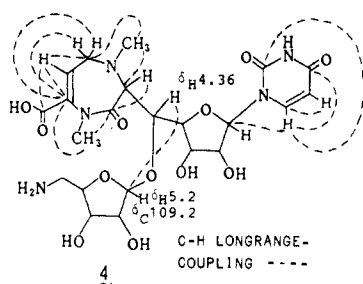


1240 cm^{-1} , 820 cm^{-1}) and by the characteristic expulsion of SO_3 (loss of 79.9517 mass units) from the MH^+ ion.¹² Negative ion MS/MS measurements¹³ on **1** demonstrated the sulfate to be bound to a C_5 unit identified as outlined below to be an amino pentose (m/z 228, amino sugar sulfate anion). The amino pentose structure is based on (i) loss of 131.0531 mass units ($\text{C}_5\text{H}_9\text{NO}_3$) from the $\text{MH}^+ - \text{SO}_3$ ion from **1**; (ii) elemental composition of the structural unit $\text{C}_5\text{H}_{11}\text{NO}_3\text{S}$ calculated as the difference between **1** and the sum of isolated hydrolysis products, having a total of three rings or double bonds and four exchangeable hydrogen atoms;⁵ (iii) ^1H NMR [$\text{CH}_2\text{-}5''$, δ 3.43 (1 H, dd, $J = 1$ Hz, $J = 15$ Hz), δ 3.24 (1 H, dd, $J = 4.4$ Hz, $J = 15$ Hz)] and ^{13}C NMR [$\text{C-}1''$, δ 110] which characterize the amino sugar as having a furanose ring;¹⁴ (iv) detailed analysis of the NMR spectra of hydrolysis product **4** (below).

Alkaline hydrolysis (0.035 M NaOH, 37 °C, 4 h) of a mixture of liposidomycins gave anhydrodeacylliposidomycins **4** (mol wt 557) and **5** (mol wt 637).⁴ Heteronuclear multiple bond cor-



relation spectroscopy (HMBC)¹⁵ of **4** shows ^1H - ^{13}C long range coupling patterns¹⁶ as indicated. The data established a seven-membered ring heterocycle as a 1,4-perhydrodiazepine and the position of the amino sugar in **4**. Phase-sensitive double-quantum-filtered COSY¹⁷ in conjunction with ^1H -detected ^1H - ^{13}C correlation (HMQC)¹⁸ from **4** permitted the complete assignments of ^1H and ^{13}C NMR signals.

Reductive cleavage (LiBH_4) of **1** gave **6** (mol wt 655),⁴ a hydrated form of **5**. The linkage of 3-acyloxy-12-methyltridecanoate was deduced by an upfield shift of $\text{H-}3'''$ (δ 4.4) in **6** compared with **1** (δ 5.4). Ester linkage of 3-methylglutaric acid to β -hydroxyl of the fatty acid was indicated by a downfield shift (1 ppm) of the fatty acid β -proton as compared with the unsubstituted hydroxy acids.¹⁸

The sulfate ester was located at $\text{C-}2''$ by comparing amino sugar assignments in ^1H and ^{13}C NMR¹⁹ of **4** with those of **1**, **5**, and

6. For example, downfield shifts of $\text{H-}2''$ (δ 4.13) and $\text{C-}2''$ (δ 74.5)²⁰ were observed in **4** compared with δ 4.63 and δ 80 in **5**, respectively.

Difference NOE spectra of **4** [e.g., 20% NOE, $\text{H-}5'$ and $\text{H-}1''$; 6.1%, N-CH_3 (δ 2.42) and $\text{H-}6'$ (δ 3.92)] supported the 1,4-perhydrodiazepine structure, amino sugar substitution at $\text{C-}5'$, and the uracil- $1'$ linkage.

