

Reactions of Primary Organosilanes on Transition Metal Surfaces. Identification of the First Surface-Bound Silylynes

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Transition metal silicides have numerous applications in the microelectronics industry, where, for example, PtSi and PtSi₂ find use as Schottky barriers, gate electrodes, and infrared radiation detectors.¹ Thin films of metal silicides can be prepared by treatment of a metal film with SiH₄,^{2,3} however, this chemical vapor deposition (CVD) method has one principal drawback: the hazards associated with handling silane, a spontaneously flammable gas. Primary organosilanes (RSiH₃) are attractive alternative silicon sources for the synthesis of metal silicides, since many of these compounds are stable in air. Studies of methylsilane on metal surfaces have shown that this molecule serves as a precursor for the deposition not of metal silicides but of silicon carbide thin films.⁴ Interestingly, "β-unstable" organosilanes such as *tert*-butylsilane have not been studied as silicon sources for metal silicides, even though clean (i.e., carbon-free) thin films are more likely to result owing to the ability of the *tert*-butyl group to undergo β-hydrogen elimination.

In order to determine whether primary organosilanes are indeed useful for the deposition of PtSi and PtSi₂ thin films via CVD, we have studied the reactions of RSiH₃ species on Pt(111) surfaces. Interestingly, we find that these molecules react to give surface-bound silylynes (RSi≡). Although there are numerous molecular complexes that contain silicon ligands bound to transition metal centers, including a recently reported base-stabilized silylyne species,⁵ the identification of silylyne units on metal surfaces has not previously been reported.⁶

A Pt(111) surface in an ultrahigh vacuum chamber (10⁻¹⁰ Torr) was treated with a 7 langmuir exposure of *t*-BuSiH₃ at 105 K, and subsequent reactions of the silane were studied by temperature-programmed reaction spectroscopy (TPRS). When the surface is heated, H₂ desorbs in a broad (recombination-limited) feature centered at ~250 K (Figure 1a). These data suggest that the Si–H hydrogen atoms of *tert*-butylsilane are transferred to the surface at temperatures below 250 K;

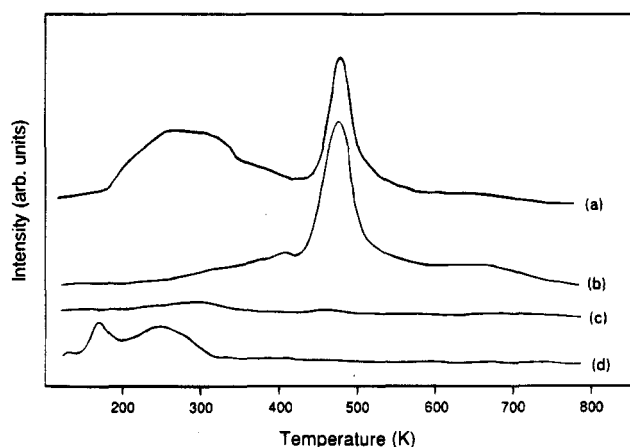


Figure 1. Temperature-programmed reaction spectra for (a) a saturation coverage of *t*-BuSiH₃ on Pt(111) at 108 K, *m/e* = 2, and a saturation coverage of *t*-BuSiD₃ on Pt(111) at 108 K, (b) *m/e* = 2, (c) *m/e* = 3, and (d) *m/e* = 4. The feature at 170 K in trace d is due to desorption of *t*-BuSiD₃ from the multilayer.

the surface hydrogen atoms then recombine to form H₂. Clear evidence that all three Si–H bonds of *tert*-butylsilane are cleaved at temperatures ≤250 K has been obtained from TPRS studies of the specifically labeled molecule *t*-BuSiD₃.⁷ When a Pt(111) surface dosed with a saturation coverage of *t*-BuSiD₃ is heated, a desorption feature for D₂ (*m/e* = 4) is seen at ~250 K. Only insignificant amounts of HD or H₂ desorb at temperatures below ~400 K (Figure 1b–d).⁸ Significantly, no further D₂ desorbs when the temperature of the surface is ramped between 250 and 800 K; the latter limit is sufficiently high to ensure the complete dehydrogenation of any adsorbed organic species. This result shows unambiguously that all three of the Si–D bonds (and none of the *tert*-butyl C–H bonds) are cleaved below 250 K. It follows that *tert*-butylsilylyne species must be formed, unless these fragments oligomerize on the surface to form products with Si–Si bonds. We will show below that this latter possibility can be ruled out.

