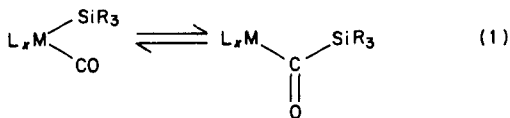


Insertion of Carbon Monoxide into a Transition-Metal-Silicon Bond. X-ray Structure of the Silaacyl ($\eta^5\text{-C}_5\text{H}_5$)₂Zr($\eta^2\text{-COSiMe}_3$)Cl

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Insertion of carbon monoxide into a transition-metal-carbon bond is a well-known reaction in organometallic chemistry.¹ Insertion of carbon monoxide into a transition-metal-silicon bond, however, is an ill-defined process which has proven difficult to study. Reactions of the latter type (e.g., eq 1) are potentially

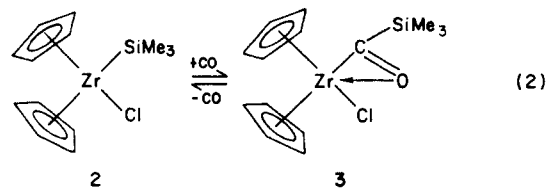


useful, in that they could provide new methods for CO activation^{2,3} and furnish pathways utilizing acylsilane derivatives.⁴

In order to develop this area of transition-metal silicon chemistry, it is important to define how silyl groups can migrate to CO within the coordination sphere of a metal. This problem has been complicated by the reluctance of many isolated carbonyl/silyl complexes to undergo migratory insertion.^{3,5} In a few cases, carbonyl/silyl compounds are known to decompose to give siloxide ($-\text{OSiR}_3$) derivatives, sometimes with complete cleavage of the C-O bond in carbon monoxide.^{3,6} To our knowledge, a direct insertion product (silaacyl) has never been observed, although the complex *fac*-Re(CO)₃(diphos)(COSiPh₃) (**1**) has been prepared and structurally characterized. Compound **1** decarbonylates above 182 °C; the resulting silyl, *mer*-Re(CO)₃(diphos)SiPh₃, could not be carbonylated with CO pressures up to 300 atm.⁷ We have been examining the reaction chemistry of early-transition-metal silyls and have recently synthesized some new zirconium and hafnium silyl complexes.⁸ Herein we report that one of these compounds, ($\eta^5\text{-C}_5\text{H}_5$)₂Zr(SiMe₃)Cl (**2**), reacts reversibly with CO, providing an insertion product which can be fully characterized.

Pressurizing red diethyl ether solutions of **2** with CO (50–100 psi) results in precipitation of a pink powder, **3**, in 90% yield. Though insoluble in diethyl ether and hydrocarbons, **3** can be crystallized from CH₂Cl₂/OEt₂ mixtures. Warming suspensions of **3** in pentane or toluene or prolonged stirring in these solvents at room temperature causes extensive conversion back to **2**. These results, along with the complete characterization of **3** (vide infra) provide evidence for the insertion and deinsertion reactions of CO with a Zr-Si bond (eq 2).

Spectroscopic properties for **3**⁹ resemble those found for **1**.⁷ The



carbonyl stretching frequency of the *bidentate* silaacyl ligand in **3** (1489 cm⁻¹ Nujol) is remarkably similar to the 1490 cm⁻¹ (KBr pellet) value observed for the *monodentate* silaacyl group of **1**. We presume that this result is fortuitous, since the carbonyl substituents in **3** and **1** are different. Consistent with the effect of silyl substitution,⁷ the carbonyl stretching frequency of **3** is lower than those found in analogous zirconium acyls (1500–1550 cm⁻¹).¹⁰ Also consistent with the presence of a $-\text{COSiMe}_3$ group is the ¹³C NMR shift of the carbonyl carbon (391.6 ppm), which appears at lower field⁷ than those of zirconium acyls (by 70–90 ppm^{10a,h,j}). The corresponding ¹³C NMR chemical shift in **1** was observed at 340.1 ppm.

The overall structure¹¹ (Figure 1) resembles that found in the acyl ($\eta^5\text{-C}_5\text{H}_5$)₂Zr($\eta^2\text{-COMe}$)Me.^{10g} Bond distances within the Zr-O-C11 triangle of **3** are identical with those found in ($\eta^5\text{-C}_5\text{H}_5$)₂Zr($\eta^2\text{-COMe}$)[(OC)₃Mo($\eta^5\text{-C}_5\text{H}_5$)],^{10a} exhibiting the same slight C-O bond elongation and Zr-O bond contraction relative to ($\eta^5\text{-C}_5\text{H}_5$)₂Zr($\eta^2\text{-COMe}$)Me. The Si-C(acyl) bond length of 1.927 (2) Å is slightly shorter than the corresponding distance in **1** (1.969 (10) Å) but considerably longer than the average of the remaining Si-C(Me) bond lengths, 1.847 (7) Å. The latter trend was observed in **1**⁷ and in Ph₃SiCOMe.¹²

