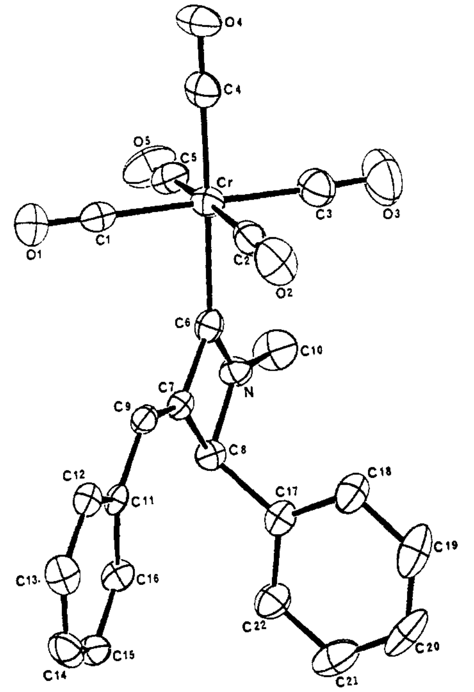

Figure 1. Perspective drawing of (1-methyl-4-phenyl-3(*E*)-(phenylmethylene)azetidinylidene)pentacarbonylchromium. The ellipsoids correspond to 50% contours of atomic displacement, and the H atoms have been omitted for the sake of clarity. Selected bond lengths (Å) are as follows: N–C6 (1.340), N–C8 (1.479), C6–C7 (1.492), C7–C8 (1.529), C6–Cr (2.034), C7–C9 (1.330). Estimated standard deviations for the bond lengths shown are all ≤0.004 Å.

Oxidation of **8a** using iodosobenzene[6] or pyridine *N*-oxide[7] in dichloromethane solution gave the β-lactam **9a**[8] (~100% and 96%, respectively). The imines **7b** and **7c** were also converted in the same way into the carbene complexes **8b** (9%) and **8c** (6%) and subsequently oxidized with pyridine *N*-oxide to produce the β-lactams **9b** (87%) and **9c** (89%).

It is possible that **8a**, **8b**, and **8c** were produced via the cycloaddition of the respective imines **7** with **3** followed by a second addition of **7** to the intermediates **10**. Alternatively, **8a**, **8b**, and **8c** may have arisen by an aldol-type mechanism via **11** and subsequent cyclization. Consistent with this stepwise mechanism, we observed that the reaction to produce **8a** was solvent dependent. Thus reaction of **1c** with toluene-4-sulfonyl chloride and imine **7a** in dry *tert*-butyl alcohol gave **8a** (22%). In contrast, reaction in dry methanol gave **8a** (9%) and **12** (9%). A detailed examination of the mechanism of the reaction and its optimization and application to more highly functionalized

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[2] Wulff has recently described the use of (1-methoxypropenylidene)pentacarbonylchromium as a dienophile in [π4s + π2s] cycloaddition reactions. Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726.

[3] For an excellent review on metal carbene complexes see: Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1.

[4] Hegedus, L. S.; McGuire, M. A.; Schultze, L. M.; Yijun, C.; Anderson, O. P. *J. Am. Chem. Soc.* **1984**, *106*, 2680.

[5] Ketenes are widely applied in β-lactam synthesis. For diverse examples, see: Mukerjee, A. K.; Singh, A. K. *Tetrahedron* **1978**, *34*, 1731.

[6] Lukehart, C. M.; Zeile, J. V. *J. Organomet. Chem.* **1975**, *97*, 421.

[7] Cotton, F. A.; Lukehart, C. M. *J. Am. Chem. Soc.* **1971**, *93*, 2672; **1973**, *95*, 3552.

[8] For the synthesis of related α-methylene-β-lactam derivatives see: Commerçon, A.; Ponsinet, G. *Tetrahedron Lett.* **1983**, *24*, 3725. Kano, S.; Shibuya, S.; Ebata, T. *J. Chem. Soc., Perkins Trans. 1* **1982**, 257. Ishida, M.; Minami, T.; Agawa, T. *J. Org. Chem.* **1979**, *44*, 2067. Agawa, T.; Ishida, M.; Ohshiro, Y. *Synthesis* **1980**, 933. Minami, T.; Ishida, M.; Agawa, T. *J. Chem. Soc., Chem. Commun.* **1978**, 12. Chiba, K.; Mori, M.; Ban, Y. *Ibid.* **1980**, 770. Mori, M.; Chiba, K.; Okita, M.; Ban, Y. *Ibid.* **1979**, 698. Fletcher, S. R.; Kay, I. T. *Ibid.* **1978**, 903. Kano, S.; Ebata, T.; Yuasa, Y.; Shibuya, S. *Heterocycles* **1980**, *14*, 589. Mayrhofer, R.; Otto, H. H. *Synthesis* **1980**, *247*. Kano, S.; Ebata, T.; Funaki, K.; Shibuya, S. *Ibid.* **1978**, 746. Corbett, D. F.; Eglington, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1083. Adlington, R. M.; Barrett, A. G. M.; Quayle, P.; Walker, A.; Betts, M. J. *J. Chem. Soc., Perkin Trans. 1* **1983**, 605.

