$\mathrm{RhCl(CO)(PMe_3)_2}$ (6.7 mg) according to the typical procedure (room temperature, 16.5 h) to give 159 mg of benzaldehyde. The reaction mixture was distilled under reduced pressure to remove benzene and low-boiling products (up to 200 °C (28 mmHg), Kugelrohr); the boiling point of benzophenone is 185 °C (28 mmHg). The weight of the residue was only 12.5 mg. Since the residue must have contained at least 2.2 mg of Rh metal coming from 6.7 mg of the starting complex, the amount of higher boiling products is estimated to be less than 10.3 mg (only 6.5% of benzaldehyde). A similar analysis for pentane carbonylation (room temperature, 16.5 h) revealed that the weight of higher boiling point products (>100 °C (28 mmHg)) was 55% of hexanal.

H/D Exchange of Ligated $\mathrm{PMe_3}$. Benzene-d_6 was carbonylated with $\mathrm{RhCl(CO)(PMe_3)_2}$ according to the typical procedure. The reaction mixture was analyzed by GC-MS (EI) to estimate the extent of deuteration of $\mathrm{RhCl(CO)(PMe_3)_2}$ (packed column OV-1, 1 m). $\mathrm{RhCl(CO)(PMe_3)_2}$-$d_0$ showed the parent ions at m/z 318 (^{35}Cl) and 320 (^{37}Cl) in the ratio of 3:1, while the complex having n deuteriums exhibited its parent ions at $(318 + n)$ and $(320 + n)$.

Typical Procedure for Wavelength-Controlled Experiment. A 0.7 mM solution of $\mathrm{RhCl(CO)(PMe_3)_2}$ in benzene was placed in a Pyrex rectangular cell (1 cm) under nitrogen. The solution was degassed under vacuum and then filled with carbon monoxide (1 atm, balloon). This process was repeated several times to exclude nitrogen. The solution was irradiated with a 500-W high-pressure mercury lamp (Ushio, USH-500D) at room temperature. The wavelength was regulated by means of glass filters (Toshiba, UV-D35, UV-35, and L-39). Wavelength ranges of these glass filters (ranges where the transmittance is over 10%) are 295-420, >325, and >375 nm, respectively.

Effect of CO Pressure and Temperature. A 0.7 mM solution of $\mathrm{RhCl(CO)(PMe_3)_2}$ in benzene (15 mL) was placed under nitrogen in a Hastelloy-C autoclave with a Pyrex window. The nitrogen atmosphere was replaced with carbon monoxide through pressurization (70 atm)-depressurization cycles. The solution was irradiated with a 500-W high-pressure mercury lamp (Ushio, USH-500D), while temperature was controlled with plate heaters attached to the side of the autoclave.

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Evidence for a Bis(alkylidene)silacyclopropane Intermediate in the Platinum-Mediated Formation of a Silacyclobutene

Anne C. Dema,[1a] C. M. Lukehart,*[,1a] Andrew T. McPhail,*[,1b] and Donald R. McPhail[1b]

Contribution from the Departments of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, and Duke University, Durham, North Carolina 27706.

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Abstract: When $\mathrm{Ph_2Si(C{\equiv}CCMe_3)_2}$ is treated with a cationic Pt-H reagent, a 4-alkylidene-1-silacyclobutenyl ring system is formed. Evidence for the presence of two intermediates in this reaction sequence is obtained by using selective trapping reactions. Acetic acid cleaves at Pt-C bond to give alkenylsilane products, indicating the intermediate formation of a Pt, Si-μ-alkenylidene complex. ROH reagents react with a proposed bis(alkylidene)silacyclopropane intermediate to initiate ring opening and to form η^3-butadienyl complexes (where R = H, Me, Et, or Ph). The structure of one of these complex ions (R = H) has been confirmed by X-ray crystallography.

Small-ring, organosilacyclic compounds are of special interest as reagents for the preparation of larger cyclic molecules or new materials due to the greater stability of these compounds relative to that of the corresponding carbocyclic compounds.[2] Silacyclobutenes undergo cycloaddition and various ring-opening reactions of interest; however, general and convenient synthetic methods for the preparation of silacyclobutenes are not available.[2-4] In recent work by Fink and co-workers, silacyclobutenes and a long-lived *o*-silaxylylene intermediate have been prepared from silacyclobutadienes.[5] In addition, the Ishikawa and Higuchi groups have prepared several analogous and highly substituted (*exo*-alkylidene)silacyclobutenes from either catalytic or stoichiometric reactions involving Ni(0) or Ni(II) species in the reaction of (phenylethynyl)polysilanes with phenyl(trimethylsilyl)acetylene. These selected (*exo*-alkylidene)silacyclobutenes are formed under high reaction temperatures (135-200°C for 15-21h), and they react with methanol to form various methoxysilacyclobutenes.[6]

