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Transformation of $Ph_2Si(C{\equiv}CCMe_3)_2$ to a 4-Alkylidene-1-silacyclobut-2-enyl Ligand by Pt-H Addition and Rearrangement Reactions

Anne C. Dema and C. M. Lukehart*

Department of Chemistry, Vanderbilt University
Nashville, Tennessee 37235

Andrew T. McPhail* and Donald R. McPhail

Department of Chemistry, Duke University
Durham, North Carolina 27706

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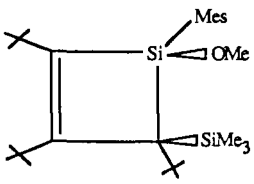
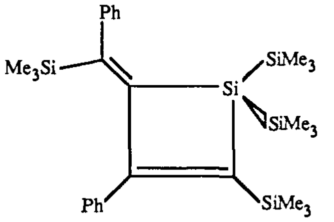
Small-ring, heterocyclic compounds are of interest because the high-strain energy within the ring system may impart exceptional reactivity to these molecules. Organosilicon compounds of this type are of special interest as reagents for the preparation of larger cyclic molecules or of new materials.[1] Silacyclobutenes, including benzosilacycloalkenes, are quite rare species which are known to undergo [4 + 2] cycloadditions to give six-membered ring siloxanes[2] or thermal-ring opening to form polymers.[1] The paucity of silacyclobutenes results from the lack of general and convenient synthetic methods for their preparation. These unsaturated rings have been prepared in earlier work by bromination and subsequent dehydrobromination of silacyclobutanes or by flash-vacuum pyrolysis.[1,3] In a recent report by Fink and co-workers, three silacyclobutenes were isolated as trapping products from reactions involving a photochemically generated silacyclobutadiene species. The structure of one of these silacyclobutenes, **1**, has been determined by X-ray diffraction.[4] Furthermore, as part of an extensive study of the formation and reactivity of silicon–carbon unsaturated compounds, the Ishikawa and Higuchi groups have prepared three analogous and highly substituted (*exo*-alkylidene)silacyclobutenes from catalytic or stoichiometric reactions involving Ni(0) or Ni(II) species in the reaction of (phenylethynyl)polysilanes with phenyl(trimethylsilyl)acetylene. The X-ray structure of one of these compounds, **2**, has been determined.[5-8] These selected (*exo*-alkylidene)silacyclobutenes are formed at high reaction temperatures (135–200 °C for 15–21 h) and in variable yields (3–77%) depending on the synthetic method used. A methoxysilacyclobutene is formed when **2** is photolyzed in the presence of methanol,[9] and subsequent thermolysis of this product in methanol affords a dimethoxysilacyclobutene and a dimethoxysilylalkene as products.[10]



1



2

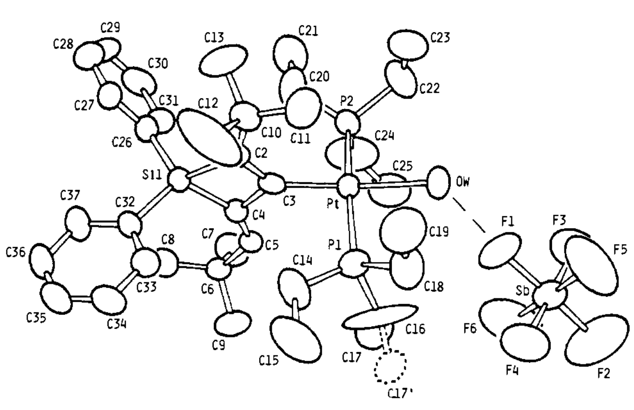
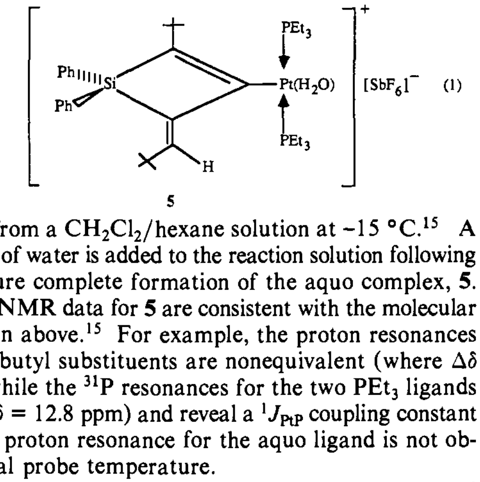