Confirmation of the formation of surface silylyne species was obtained by reflection-absorption infrared (RAIR) spectroscopy. For *t*-BuSiH₃ on Pt(111), the bands seen at temperatures below 400 K are consistent with the presence of intact *t*-Bu structures. Absorptions are seen in the Si–H stretching and bending regions (2147 and 937 cm⁻¹, respectively) at 132 K; these bands disappear when the surface is heated to ~160 K. The *tert*-butyl group is evidently still intact, since little change is seen in the C–H stretching bands (2945, 2928, 2891, and 2860 cm⁻¹), the antisymmetric CH₃ deformation band (1470 cm⁻¹), and the weak symmetric CH₃ deformation band (1260 cm⁻¹) over the temperature range 110–410 K, after which decomposition occurs (see below). Since surface-bound *tert*-butyl groups should not be stable over such a temperature range,⁹ the Si–C bond must remain intact at temperatures up to 400 K.

Methylsilane also dehydrogenates on Pt(111) surfaces to give a stable organosilylyne product. Adsorption proceeds dissociatively even at temperatures as low as 108 K, but the nature of the products formed depends sensitively on the coverage. At the lowest exposures used (0.5 langmuir, Figure 2a), the spectra suggest that methylsilylyne is the predominant surface-bound species present: the mode at 760 cm⁻¹ is assigned to the Si–C stretch, the mode at 1231 cm⁻¹ is assigned to the

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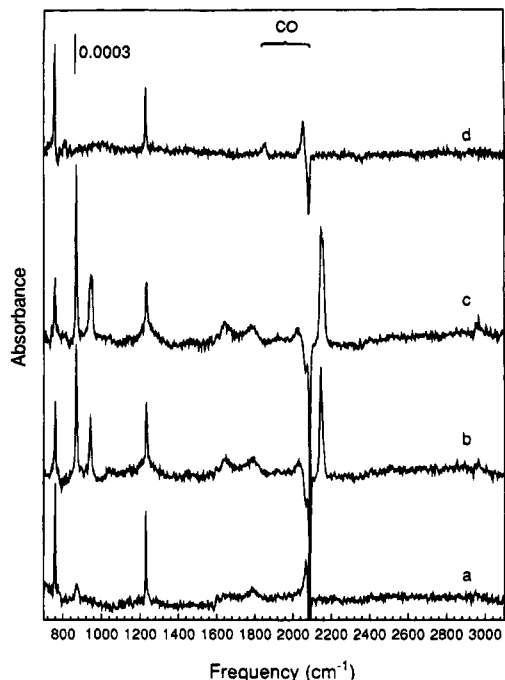


Figure 2. Reflection-absorption infrared spectra of MeSiH₃ on Pt(111): (a) 0.5 langmuir at 108 K, (b) 1.0 langmuir at 108 K, (c) 2.0 langmuirs at 108 K and (d) 1.0 langmuir at 260 K. Background CO is present in very small quantities; the RAIR features appear intense due to the large oscillator strength of the C–O stretch.

CH₃ symmetric deformation, and the weak band at ~ 2949 cm⁻¹ is assigned to the symmetric C–H stretch. The RAIR spectrum of the MeSi≡ fragment closely resembles that of ethynyl (MeC≡) on Pt(111) at 82 K: the latter exhibits a C–CH₃ stretch at 1118 cm⁻¹, a symmetric CH₃ deformation at 1339 cm⁻¹, and a symmetric C–H stretch at 2884 cm⁻¹.¹⁰ The absence of the strong CH₃ rocking mode in the IR spectrum establishes that the Si–C vector is oriented nearly perpendicularly to the surface.¹¹ This result is consistent with the formation of a methylsilylyne species, but is inconsistent with the presence of MeHSi≡, MeH₂Si–, or oligomeric (MeSi)_n species, all of which would have methyl groups tilted with respect to the surface normal that should give strong CH₃ rocking modes in the RAIR spectrum.