We reported recently a facile, *low-temperature* synthesis of an (*exo*-alkylidene)silacyclobutenyl ring system from readily available dialkynylsilane-utilizing platinum-mediated addition and insertion reactions.[7] Specifically, when the dialkynylsilane, **1**, is treated with the platinum hydride complex, **2**, under anhydrous conditions, the silacyclobutenyl complex **5** is isolated in good yield (see Scheme I). The molecular structure of **5** has been confirmed by X-ray crystallography.[7]

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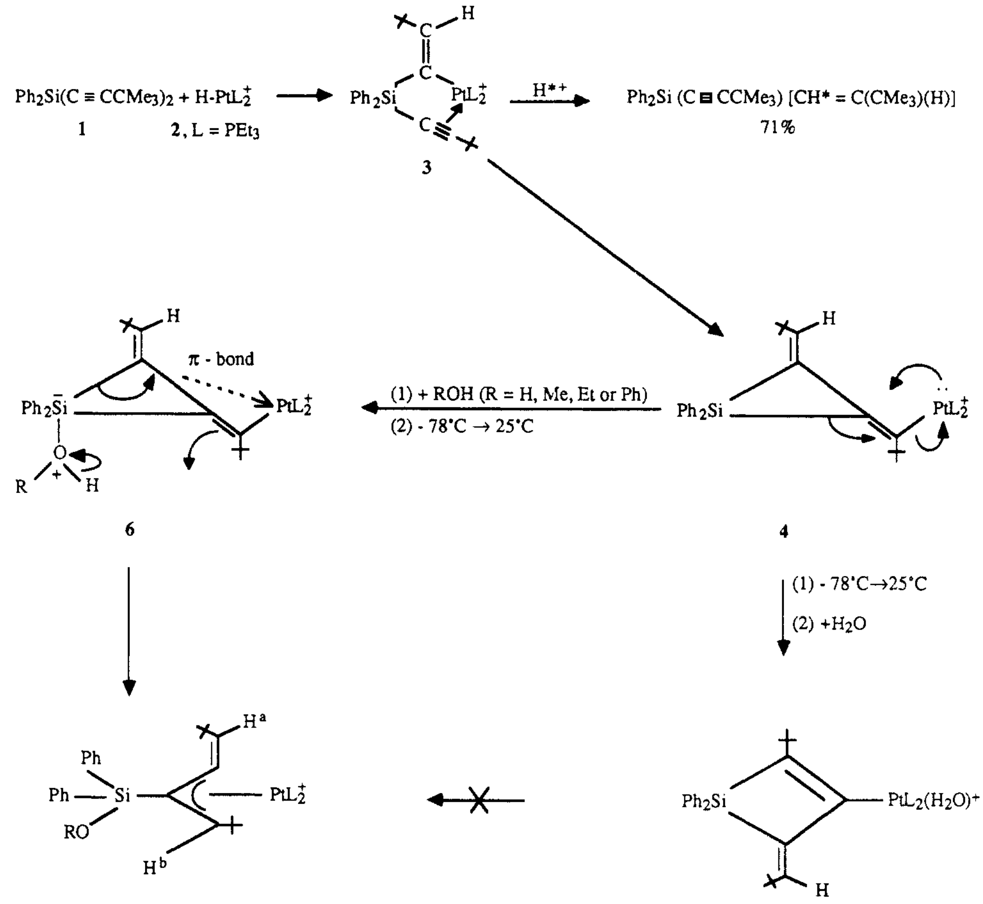
Scheme I



Cpd.	R,	Yield
7	H,	84%
8	Me,	57%
9	Et,	62%
10	Ph,	66%

5, 51%

We now report the results of a mechanistic study of this reaction providing evidence for the intermediate existence of the species **3** and **4**. Most importantly, stereo- and regioselective trapping reactions of the bis(alkylidene)silacyclopropane intermediate **4** by hydroxylic reagents is supported by the isolation of silyl-substituted, η^3-butadienyl compounds. The isolation of these complexes also demonstrates the importance of having a platinum functionality present in an intermediate species to stabilize the resulting organosilane fragment that is produced from an initiated ring-opening reaction.

Experimental Section

Materials and Methods. All manipulations were performed under an atmosphere of dry, prepurified nitrogen and at room temperature unless otherwise indicated. Diethyl ether, hexane, pentane, and tetrahydrofuran (THF) were dried over Na/K alloy with benzophenone having been added to the diethyl ether and THF. Methylene chloride was dried over CaH_2. All solvents were distilled under nitrogen prior to use. ^1H NMR spectra were recorded on an IBM NR-300 spectrometer (300 MHz), using the ^2H signal of the solvent as an internal lock frequency. Chemical shifts (δ) were measured with respect to the residual solvent peak as an internal reference. ^{31}P NMR spectra were recorded on an IBM NR-200 spectrometer operating at a frequency of 81 MHz. Chemical shifts were measured with respect to the external reference of 85% H_3PO_4. Microanalyses were performed by Galbriath Laboratories, Inc., Knoxville, TN.

The cationic platinum hydride (**2**) and organosilane (**1**) reagents were prepared as previously reported.[7] All other reagents were obtained commercially.