Figure 1. An ORTEP diagram of **5** (thermal ellipsoids at the 40% probability level) showing the atomic numbering scheme; one methyl group is disordered over two positions, C17 and C17′. Hydrogen atoms have been omitted for clarity. Values of selected interatomic distances (Å) and angles (deg) are as follows: Pt-P(1) 2.320 (4), Pt-P(2) 2.326 (3), Pt-O(W) 2.273 (8), Pt-C(3) 1.955 (9), Si(1)-C(2) 1.86 (1), Si(1)-C(4) 1.88 (1), Si(1)-C(26) 1.88 (1), Si(1)-C(32) 1.87 (1), C(2)-C(3) 1.40 (1), C(2)-C(10) 1.52 (1), C(3)-C(4) 1.51 (1), C(4)-C(5) 1.35 (1), C(5)-C(6) 1.52 (1); P(1)-Pt-P(2) 169.3 (1), C(3)-Pt-O(W) 176.1 (3), C(2)-Si(1)-C(4) 75.3 (4), Si(1)-C(2)-C(3) 92.8 (6), Si(1)-C(2)-C(10) 134.0 (7), C(3)-C(2)-C(10) 133.0 (8), C(2)-C(3)-C(4) 103.1 (7), Si(1)-C(4)-C(3) 88.7 (5), Si(1)-C(4)-C(5) 144.9 (7), C(3)-C(4)-C(5) 126.4 (8), C(4)-C(5)-C(6) 128.8 (8).

We wish to report a facile, *low-temperature* synthesis of an (*exo*-alkylidene)silacyclobutenyl ring system utilizing transition-metal, organometallic addition and rearrangement reactions, as shown in eq 1. When the dialkynylsilane, **3**,[11] is treated with the cationic platinum hydride complex, **4**,[14] under anhydrous conditions, the product, **5**, is isolated as colorless needles by crystallization from a CH_2Cl_2/hexane solution at −15 °C.[15] A moderate excess of water is added to the reaction solution following reaction to ensure complete formation of the aquo complex, **5**. The ^1H and ^{31}P NMR data for **5** are consistent with the molecular symmetry shown above.[15] For example, the proton resonances of the two *tert*-butyl substituents are nonequivalent (where $\Delta\delta = 0.31$ ppm), while the ^{31}P resonances for the two PEt_3 ligands are equivalent ($\delta = 12.8$ ppm) and reveal a $^1J_{PtP}$ coupling constant of 2951 Hz. A proton resonance for the aquo ligand is not observed at normal probe temperature.

$$\underset{\textbf{3}}{Ph_2Si(C{\equiv}CCMe_3)_2} + \underset{\textbf{4}}{[\textit{trans}\text{-}Pt(H)(PEt_3)_2(THF)]^+[SbF_6]^-} \xrightarrow[\text{(2) } H_2O \text{ (moderate excess)}]{\text{(1) } CH_2Cl_2,\ -78° \to 25\ °C}$$



5 (1)

In addition, the molecular structure of **5** has been confirmed by X-ray diffraction.[16] An ORTEP diagram of **5** showing the

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(1) Barton, T. J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 2, pp 205–303.

(2) Tzeng, D.; Fong, R. H.; Soysa, H. S. D.; Weber, W. P. *J. Organomet. Chem.* **1981**, *219*, 153–161.

(3) Burns, G. T.; Barton, T. J. *J. Organomet. Chem.* **1981**, *216*, C5–C8.