Insertion reactions of the type observed here (eq 2) may be particularly favorable with early metal complexes such as **2**, in which an increase in electron count for the metal and formation of a strong metal-oxygen bond occurs. It remains uncertain whether this insertion reaction represents an early event in reactions that proceed to siloxide derivatives in other silyl complexes. It is worth noting, however, that acylsilanes such as Me₃SiCOR are known to photochemically or thermally rearrange to the siloxycarbenes Me₃SiOCR.¹³ This 1,2-shift can also result from nucleophilic attack at the carbonyl carbon.^{4b} With respect to these considerations, we are currently investigating the reactivity of **3** and searching for similar CO insertions in related systems.

Preliminary results indicate that nucleophiles and electrophiles react at the Zr-Cl bond of **3** rather than with the silaacyl ligand. The reaction of **3** with LiOCMe₃ in diethyl ether proceeds via decarbonylation to the silyl complex ($\eta^5\text{-C}_5\text{H}_5$)₂Zr(SiMe₃)-

(9) For **3**: ¹H NMR (CD₂Cl₂, 20 °C, 360 MHz) δ 0.47 (s, 9 H, SiMe₃), 5.78 (s, 10 H, C₅H₅); ¹³C{¹H} NMR (CD₂Cl₂, 20 °C, 50.3 MHz) δ -2.90 (s, SiMe₃), 109.2 (s, C₅H₅), and 391.6 (s, ZrCOSi). Anal. (C₁₄H₁₉O₂SiZr) C, Cl, H. Mp 130–133 °C.

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(11) The crystal structure was determined by Dr. F. J. Hollander, staff crystallographer at the U.C. Berkeley X-Ray Crystallographic Facility (CHEX-RAY). **3** crystallizes in the monoclinic space group *P2₁/n* with cell dimensions *a* = 9.7608 (12) Å, *b* = 12.8694 (16) Å, *c* = 12.6837 (15) Å, β = 91.074 (10)°, and *V* = 1593.0 (6) Å³, with *Z* = 4 and *d*(calcd) = 1.49 g cm⁻³. The data were collected on a Nonius CAD-4 automated diffractometer with Mo K α X-rays (λ = 0.7103 Å). The structure was solved by Patterson methods and refined by full-matrix least-squares to a conventional *R* factor of 0.024 (*R_w* = 0.037; GOF = 1.96) by using 1836 data, where *F*² > 3 σ (*F*²), against 164 variables. The *R* value for all 2081 data was 0.031.

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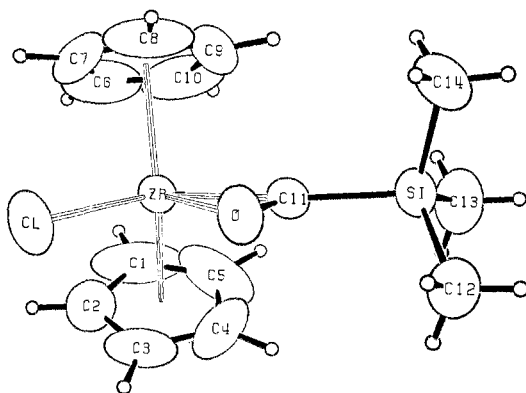


Figure 1. ORTEP view of **3**. Additional distances (Å) and angles (deg): Zr-Cl, 2.536 (1); Zr-O, 2.248 (1); Zr-C11, 2.183 (2); C11-O, 1.244 (3); Cl-Zr-O, 80.86 (4); Cl-Zr-C11, 113.42 (6); Zr-C11-Si, 163.87 (13); O-C11-Si, 119.56 (16).

OCMe₃.⁸ This presumably reflects competition between lone pairs on the silylacyl oxygen and the butoxide ligand for the same orbital on zirconium.^{10b} In contrast, the triflate complex (η^5 -C₅H₅)₂Zr(η^2 -COSiMe₃)(OSO₂CF₃)¹⁴ (**4**) was obtained in high yield after stirring **3** with an excess of Me₃SiOSO₂CF₃ in dichloromethane. We are examining further aspects of the insertion chemistry of **2** but have been unable to observe reactions with ethylene (90 psi, diethyl ether, 2 days), phenylacetylene (excess, hexane, 1 day), carbon dioxide (100 psi, diethyl ether, 2 days), and carbon disulfide (excess, C₆D₆, 1 day).

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Supplementary Material Available: A listing of bond lengths, bond angles, positional and thermal parameters, and observed and calculated structure factors for **3** (14 pages). Ordering information is given on any current masthead page.