Preparation of $Ph_2Si(C{\equiv}CCMe_3)[CH{=}C(CMe_3)(H)]$. To a THF solution of 0.094 g (0.20 mmol) of *trans*-$[Pt(PEt_3)_2\ HCl]$ was added 0.069 g (0.20 mmol) of $Ag[SbF_6]$ in 2 mL of THF. The resulting AgCl was removed by filtration, and the solvent was removed at reduced pressure to give $[Pt(H)(PEt_3)_2(THF)][SbF_6]$. This cationic platinum hydride reagent was dissolved in CH_2Cl_2, and this solution was added to a solution of 0.069 g (0.20 mmol) of $Ph_2Si(C{\equiv}CCMe_3)_2$ (**1**) and 0.15 mL (2.62 mmol) of acetic acid in CH_2Cl_2 at −78°C. The reaction solution was stirred at −78 °C for 1 h and then at 25 °C for 19 h. The solvent was removed at reduced pressure. The residue was extracted with 2 × 10 mL portions of diethyl ether, and removal of the ether from these extractions at reduced pressure gave 0.07 g of a colorless oil: ^1H NMR ($CDCl_3$) δ 1.05 (s, 9 H, CMe_3), 1.31 (s, 9 H, CMe_3), 5.80 (d, 1 H, H^α, $^3J_{HH}$ = 19 Hz, $^2J_{SiH}$ = 7.0 Hz), 6.37 (d, 1 H, H^β, $^3J_{HH}$ = 19 Hz, $^3J_{SiH}$ = 9.5 Hz), 7.3–7.65 (m, 10 H, Ph). Exact mass calcd for $C_{24}H_{30}Si$ 346.212, found 346.214.

Preparation of $Ph_2Si(C{\equiv}CCMe_3)[CD{=}C(CMe_3)(H)]$. This monodeuterated organosilane was obtained by quenching the above reaction solution with acetic acid-d^4 by using a procedure similar to that reported above: ^1H NMR ($CDCl_3$), vinylic region only, δ 6.36 (t, H^β, $^3J_{HD}$ = 2.6 Hz).

Preparation of $Ph_2Si[CH{=}C(CMe_3)(H)]_2$. A solution of 0.43 mmol of $[Pt(H)(PEt_3)_2(THF)][SbF_6]$ in CH_2Cl_2 (prepared as reported above) was added to a CH_2Cl_2 solution of 0.059 g (0.17 mmol) of **1** and 0.25 mL (4.37 mmol) of acetic acid at −78 °C. The reaction mixture was kept at −78 °C for 2 h and then was warmed to 25 °C for 18.5 h. The solvent was removed at reduced pressure. The organosilane product was isolated in 68% yield by extraction with pentane: ^1H NMR ($CDCl_3$) δ 1.05 (s, 18, H, CMe_3), 5.84 (d, 2 H, H^α, $^3J_{HH}$ = 19 Hz, $^2J_{SiH}$ = 6.18 Hz), 6.16 (d, 2 H, H^β, $^3J_{HH}$ = 19 Hz, $^3J_{SiH}$ = 8.43 Hz). Exact mass calcd for $C_{24}H_{32}Si$ 348.227, found 348.225.

Preparation of $\{Pt[\eta^3\text{-}C(H)(CMe_3)C(SiPh_2OH)C{=}C(H)(CMe_3)](PEt_3)_2\}[SbF_6]$ (7). A solution of 0.64 mmol of $[Pt(H)(PEt_3)_2(THF)][SbF_6]$ in 5 mL of CH_2Cl_2 (prepared as reported above) was added to a CH_2Cl_2 mixture of 0.222 g (0.64 mmol) of **1** and 0.2 mL (11.1 mmol) of water at −78 °C. The reaction mixture was stirred at −78 °C for 1.5 h and then was warmed to 25 °C for 48 h. The solvent was removed at reduced pressure to give a yellow residue. This residue was washed with 2 × 5 mL portions of pentane. The crude product yield was 0.557 g (84%), and **7** was purified by crystallization from a CH_2Cl_2/hexane solution at −15 °C as colorless crystals: mp 185–190 °C dec; ^1H

NMR ($CDCl_3$) δ 0.87 (m, 9 H, PCH_2CH_3), 0.93 (s, 9 H, CMe_3), 1.07 (m, 9 H, PCH_2CH_3), 1.10 (s, 9 H, CMe_3), 1.9–2.16 (m, 12 H, PCH_2CH_3), 3.24 (s, 1, OH), 5.51 (dd, 1 H, H^b, $^3J_{PH}$ = 11, 3 Hz, $^2J_{PtH}$ = 14 Hz). 5.59 (d, 1 H, H^a, $^4J_{PH}$ = 4 Hz, $^3J_{PtH}$ = 6 Hz), 7.35–7.70 (m, 10 H, Ph); $^{31}P\{H\}$ NMR ($CDCl_3$) δ 4.01 (d, PEt_3 $^1J_{PtP}$ = 3228 Hz, $^2J_{PP}$ = 10 Hz), 8.83 (d, PEt_3, $^1J_{PtP}$ = 3789 Hz, $^2J_{PP}$ = 10 Hz). Anal. Calcd for $C_{36}H_{61}F_6OP_2PtSbSi$: C, 41.95; H, 5.97. Found: C, 41.82; H, 5.91.