(4) Fink, M. J.; Puranik, D. B.; Johnson, M. P. *J. Am. Chem. Soc.* **1988**, *110*, 1315–1316.

(5) Ishikawa, M.; Ohshita, J.; Ito, Y.; Iyoda, J. *J. Am. Chem. Soc.* **1986**, *108*, 7417–7419.

(6) Ishikawa, M.; Ohshita, J.; Ito, Y. *Organometallics* **1986**, *5*, 1518–1519.

(7) Ishikawa, M.; Matsuzawa, S.; Higuchi, T.; Kamitori, S.; Hirotsu, K. *Organometallics* **1985**, *4*, 2040–2046.

(8) Ishikawa, M.; Matsuzawa, S.; Hirotsu, K.; Kamitori, S.; Higuchi, T. *Organometallics* **1984**, *3*, 1930–1932.

(9) Ishikawa, M.; Sugisawa, H.; Matsuzawa, S.; Hirotsu, K.; Higuchi, T. *Organometallics* **1986**, *5*, 182–184.

(10) Ishikawa, M.; Sugisawa, H.; Akitomo, H.; Matsusaki, K.; Kamitori, S.; Hirotsu, K.; Higuchi, T. *Organometallics* **1986**, *5*, 2447–2451.

(11) Compound **3** was prepared from Ph_2SiCl_2 and $LiC{\equiv}CCMe_3$ in THF solution according to standard procedures[12,13] (64%); mp 84–87 °C; IR (KBr, cm^{-1}) $\nu(C{\equiv}C)$ 2205 (s), 2163 (vs); ^1H NMR ($CDCl_3$) δ 1.28 (s, 18, CMe_3), 7.55 (m, 10, Ph). Anal. Calcd for $C_{24}H_{28}Si$: C, 83.66; H, 8.19. Found: C, 83.85; H, 8.19.

(12) Pant, B. C.; Reiff, H. F. *J. Organomet. Chem.* **1968**, *15*, 65–68.

(13) Hartmann, H.; Niemöller, H.; Reiss, W.; Karbstein, B. *Naturwissenschaften* **1959**, *46*, 321.

(14) Clark, H. C.; Kurosawa, H. *Inorg. Chem.* **1972**, *11*, 1275–1280.

(15) Complex **5** (51% unoptimized yield): dec 170–175 °C; ^1H NMR ($CDCl_3$) δ 0.90 (s, 9, CMe_3), 1.10–1.26 (m, 18, PCH_2CH_3), 1.21 (s, 9, $CHMe_3$), 1.75–2.00 (m, 12, PCH_2CH_3), 6.45 (s, 1, CH, $^4J_{PtH}$ <1.5 Hz), 7.35–7.65 (m, 10, Ph); $^{31}P\{H\}$ NMR ($CDCl_3$) δ 12.8 (s, PEt_3, $^1J_{PtP}$ = 2951 Hz). Anal. Calcd for $C_{36}H_{61}OP_2SiPtSbF_6$: C, 41.95; H, 5.97. Found: C, 42.04; H, 6.01.