(14) For **4**: ¹H NMR (CD₂Cl₂, 20 °C, 360 MHz) δ 0.51 (s, 9 H, SiMe₃), 5.90 (s, 10 H, C₅H₅); ¹³C{¹H} NMR (CD₂Cl₂, 20 °C, 50.3 MHz) δ -2.85 (s, SiMe₃), 110.0 (s, C₅H₅), 389.7 (s, ZrCOSi); IR (Nujol, cm⁻¹) ν_{CO} = 1500. Anal. (C₁₅F₇H₁₉O₄SSiZr) C, H, S.

Fluoride Ion Catalyzed Aldehyde Addition of Labile α - or β -Halocarbanion Species Generated from the Corresponding α - or β -Halo Organosilanes

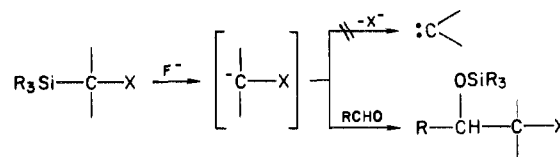
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Organometallic compounds having such leaving group(s) as halogen at the α -position to the metal are called carbenoids and are labile and decompose to carbenes readily.¹ Though uniquely versatile in organic synthesis,^{1,2} carbenoid reactions require generally extremely low temperatures.³ The instability of the carbenoid species is attributed to coordination of the halogen(s) to the metal (e.g., Li⁺ and Mg²⁺) to produce a metal-halogen bond

and induce its decomposition to carbene. In spite of attempts at stabilization of the carbenoids by employing basic solvents^{1b,4} or by adding metal halide salts,⁵ handling the reactive organometallics still needs careful experimentations.⁶ We assumed that in the absence of a metal gegen cation, the interaction between the metal cation and the leaving group halogen(s) should be completely neglected, and the corresponding carbanions having α -halogens should have longer lifetimes to undergo synthetic reactions before decomposition. Herein we report that such naked carbanion species can be generated from the corresponding α -halo organosilanes by the action of fluoride ion catalyst and add to aldehydes at ambient temperature without appreciable decomposition.



When tris(diethylamino)sulfonium difluorotrimethylsilicate (TASF)^{7,8} (1 M tetrahydrofuran (THF) solution, 0.25 mmol) was added to a THF (2 mL) solution of benzaldehyde (1 mmol) and (dichloromethyl)trimethylsilane (1.2 mmol) at room temperature, exothermic reaction took place. After being stirred for 8 h, the reaction mixture was treated with acid (1 M HCl-MeOH solution, room temperature, 0.25 h). Workup followed by chromatographic purification (silica gel, CH₂Cl₂-hexane) gave 2,2-dichloro-1-phenylethanol in 74% yield. Experiments using *N,N*-dimethylformamide (DMF) or hexamethylphosphoric triamide (HMPA) as the solvent or tetrabutylammonium fluoride (TBAF) as the catalyst gave somewhat lower yields. Various (polyhalomethyl)silanes gave the corresponding aldehyde adducts in good yields (Table I) except Me₃SiCH₂Cl and PhMe₂SiCF₂H which were recovered unchanged. Since the corresponding (polyhalomethyl)lithium compounds decompose even at -78 °C,³ the procedure described herein should be of great significance from a practical viewpoint. For example, introduction of dichloromethyl unit to 3,4-dichlorobenzaldehyde gave an insecticide (run 13),⁹ whereas the product of run 14 is a precursor of 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid, an acid part of permethrin and its derivatives.¹⁰ Ketone adducts were not isolated thus far.¹¹

Stereoselectivity of the carbonyl addition is worthy of note. In the reaction of 2-phenylpropanal with Me₃SiCCl₃ the erythro isomer of the adduct was formed as the major product (87% selectivity).^{12,13} The erythro:threo ratio (87:13) did not change significantly on employment of PhMe₂SiCCl₃ (87:13) or *t*-BuMe₂SiCCl₃ (90:10). Thus, the observed selectivity seems to be an intrinsic value of a naked trichloromethyl anion. A possibility that a pentavalent silicate species is involved may be rejected on the basis of the lack of the substituent effect at silicon

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(11) In the reaction of acetophenone and Me₃SiCHCl₂, the enol silyl ether, α -trimethylsilyloxystyrene, was formed, suggesting that the dichloromethyl anion species generated in the present reaction has considerable basicity (see: Nakamura, E.; Murofushi, T.; Shimizu, M.; Kuwajima, I. *J. Am. Chem. Soc.* **1976**, 98, 2346).

(12) The relative configuration is assigned as "erythro" or "threo" according to the definition of Noyori (Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1983**, 105, 1598).

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(3) For instance, LiCH₂Cl decompose even at -130 °C^{2b,c} and preparation of LiCHCl₂ or LiCCl₃ must be carried out at -110 or -78 °C, respectively.¹