Preparation of $\{Pt[\eta^3\text{-}C(H)(CMe_3)C(SiPh_2OMe)C{=}C(H)(CMe_3)](PEt_3)_2\}[SbF_6]$ (8). The synthetic procedure reported above for the preparation of **7** was followed using 1 mL (24.5 mmol) of methanol in place of water and reaction times of 2 h at −78 °C and 48 h at 25 °C. Colorless crystals of **8** were isolated by crystallization from a CH_2Cl_2/pentane solution at −15 °C to give 0.38 g (57%, unoptimized yield): mp 187–205 °C dec; ^1H NMR ($CDCl_3$) δ 0.85 (m, 9 H, PCH_2CH_3), 0.95 (s, 9 H, CMe_3), 1.1 (s, 9 H, CMe_3), 1.18 (m, 9 H, PCH_2CH_3), 1.85–2.25 (dm, 12 H, PCH_2CH_3), 3.4 (s, 3 H, OCH_3), 5.45 (d, 1 H, H^a, $^4J_{PH}$ = 4 Hz), 5.455 (dd, 1 H, H^b, $^3J_{PH}$ = 9, 3 Hz), 7.35–7.43 (m, 10 H, Ph); $^{31}P\{H\}$ NMR ($CDCl_3$) δ 4.21 (d, PEt_3, $^1J_{PtP}$ = 3, 226 Hz, $^2J_{PP}$ = 10 Hz), 8.02 (d, PEt_3, $^1J_{PtP}$ = 3791 Hz, $^2J_{PP}$ = 10 Hz). Anal. Calcd for $C_{38}H_{65}Cl_2F_6OP_2PtSbSi$ (**8**·CH_2Cl_2): C, 40.40; H, 5.80. Found: C, 40.86; H, 6.18.

Preparation of $\{Pt[\eta^3\text{-}C(H)(CMe_3)C(SiPh_2OEt)C{=}C(H)(CMe_3)](PEt_3)_2\}[SbF_6]$ (9). The synthetic procedure reported above for the preparation of **7** was followed using 0.25 mmol of the Pt–H and organosilane reagents with 0.15 mL (2.56 mmol) of ethanol in place of the water and reaction times of 1.5 h at −78 °C and 14 h at 25 °C. The crude yield of **9** was 0.177 g (62%), and pure product was obtained by crystallization from a CH_2Cl_2/hexane solution at −15 °C: mp 190–195 °C dec; ^1H NMR ($CDCl_3$) δ 0.83 (m, 9 H, PCH_2CH_3), 0.92 (s, 9 H, CMe_3), 1.10 (s, 9 H, CMe_3), 1.0–1.28 (m, 12 H, PCH_2CH_3 and OCH_2CH_3), 1.8–2.3 (dm, 12 H, PCH_2CH_3), 3.68 (dq, 2 H, OCH_2CH_3, $^2J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 6.8 Hz, $^3J_{SiH}$ = 13 Hz), 5.48 (dd, 1 H, H^b, $^3J_{PH}$ = 3.3, 11 Hz), 5.52 (d, 1 H, H^a, $^4J_{PH}$ = 4Hz), 7.35–7.60 (m, 10 H, Ph); $^{31}P\{H\}$ NMR ($CDCl_3$) δ 4.14 (d, PEt_3, $^1J_{PtP}$ = 3219 Hz, $^2J_{PP}$ = 10 Hz), 7.98 (d, PEt_3, $^1J_{PtP}$ = 3790 Hz, $^2J_{PP}$ = 10 Hz. Anal. Calcd for $C_{38}H_{67}Cl_2F_6OP_2PtSbSi$ (**9**·CH_2Cl_2): C, 40.96; H, 5.90. Found: C, 40.84; H, 5.79.