The overall arrangement of structural units in **1** was supported by tandem mass spectrometry.¹³ For example, the decomposition pathway from MH^+ of **1**, $1010^+ \rightarrow 930^+ \rightarrow 799^+ \rightarrow 687^+ \rightarrow 555^+ \rightarrow 373^+ \rightarrow 245^+$ represents sequential losses of SO_3 , amino sugar, uracil, ribose, 1,4-perhydrodiazepine moiety, and 3-methylglutaric acid. This order was established by determination of product ions following sequential mass selection and collision-induced dissociation of each of the foregoing ions, thus placing constraints on the interconnectivity of the subunits.

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Oxidative Addition of Halosilanes to Zero-Valent Platinum Complexes

Hiroshi Yamashita, Teruyuki Hayashi, Toshi-aki Kobayashi, Masato Tanaka,* and Midori Goto

National Chemical Laboratory for Industry
Tsukuba, Ibaraki 305, Japan

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The oxidative addition reactions of C-X bonds in organic halides to transition-metal complexes have been widely developed and applied to various organic syntheses.¹ Ge-X or Sn-X bonds in halogermanes or halostannanes are also known to be able to oxidatively add to some transition-metal complexes.^{2,3} Unlike these reactivities of group IV element-halogen bonds, Si-X bonds in halosilanes have never been observed to undergo similar oxidative addition reactions though some attempts have been made.^{2,4,5} This is, however, peculiar, because bond dissociation energies of Si-X bonds in Me_3SiX (76 or 57 kcal/mol for X = Br or I, respectively)⁶ are comparable with that of C-Br or C-I in halobenzenes (71 or 61 kcal/mol, respectively)⁷ which are capable of the oxidative addition. In addition, silicon-transi-

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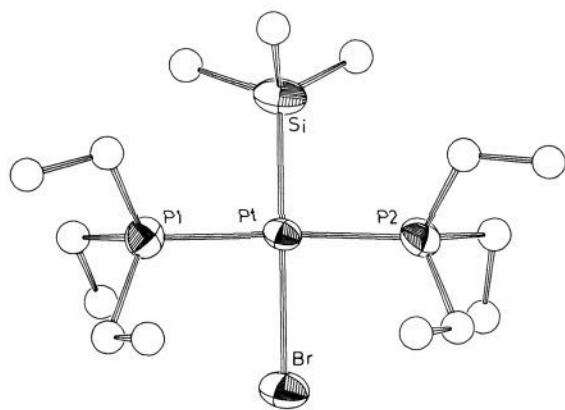
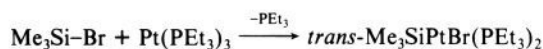


Figure 1. ORTEP drawing of the molecular structure of *trans*-Me₃SiPtBr(PET₃)₂ (**1**). Selected interatomic distances (Å): Pt–Si, 2.330 (17); Pt–Br, 2.604 (6); Pt–P1, 2.299 (15); Pt–P2, 2.296 (15).

tion-metal bonds are usually anticipated to be more stable than the carbon analogues.⁸ These considerations have prompted us to reinvestigate the reactions of halosilanes with metal complexes. We wish to report herein the first examples of the oxidative addition of Si–X bonds to zero-valent platinum complexes.

The reactions were conducted in sealed NMR tubes with benzene as a solvent⁹ and were monitored by means of ¹H NMR. PtL₄ (L = PPh₃, PMe₂Ph) and Pt(Ph₂PCH₂CH₂PPh₂)₂ did not react with Me₃SiBr even at elevated temperatures up to 120 °C. However, when Pt(PET₃)₃ was subjected to the reaction with Me₃SiBr, the color changed from orange to yellow after heating at 90 °C for 2 h. In addition, new ¹H NMR signals emerged at 0.73, 0.59, and 0.45 ppm, the relative intensity being about 1:4:1. The signals at 0.73 and 0.45 ppm are considered to be the satellite arising from ¹H–¹⁹⁵Pt coupling of the H₃C–Si–Pt moiety of the product.¹⁰ The solvent and the excess halosilane in the reaction mixture were removed, and the residue was extracted with pentane. When the pentane solution was slowly cooled to –50 °C, pale yellow needles were obtained. Single-crystal X-ray diffraction analysis revealed the structure shown in Figure 1. Thus, oxidative addition of the Si–Br bond of Me₃SiBr to Pt(PET₃)₃ really took place, and *trans*-Me₃SiPtBr(PET₃)₂ (**1**) was formed.¹²