systems is currently under investigation.

Acknowledgment. We thank NIH under Grant 1 S10 RR-01672-01 and NSF under Grant CHE8300958 for the provision of the Enraf-Nonius CAD4 single-crystal diffractometer and G.D. Searle and Co. for a generous unrestricted grant.

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)$_5$WC(SEt)SiPh$_3$[†]

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Received June 13, 1985

Summary: Thermal decomposition of the carbene complex (CO)$_5$WC(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$_3$Si)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)$_5$MC(OEt)SiPh$_3$[6] (M = Cr, Mo, W) are totally different to those obtained from the corresponding alkyl- or arylalkoxycarbene complexes (CO)$_5$MC(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)$_5$WC(SEt)SiPh$_3$ (1)[8] is prepared in 96% yield by reaction of (CO)$_5$WC(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)$_5$WS(H)Et[9] are formed with increasing temperature and time.

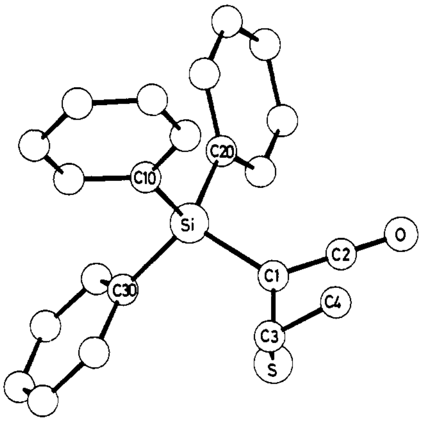
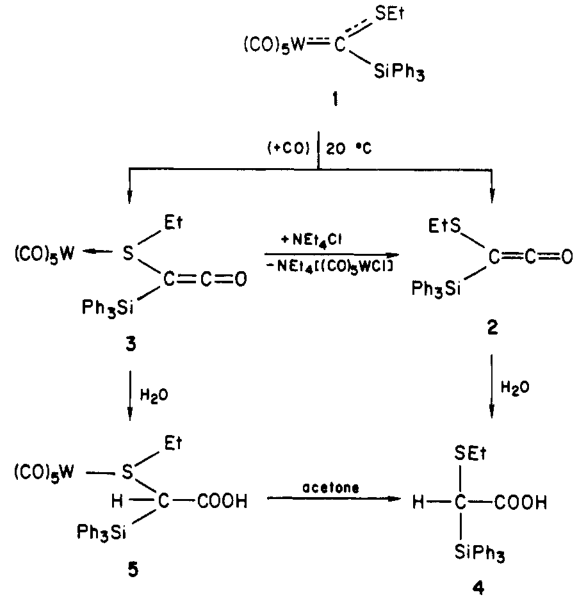


Figure 1. ORTEP diagram of 2. Hydrogen atoms have been omitted. Important bond lengths (pm) and angles (deg) are as follows: Si–C1 = 184.9 (6), Si–C10 = 184.9 (6), Si–C20 = 186.7 (6), Si–C30 = 185.5 (6), C1–S = 177.7 (6), S–C3 = 176.2 (10), C1–C2 = 130.8 (10), C2–O = 116.1 (10); C1–C2–O = 179.4 (8), 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)$_5$W fragment (Scheme I). No products of the type obtained by thermolysis of (CO)$_5$WC(*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$_4$Cl in CH$_2$Cl$_2$ and subsequent separation from NEt$_4$ [(CO)$_5$WCl] (Scheme I).

The small difference in the ν(CCO) frequencies and the somewhat different ^{1}H 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; ^{1}H 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$_5$SSiW: C, 47.56; H, 3.05. Found: C, 47.69; H, 3.13. We found that the reaction of (CO)$_5$WC(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; ^{1}H 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; ^{1}H 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: ^{1}H 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}.

0276-7333/85/2304-1905$01.50/0