Preparation of $\{Pt[\eta^3\text{-}C(H)(CMe_3)C(SiPh_2OPh)C{=}C(H)(CMe_3)](PEt_3)_2\}[SbF_6]$ (10). The synthetic procedure reported above for the prepartion of **7** was followed using 0.42 mmol of the Pt–H and organosilane reagents with 0.049 g (0.52 mmol) of phenol in place of the water and reaction times of 1 h at −78 °C and 16 h at 25 °C. The reaction residue was washed with 2 × 5 mL portions of diethyl ether to give 0.31 g (66%) of **10** as a crude product. Colorless crystals of **10** were obtained by crystallization from a CH_2Cl_2/hexane solution at −15 °C: mp 185–190 °C dec; ^1H NMR ($CDCl_3$) δ 0.9–1.15 (m, 18 H, PCH_2CH_3), 0.94 (s, 9 H, CMe_3), 1.15 (s, 9 H, CMe_3), 1.90–2.17 (m, 12 H, PCH_2CH_3), 5.55 (d, 1 H, H^a, $^4J_{PH}$ = 3.5 Hz), 5.56 (dd, 1 H, H^b, $^3J_{PH}$ = 3.5, 11 Hz), 6.65 (d, 2 H, ortho H, $^3J_{HH}$ = 9 Hz), 6.90 (t, 1 H, para H, $^3J_{HH}$ = 9 Hz), 7.10 (t, 2 H, meta H, $^3J_{HH}$ = 9 Hz), 7.26–7.68 (m, 10 H, Ph); $^{31}P\{H\}$ NMR ($CDCl_3$) δ 4.41 (d, PEt_3, $^1J_{PtP}$ = 3216 Hz, $^2J_{PP}$ = 10 Hz), 7.88 (d, PEt_3, $^1J_{PtP}$ = 3763 Hz, $^2J_{PP}$ = 10 Hz). Anal. Calcd for $C_{42}H_{65}F_6OP_2PtSbSi$: C, 45.58; H, 5.92. Found: C, 45.78; H, 6.18.

X-ray Crystal Structure Analysis of Complex 7. Crystal, data collection, and refinement parameters for this analysis are provided in Table I. Intensity data were recorded on an Enraf-Nonius CAD-4 diffractometer with Cu Kα radiation using an incident-beam graphite monochromator. The data were corrected for the usual Lorentz and polarization effects, and an empirical absorption correction was also applied. The crystal structure was solved by direct methods (MULTAN-11/82). Refinement consisted of full-matrix, least-squares adjustment of atomic parameters (anisotropic C, O, P, Pt, Si, Sb, and F; fixed H contributions) and an extinction correction. Crystallographic calculations were performed on PDP 11/44 and Micro VAX computer by use of the Enraf-Nonius Structure Determination Package.

Results and Discussion

The regio- and stereoselective formation of intermediate **3** from reaction of **1** and **2** is expected to occur based on our results obtained from reaction of **2** with alkynyl phosphine oxides or alkynyl transition-metal complexes.[8] Reaction of **1** and **2** in the presence of an excess of acetic acid gives a quantitative recovery of organosilanes consisting of the (monoalkynyl)(monoalkenyl)diphenylsilane (in 71% yield), as shown in Scheme I, recovered **1** (in 25% yield), and a small amount of the corresponding (dialkenyl)silane, $Ph_2Si[CH{=}C(CMe_3)(H)]_2$ (in 4% yield). Acetic acid effectively intercepts intermediate **3** presumably through electrophilic cleavage of the Pt-C (alkenylidene) bond. When acetic acid-d^4 is used as the trapping agent, the (monoalkynyl)(monoalkenyl)diphenylsilane is formed stereo- and regioselectively with deuteration only at the Si-C(α) position, as confirmed by NMR.[9] When **1** and **2** react under similar conditions in a 1:2.5 stoichiometry, the (dialkenyl)diphenylsilane product is obtained in 68% yield (along with a 32% yield of the monoalkenylsilane product and no recovered **1**). This result indicates that both alkynyl substituents of **1** can undergo nearly independent reaction with **2**.

Table I. Crystal Data Collection and Selected Refinement Parameters for the X-ray Crystal Structure Analysis of Complex 7

molecular formula	$C_{36}H_{61}F_6OP_2PtSbSi$
formula weight	1030.75
crystal system	orthorhombic
space group	$P2_12_12_1(D_2^4)$, No. 19
a, Å	19.054 (3)
b, Å	19.221 (3)
c, Å	11.680 (2)
no. of orientatn reflctns; θ (°) range	25; 33–38
V, Å^3	4277.6
Z	4
D_{calcd}, g cm^{-3}	1.600
μ(Cu Kα radiation, (λ = 1.5418 Å), cm^{-1}	126.7
temp, °C	25
crystal dimensions, mm	0.020 × 0.035 × 0.43
T_{max}:T_{min}	1.00:0.82
scan type; scan width, deg; θ_{max}, deg	ω–2θ; 1.00 + 0.14 tan θ; 67
intensity control reflctns; variation; repeat time, h	432, $4\bar{3}2$; <2%; 2
total no. of reflctns (+h,+k,+l) recorded	4238
no. of reflctns [$I > 3.0\sigma(I)$] retained	3038
no. of parameters refined	443
extinction correction	1.5 × 10^{-7}
goodness of fit[a]	1.03
R (R_w)[a]	0.042 (0.054)
max shift (esd in final least-squares cycle)	<0.10
max in final difference Fourier synthesis, e/Å^3; location	1.04; 0.87 Å from Pt

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $\sum w\Delta^2[w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$ was minimized; goodness of fit $= [\sum w\Delta^2/(N_{observations} - N_{parameters})]^{1/2}$