On the basis of the thermochemical considerations of the reactions of platinum(0) complexes with organo group IV metal halides, Eaborn et al. predicted that, in the oxidative addition of organohalosilanes, the cleavage of the Si–C bond would be preferable to that of the silicon–halogen bond.¹³ However, the present result shows that Pt(PET₃)₃ selectively undergoes the insertion into the Si–Br bond and that Me₃SiBr behaves like organic halides. The yield of **1** was estimated to be about 90% from the ¹H NMR spectrum of the reaction mixture. The structure of **1** is notable in that the distance of the Pt–Br bond (2.61 Å, average value of two Pt–Br bonds) is longer than that of *trans*-PtBr₂(PET₃)₂¹⁴ or *trans*-PtHBr(PET₃)₂¹⁵ (2.428 or 2.56

Å, respectively). The result is consistent with the strong trans influence of the Me₃Si group¹⁶ as compared with the bromide or hydride ligand.

In place of Pt(PET₃)₃, Pt(PET₃)₄ also gave the same product when treated with Me₃SiBr, though the reaction rate was lower. Me₃SiI reacted more easily with Pt(PET₃)₃ than Me₃SiBr and afforded *trans*-Me₃SiPtI(PET₃)₂ (**2**).¹⁷ Me₃SiCl, however, did not react with Pt(PET₃)₃ even at 120 °C, probably because of the strong Si–Cl bond (98 kcal/mol for Me₃SiCl bond)⁹ as compared with the Si–Br bond. The treatment of Pt(PET₃)₃ with Me₃PhSiBr and the treatment of Pt(PMe₃)₄ with Me₃SiBr also showed new ¹H NMR signals which were considered to arise from the formation of disilanes was not observed in ¹H NMR, though the formation of Me₃SiSiMe₃ was reported in the reaction of Pd(PPh₃)₄ with Me₃SiX (X = Cl or Br).¹⁸

In conclusion, this paper has established the first example of the oxidative addition of Si–X bond. Further investigations using other metal complexes and halosilanes as well as mechanistic studies are now under way.

Registry No. **1**, 114595-43-6; **2**, 114595-44-7; Me₃SiBr, 2857-97-8; Pt(PET₃)₃, 39045-37-9; Pt(PET₃)₄, 33937-27-8; Me₃SiI, 16029-98-4; Me₃PhSiBr, 13247-99-9; Me₃SiCl, 75-77-4.

Supplementary Material Available: Crystal data for **1**, microanalytical data for **1** and **2** and tables of atomic coordinates, thermal parameters, and bond lengths and angles for **1** (6 pages); listing of structure factor amplitudes for **1** (9 pages). Ordering information is given on any current masthead page.

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The Remarkably Low Second pK_a of 1-Naphthylacetic Acid. Lithium Ion Pair Acidity in Tetrahydrofuran¹

Scott Gronert and Andrew Streitwieser*

Department of Chemistry, University of California
Berkeley, California 94120
Received February 29, 1988

Dianions derived from carboxylic acids (carboxylates deprotonated at the α carbon) have proven to be synthetically useful enolate equivalents in a number of carbon–carbon bond-forming reaction sequences.^{2–14} They are readily prepared by the met-

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(9) Typical reaction condition: platinum complex 0.15 mmol, halosilane 0.45–0.60 mmol, benzene 0.3 mL, 90–120 °C.

(10) The coupling constant of ¹H–¹⁹⁵Pt is 25.2 Hz which is similar to the value reported for *trans*-Me₃SiPtCl(PET₃)₂ (24.6 Hz).¹¹

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