At higher coverages, the bands for methylsilylyne persist but decrease somewhat in intensity and new bands appear (Figure 2b,c). We assign the strong band at 870 cm⁻¹ and the bands at 941 and 2145 cm⁻¹ to the methyl rocking motion and the Si–H bending and stretching modes,¹¹ respectively, of a methylsilylyne species (MeHSi≡). At coverages approaching saturation of the monolayer,¹² additional bands appear in the C–H stretching region at 2965 cm⁻¹ and in the Si–H bending and stretching regions at 951 and 2154 cm⁻¹, respectively, that we attribute to the presence of either methylsilyl units (MeH₂Si–) or intact methylsilane molecules. The pair of broad, weak bands at 1645 and 1776 cm⁻¹ may be due to soft modes of the Si–H stretching vibrations (Figure 2c).^{13,14} When a Pt(111) surface dosed at

108 K with a near saturation coverage of MeSiH₃ is heated above 170 K, the modes associated with the Si–H bonds disappear and the only bands which persist are those assignable to methylsilylyne (Figure 1d).

For phenylsilane on Pt(111), the predominant features in the IR spectrum at 132 K are the Si–H stretching and bending vibrations (2154 and 937 cm⁻¹). When the dosed surface is heated to 220 K, the Si–H vibrations disappear and the intensities of the C–H stretching vibration at 3055 cm⁻¹ and the Si–C stretching vibration at 1107 cm⁻¹ increase significantly. We conclude that phenylsilane chemisorbs at least in part to the Pt(111) surface via a π interaction with the phenyl ring, so that the C–H and Si–C stretching motions are parallel to the surface and thus weak owing to the dipole selection rule for RAIRS.¹⁵ In contrast, when the Si–H bonds dissociate, the C–H and Si–C modes are strong because the PhSi≡ unit is bound to the surface through the silicon atom and the phenyl groups are thus perpendicular to the surface.

At higher temperatures, all of the organosilylyne species decompose. RAIRS and TPRS studies of *t*-BuSiH₃ at saturation coverage show that the *tert*-butyl groups disappear above 410 K and that isobutylene desorbs from the surface at ~ 460 K.¹⁶ It is unclear whether isobutylene is formed directly from the *tert*-butylsilylyne group or by an initial transfer of the *tert*-butyl group to the platinum surface followed by β -hydrogen elimination. For *t*-BuSiD₃, the TPRS features seen above 250 K are essentially identical to those seen for the unlabeled molecule: no D₂ desorbs, and negligible amounts of HD desorb at 291 and 460 K, but strong desorption features for H₂ are seen at 460 and 632 K (Figure 1c). For MeSi≡, decomposition occurs to give methane (300, 450 K) and H₂ (450, 645 K), while for PhSi≡, decomposition occurs to give benzene (~ 450 K) and H₂ (490, 645 K).¹⁶ Taken together, the data suggest that the cleavage of the Si–C bonds of the organosilylyne species is facile above ~ 400 K.¹⁷

The present data reveal that the Si–H bonds of primary organosilanes readily cleave on Pt surfaces. The number of Si–H bonds cleaved is dependent on the temperature and coverage, but by 250 K all three are cleaved to yield organosilylyne units. Like alkynyl units, with which they are isoelectronic, the organosilylyne species are probably bound to 3-fold hollow sites.¹⁸ The high activity of Pt toward Si–H bonds and the relative kinetic stability of Si–C bonds in the surface adducts have implications regarding the utility of primary silanes as silicon sources for the CVD deposition of metal silicides. Further studies will be reported separately.

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Supplementary Material Available: Temperature-dependent RAIR spectra of *tert*-butylsilane and phenylsilane (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(11) The C–H stretching modes and the CH₃ antisymmetric deformation mode of methylsilane are quite weak. Wilde, R. E. *J. Mol. Spectrosc.* **1962**, *8*, 427–454. It is expected that this will also hold true for the MeH₂Si fragments on Pt(111).

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(13) Although softened Si–H modes have not been previously observed on transition metal surfaces, softened C–H modes are relatively common; see, for example: Raval, R.; Chesters, M. A. *Surf. Sci.* **1989**, *219*, L505–L514.

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(16) The peak temperatures and intensities of these desorption features are coverage dependent.

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