Insertion of the remaining alkynyl C≡C bond of **3** into the Pt-C (alkenylidene) σ bond would give the bis(alkylidene)silacyclopropane intermediate, **4**.[10,11] Ring expansion and a 1,2 metal migration, as shown, would form the isolated (*exo*-alkylidene)silacyclobutenyl product, **5**.[7] However, the high oxophilicity of the silicon atom in the highly strained ring system of **4** permits the interception of this intermediate by reacting **1** and **2** in the presence of hydroxylic trapping agents, such as H_2O, MeOH, EtOH, or phenol. Nucleophilic attack by ROH at the Si atom of **4** would produce **6**. Ring opening to a formal allenyl intermediate, as shown in Scheme I, is stabilized by complexation of one of the double bonds of the allene fragment to the very electron-deficient PtL_2 moiety that is already present in the molecule

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(10) For a discussion of alkyne insertions into M–C bonds, see: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; Univeristy Science Books: Mill Valley, CA, 1987.

(11) On the basis of the trapping reactions reported in this work, a reviewer has suggested that *nonprotic* nucleophiles present in the reaction could also account for the formation of **5** from intermediate **4**. Such nucleophilic activation might occur via nucleophilic attack at Si, heterolytic cleavage of a Si–C bond to give a carbanion β to the Pt moiety, and 1,2-migration of the PtL_2^+ fragment followed by ring closure to afford the deaquo derivative of **5**.

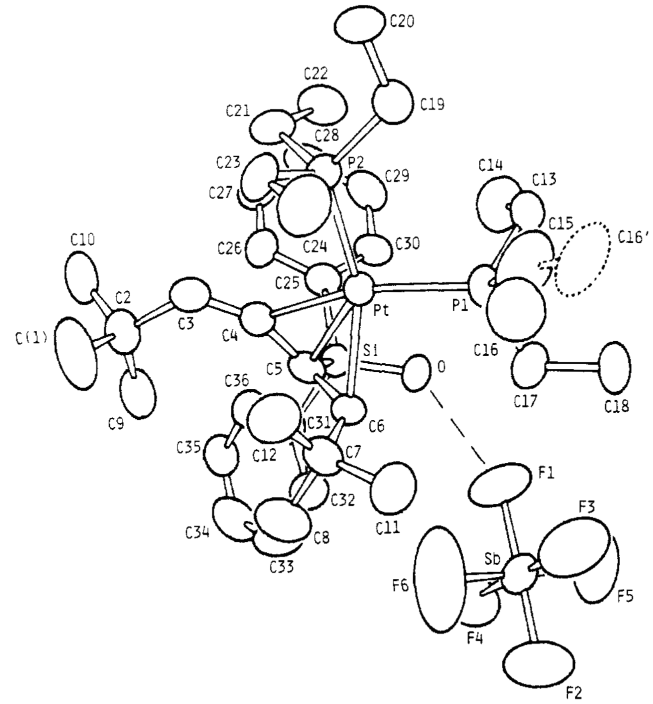

Figure 1. ORTEP diagram of the SbF_6^- salt of **7** showing the atomic numbering scheme; one methyl group is disordered over two positions, C(16) and C(16′). Hydrogen atoms have been omitted for clarity.

Table II. Selected Bond Distances (Å)[a] and Angles (deg)[a] in complex **7**

Pt–P(1)	2.323 (4)	C(4)–C(5)	1.43 (2)
Pt–P(2)	2.304 (4)	C(5)–C(6)	1.42 (2)
Pt–C(4)	2.106 (12)	C(6)–C(7)	1.53 (2)
Pt–C(5)	2.186 (13)	P(1)–Pt–P(2)	101.7 (2)
Pt–C(6)	2.272 (13)	C(2)–C(3)–C(4)	128 (1)
Si–C(5)	1.88 (2)	C(3)–C(4)–C(5)	150 (1)
Si–O	1.63 (1)	C(4)–C(5)–C(6)	117 (1)
Si–C(25)	1.83 (1)	C(5)–C(6)–C(7)	128 (1)
Si–C(31)	1.87 (1)	Si–C(5)–C(4)	123 (1)
C(2)–C(3)	1.54 (2)	Si–C(5)–C(6)	118 (1)
C(3)–C(4)	1.34 (2)	O–Si–C(31)	110.5 (6)

[a] Numbers in parentheses are estimated standards deviations in the least significant digits.

to give the η^3-butadienyl complexes **7–10** in excellent yields.[12] Of these, complex **7** contains a silanol substituent, while in **8–10**, an alkoxysilyl substituent is attached to the central carbon atom of the η^3-allyl fragment.