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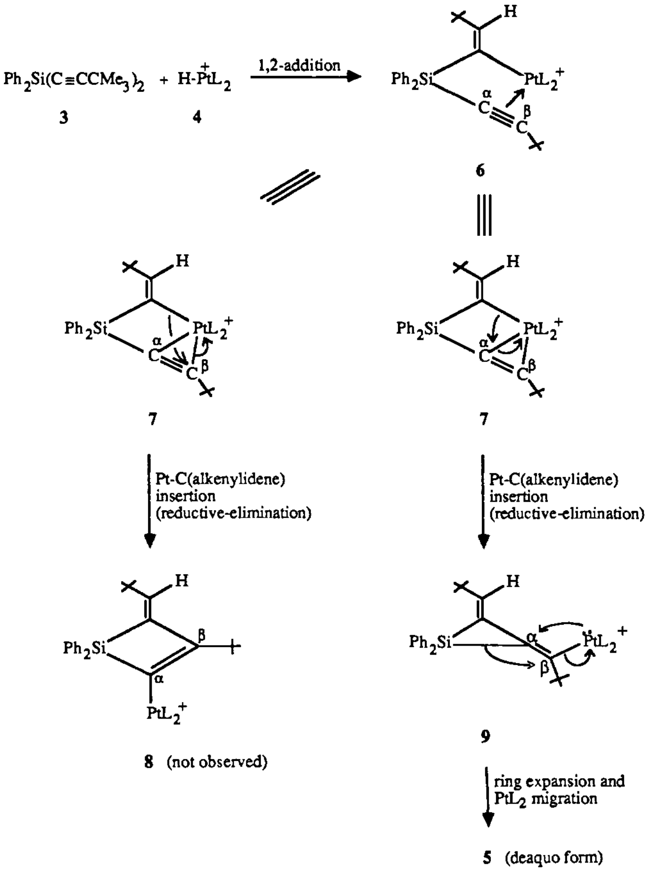
Scheme I



atomic numbering scheme is presented in Figure 1. The *trans*-$Pt(PEt_3)_2(H_2O)^+$ unit has the expected structural features and is bonded to the silacyclobutenyl ring through a Pt-C(3) alkenyl single bond of length 1.955 (9) Å.[17] The 4-alkylidene-1-silacyclobut-2-enyl ring system is characterized by an endocyclic C(2)-C(3) double bond distance of 1.40 (1) Å, an exocyclic C(4)-C(5) double bond distance of 1.35 (1) Å, and by a strained, intraring angle, C(2)-Si-C(4), of 75.3 (4)° centered at the Si atom. The corresponding distances and angle of the silacyclobutene ring in **2** are, respectively, 1.367 (11) Å, 1.334 (12) Å, and 74.0 (4)°.[8] Similarly, the values of the endocyclic C-C double bond distance and the internal angle centered at Si for compound **1** are 1.367 (4) Å and 78.6 (3)°, respectively. In complex **5**, both hydrogen atoms of the aquo ligand are involved in $O-H\cdots FSbF_5^-$ hydrogen bonding. The O(W)···F(1) and O(W)···F(3′) [symmetry-related to F(3)] interatomic distances are 2.72 (1) Å and 2.75 (1) Å, respectively. These values fall within the normal range of 2.72 ± 0.09 Å for O···F interatomic distances in systems exhibiting $O-H\cdots F^-$ hydrogen bonding.[18]

A proposed mechanism for the formation of complex **5** is shown in Scheme I. Regioselective cis addition of the Pt-H bond of **4** across the C≡C bond of one of the alkynyl substituents of **3** would give a Pt, Si μ-alkenylidene intermediate, like **6**, in which the second alkynyl substituent of **3** coordinates to the cationic Pt(II) center. Reaction of **4** with the monoalkynyl phosphine oxide, $Ph_2(PhC{\equiv}C)P{=}O$, gives a complex of similar structure to **6** with the same regioselectivity for the Pt-H addition, $[Ph_2P(\mu\text{-}C{=}CPhH)(\mu\text{-}O)PtL_2]^+$.[19] Intermediate **6** can be represented formally as the oxidative-addition structure **7**. Direct insertion of the second alkynyl bond into the Pt-C(alkenylidene) bond of **7** can occur with two regioselectivities, as shown. Insertion whereby the Pt atom adds to C(α) of the alkynyl substituent would give the heterocyclic complex **8**. This compound is a structural isomer of **5**, and its formation is not observed. Insertion of the alkynyl substituent into the Pt-C(alkenylidene) bond whereby the Pt atom adds to C(β) of the alkynyl substituent would give a highly strained, silacyclopropane intermediate, such as **9**. Ring expansion and migration of the PtL_2 moiety, as shown, would give **5** prior to coordination of the water molecule. Other mechanisms which could effect the conversion of **3** and **4** to **5** have been proposed previously to rationalize the conversion of $O{=}P(C{\equiv}CCMe_3)_3$ and **4** to a similar Pt complex containing a 2-alkylidene-1,2-dihydro-3-phosphete *P*-oxide ligand.[19]

The general scope of this synthetic method and the chemical reactivity of compound **5** are under current investigation.