The structure of **7** as the SbF_6^- salt has been determined by X-ray crystallography. An ORTEP diagram of **7** showing the atomic numbering scheme is presented in Figure 1, and the values of selected bond distances and angles are reported in Table II. The (η^3-butadienyl)PtL_2 fragment has an expected geometry with Pt–C(allyl) distances of 2.106 (12), 2.186 (13), and 2.272 (13) Å, and an exo-alkylidene C(3)–C(4) double-bond distance of 1.34 (2) Å. The relative stereochemical locations of the *tert*-butyl substituents are mechanistically important. The C(2) *tert*-butyl group on the exo-alkylidene fragment retain a syn relative orientation to the silanol moiety as is observed in **5**. Also, the C(7) *tert*-butyl group on the C(6) allyl terminus occupies an anti orientation relative to the silanol moiety, as is expected in converting **6** to **7**. These results are consistent with the proposed mechanism, assuming that H^a is derived solely from the Pt-H reagent, **2**, and that H^b originates solely in the H_2O (or ROH) trapping reagent. In crystals of the SbF_6^- salt of **7**, the $Ph_2Si(OH)$ substituent on the central allyl carbon C(5) is involved in an O–H···F hydrogen bond to F(1). the O···F(1) distance of 2.77 (2) Å falls within the normal range of 2.72 ± 0.09 Å for O···F interatomic distances in systems exhibiting O–H···F hydrogen bonding.[13]

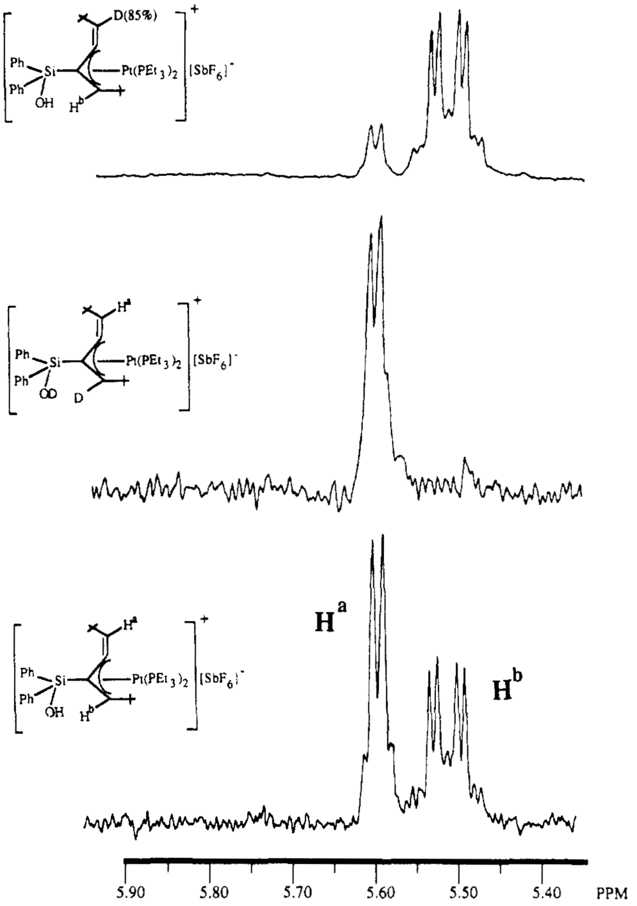

Figure 2. Alkenyl portion of the ^1H NMR spectra of **7** with selected isotopic labeling taken at 300 MHz in $CDCl_3$ solution at normal probe temperature.

To test the proposed mechanism further and to examine the structural integrity of the proposed intermediate **4**, we repeated the above reactions under conditions of selective isotopic labeling. The principal results of this study are shown in Figure 2. The bottom spectrum shows the alkenyl portion of the ^1H NMR spectrum of **7** with the resonances assigned to protons H^a and H^b. When **1** is reacted with **2** in the presence of D_2O as a trapping reagent, the product obtained gives the middle spectrum. The resonance of the exo-alkylidene proton, H^a, is present at full intensity; however, the resonance for the allyl proton H^b is absent, indicating deuteration only at this site. The singlet resonance of the silanol OH proton is also absent from the spectrum of this product. When **1** is treated with the Pt–D$^+$ reagent analogous to **2** (with ca. 85% Pt–D incorporation) in the presence of H_2O as a trapping reagent, the product obtained gives the top spectrum. In this product, the resonances for the allyl proton, H^b, and for the SiOH group are observed at full intensity, while the resonance for the exo-alkylidene proton, H^a, shows reduced intensity due to the regioselective, deuterium labeling at this site. In addition, all of these η^3-butadienyl complexes appear to be stereochemically rigid species under the experimental conditions employed. Also, although cations **5** and **7** are structural isomers, independent experiments confirm not only that **5** does not react with water,

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(12) For examples of other η^3-butadienyl complexes, see: (a) Bruce, M. I.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *Organometallics* **1988**, *7*, 343–350. (b) Bruce, M. I.; Hambly, T. W.; Snow, M. R.; Swincer, A. G. *Organometallics* **1985**, *4*, 501–508. (c) Bruce, M. I.; Hambly, T. W.; Snow, M. R.; Swincer, A. G. *Organometallics* **1985**, *4*, 494–500. (d) Nesmeyanov, A. N.; Aleksandrov, G. G.; Bokii, N. G.; Zlotina, I. B.; Struchkov, Yu. T.; Kolobova, N. E. *J. Organomet. Chem.* **1976**, *111*, C9–C12. (e) Nesmeyanov, A. N.; Kolobova, N. E.; Zlotina, I. B.; Lokshin, B. V.; Leshcheva, I. F.; Znobina, G. K.; Anisimov, K. N. *J. Organomet. Chem.* **1976**, *110*, 339–344.

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but also that it does not convert to **7**.

We believe that these results strongly indicate that a bis(alkylidene)silacyclopropane intermediate like **4** is present in this reaction sequence. (*Mono*alkylidene)silacyclopropanes have been recently prepared and characterized as stable molecules.[14] Among other interesting reactions, these compounds react quantitatively with methanol to give (allyl)methoxysilanes by cleavage of the Si–C(alkenyl) intraring bond of the (alkylidene)silacyclopropane.[14] The same mechanism is postulated above for the conversion of **4** to **6**. We have also demonstrated the utility of having a PtL_2 substituent present in silacyclic systems to stabilize internally products obtained from chemically initiated, ring-opening reactions. This latter observation might have general application to the study of the chemistry of heterocyclic compounds.

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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 the SbF_6^- salt of **7** (13 pages); table of observed and calculated structure factors for this salt (21 pages). Ordering information is given on any current masthead page.

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Interaction of Zn^{2+}, Cd^{2+}, and Hg^{2+} with 2-(α-Hydroxybenzyl)thiamin and 2-(α-Hydroxy-α-cyclohexylmethyl)thiamin. Crystal Structure of the Complex $Hg(2\text{-}(\alpha\text{-hydroxybenzyl})thiamin)Cl_3 \cdot H_2O$

Maria Louloudi,[†] Nick Hadjiliadis,[*,†] Jin-An Feng,[‡] Sunanda Sukumar,[‡] and Robert Bau[‡]

Contribution from the Department of Chemistry, University of Ioannina, Ioannina 45-110, Greece, and the Department of Chemistry, University of Southern California, Los Angeles, California 90089-0744. *Received October 23, 1989*

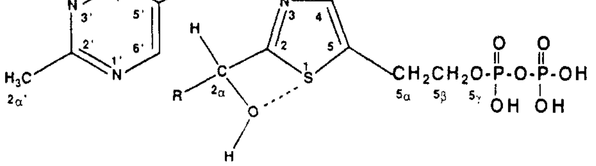
Abstract: The reactions of $ZnCl_2$, $CdCl_2$, and $HgCl_2$ with the "active aldehyde derivatives" of thiamin, 2-(α-hydroxybenzyl)thiamin (HBT) and 2-(α-hydroxycyclohexylmethyl)thiamin (HCMT) were studied in methanolic and aqueous solutions. Complexes of the formulas $M(HBT)Cl_3$ and $M(HCMT)Cl_3$, ($M = Zn^{2+}, Cd^{2+}, Hg^{2+}$) were isolated and characterized as solid adducts with elemental analyses, conductivity measurements, and IR spectra. The crystal structure of the complex $Hg(HBT)Cl_3$ was also solved. The compound is monoclinic ($P2_{1/n}$) with a = 9.588 (6) Å, b = 7.644 (3) Å, c = 31.412 (20) Å, β = 90.41 (5)°, V = 2302 (2) Å^3, and Z = 4. The HBT ligand is found in the *S* conformation, as expected for C(2)-substituted derivatives of thiamin, with $\phi_P = 172.7°$ and $\phi_T = -100.0°$. It is concluded from the IR spectra that all the isolated complexes are isostructural and in the same *S* conformation, as in the compound $Hg(HBT)Cl_3$, in the solid state. The facile formation of complexes of bivalent metals with the active aldehyde derivatives of thiamin, which contain direct metal–ligand (M–N(1′)) bonding, may indicate that the intervention of metal ions could follow the formation of these intermediates in the enzymatic action of thiamine.

Introduction

The pyrophosphate ester of thiamin (TPP) is the coenzyme for the enzymes carboxylase, pyruvic dehydrogenase, transketolase, and phosphoketolase that catalyze either the decarboxylation of α-keto acids or the formation of α-ketols.[1] For its catalytic action, a bivalent metal ion such as Mg^{2+} is required.[1,2] Other bivalent metal ions such as Co^{2+}, Zn^{2+}, Mn^{2+}, and Cd^{2+} have also been shown to catalyze the various enzymatic reactions in vitro,[1] but not as efficiently as Mg^{2+}.

It is known today that the mechanism of action of TPP involves the formation of the so-called "active aldehyde" intermediates (I) formed with subsequent ionization of a proton from the C(2) atom of the thiazole ring.[3] However, the role played by the bivalent metal ion is not yet clear.[4]

It was proposed that the metal ions are used to bind the coenzyme to the apoenzyme, either through the N(1′) atom of the pyrimidine ring,[5] or through the pyrophosphate group.[6] The N(1′) of the pyrimidine moiety was also proposed to coordinate with the metal ion indirectly through a water molecule and simulta-



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[*] Author to whom correspondence should be addressed. On leave: Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, PQ, Canada H3A 2K6.

[†] University of Ioannina.

[‡] University of Southern California.

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