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Supplementary Material Available: Tables of crystallographic data, atomic positional and thermal parameters, bond lengths and angles, torsion angles, and least-squares planes for complex **5** (14 pages); table of observed and calculated structure factors for complex **5** (34 pages). Ordering information is given on any current masthead page.

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(16) Crystal data: $C_{36}H_{61}OP_2PtSiSbF_6$ (**5**), $M = 1030.75$, monoclinic, space group $P2_1/c(C_{2h}^5)$ - No. 14, $a = 11.696$ (4) Å, $b = 17.341$ (4) Å, $c = 21.938$ (9) Å, $\beta = 91.40(2)°$ (from 25 orientation reflections, $33° < \theta < 43°$), $V = 4448$ (4) Å^3, $Z = 4$, $d_{calcd} = 1.539$ g cm^{-3}, μ(Cu Kα) = 121.8 cm^{-1}. Crystal dimensions: 0.11 × 0.15 × 0.20 mm. Intensity data ($+h$, $+k$, $\pm l$; 7942 nonequivalent, absorption-corrected reflections; $\theta_{max} = 67°$) were recorded on an Enraf-Nonius CAD-4 diffractometer (Cu Kα radiation, $\lambda = 1.5418$ Å; graphite monochromator; $\omega-2\theta$ scans). The crystal structure was solved by direct methods (MULTAN-11/82). Full-matrix least-squares refinement of atomic parameters (anisotropic C, O, P, Pt, Si, Sb, F; fixed H contributions) converged (max. shift 0.02σ) at $R = 0.050$ ($R_w = 0.064$, GOF = 1.52) over 4980 reflections with $I > 3.0\sigma(I)$. Further details are provided as Supplementary Material.

(17) Pt^{II}-C(alkenyl) distances normally fall within the range of 2.022 (8)-2.08 (2) Å. See: Hartley, F. R. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, pp 471-762.

(18) Joesten, M. D.; Schaad, L. J. In *Hydrogen Bonding*; Marcel Dekker: New York, 1974.

(19) Lukehart, C. M.; McPhail, A. T.; McPhail, D. R.; Meyers, J. B., Jr.; Soni, H. K. *Organometallics* **1989**, *8*, 1007-1014.

Acyl Thrombin Photochemistry: Kinetics for Deacylation of Enzyme Cinnamate Geometric Isomers

Ned A. Porter* and John D. Bruhnke

Department of Chemistry, Duke University
Durham, North Carolina 27706

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We recently reported[1] a means for photocontrol of the activity of the blood coagulation enzymes thrombin and Factor Xa. Compound **1a** was thus shown to inhibit thrombin and Factor Xa, and the inhibition was reversed by photolysis. There were, however, several problems with this inhibition-photoactivation strategy utilizing **1a**. The inhibition was temporary and enzyme activity returned after a few hours in the dark. Furthermore, the photoactivation of these enzymes was slow and required light intensities and wavelengths such that appreciable enzyme degradation occurred during photoactivation. Because of these problems, we have prepared several derivatives of **1a** and have studied the kinetics of the inhibition-photoactivation sequence in detail. We report here rate constants for our best inhibitor, **1b**,[2] and these

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(1) Turner, A. D.; Pizzo, S. V.; Rozakis, G.; Porter, N. A. *J. Am. Chem. Soc.* **1988**, *110*, 244.

(2) The inhibitor **1b** was prepared by the procedures described for the preparation of **1a** in ref 1. All new compounds were fully characterized by spectroscopy and elemental analysis, and the details of the synthesis of **1b** and other analogues will be published in due course.

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