

Quaternization of the Bridgehead Nitrogen in Silatranosmium(II) Complexes and Reestablishment of the Transannular N–Si Bond following Migratory Insertion of the Silatranyl Ligand

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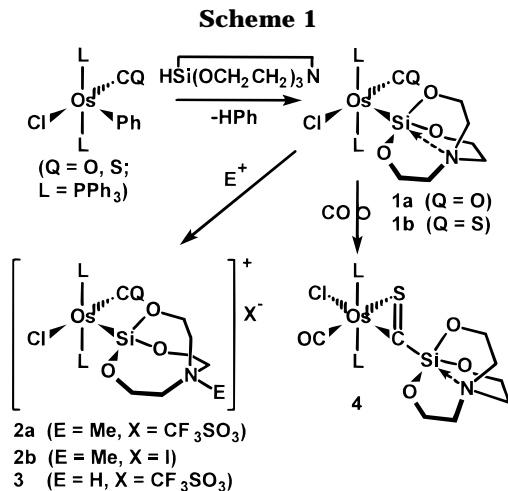
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Received December 16, 1997

Summary: The Si–N distance in the five-coordinate silatranyl complex $\text{Os}(\text{Si}\{\text{OCH}_2\text{CH}_2\}_3\text{N})\text{Cl}(\text{CQ})(\text{PPh}_3)_2$ (**1a**, Q = O) is very long, and the geometry about nitrogen is planar. Accordingly, the nitrogen atom readily undergoes methylation or protonation, and this increases the Si–N separation even further. On addition of CO to **1b** (Q = S), the coordinated CS inserts into the Os–Si bond and the normal silatrane N–Si interaction is restored in the product, $\text{Os}(\eta^2\text{-C}\{\text{S}\}\text{Si}\{\text{OCH}_2\text{CH}_2\}_3\text{N})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (**4**).

Silatranes, cyclic organosilicon ethers of tris(2-oxy-alkylamine), are among the most interesting examples of hypervalent silicon compounds and they have been intensively studied since their discovery in 1961.¹ They are part of a larger family of compounds which have been called "atranes".² The silatranes have aroused interest because of questions relating to the nature of the N–Si bond, variation in the transannular N–Si distance and the dependence of this on the axial silicon substituent, biological activity, and their architectural beauty.³ The nature of the N–Si bond in silatranes has been the subject of several recent theoretical papers, and the results suggest that it is best described in terms of a dative N→Si bond with some small contribution from a three-center, four-electron interaction.^{4–6} Furthermore, the calculated potential curve for deformation of the N–Si distance is very shallow.⁶

In this paper, we report the synthesis of a silatrane that bears an osmium substituent at silicon. The N–Si distance is exceptionally long in this compound, and this allows, for the first time, the isolation of derivatives resulting from the addition of electrophiles to the silatrane nitrogen atom. The transannular N–Si bond within the silatranyl ligand is reestablished when this



group undergoes a migratory insertion reaction, which has the effect of replacing the osmium substituent on silicon by carbon.

We have reported previously that a convenient route to coordinatively unsaturated silyl compounds of ruthenium and osmium involves treatment of the five-coordinate phenyl derivatives $\text{M}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (M = Ru, Os) with silanes.^{7,8} We now report that heating

$\text{Os}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ with silatrane ($\text{HSi}\{\text{OCH}_2\text{CH}_2\}_3\text{N}$) in toluene results in the formation of the yellow, air-stable, five-coordinate silatranyl complex $\text{Os}(\text{Si}\{\text{OCH}_2\text{CH}_2\}_3\text{N})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (**1a**)⁹ in good yield (see Scheme 1). The single-crystal X-ray structure of this product has been determined, and the molecular structure is depicted in Figure 1.¹⁰ The five ligands are arranged about the osmium center in a distorted square-pyramidal geometry with the silatranyl group in the apical position. The Os–Si distance and the Os–Si–O angles are very similar to the corresponding parameters found for the closely related trihydroxysilyl complex $\text{Os}(\text{Si}\{\text{OH}\}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$.⁷ The most striking feature of the structure of **1a** is the long N–Si distance of 3.000(7) Å, which is the longest distance recorded for a silatrane.¹¹ The separation between the silicon and nitrogen atoms

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in the solid-state structures of silatranes generally falls in the range 2.00–2.26 Å with the less electronegative axial substituents on silicon favoring longer transannular N–Si distances.¹² In some cases, these weak, easily deformed bonds have been shown to increase in length somewhat in the gas phase.¹³ The longest N–Si silatrane distance that has been described in the literature is that found in the platinum silatranyl complex *trans*-Pt(Si{OCH₂CH₂}₃N)Cl(CO)(PMe₂Ph)₂ (2.89(1) Å).¹⁴ This appears to be the only metal-substituted silatrane that has been reported.

One consequence of the very long N–Si distance within the silatrane cage of **1a** is that the bonds about nitrogen are almost perfectly trigonal planar. The sum of the angles at N is 360.0°, and the nitrogen atom sits within 0.015(8) Å of the plane defined by C(2), C(4), and C(6). The trigonal-planar geometry about nitrogen and the very long N–Si distance suggest that the nitrogen could be available for reaction with electrophiles. In-

(9) The experimental details and spectroscopic data for the representative compounds **1a**, **2a**, and **4** follows, and the information for compounds **1b** and **3** is provided as Supporting Information. Os(Si{OCH₂CH₂}₃N)Cl(CO)(PPh₃)₂ (**1a**): Freshly degassed toluene (20 mL) was added via a syringe to a Schlenk tube containing Os(Ph)Cl(CO)-

(PPh₃)₂ (200 mg, 0.234 mmol) and HSi(OCH₂CH₂)₃N (82 mg, 0.468 mmol). The purple solution was refluxed for 3 h, during which time a yellow color developed. The Schlenk tube was allowed to cool, and the solvent volume was reduced in vacuo. Ethanol (30 mL) was added to precipitate a bright yellow product. The product was filtered, washed with hexane (20 mL), and recrystallized from dichloromethane:ethanol to yield bright yellow needles of pure **1a** (209 mg, 94%): mp 214–217 °C; *m/z* 917 (M⁺); IR 1913 ν(CO) 1365, 1263, 1109, 998, 911, 878, 862, 702, 662, 608 cm⁻¹; ¹H NMR (400.1 MHz, CDCl₃, TMS = 0.00) 2.63 (t, 6H, CH₂N, ³J_{HH} = 5.1 Hz) 3.30 (t, 6H, OCH₂, ³J_{HH} = 5.1 Hz) 7.34–7.66 (m, 30H, PPh₃); ¹³C NMR (100.6 MHz, CDCl₃, TMS = 0.00) 52.89 (CH₂N), 61.75 (OCH₂), 127.86 (t, PPh₃ *ortho*-C, ^{2,4}J_{CP} = 10.1 Hz), 129.71 (s, PPh₃ *para*-C), 134.82 (t, PPh₃ *meta*-C, ^{2,4}J_{CP} = 10.1 Hz), *ipso*-C of PPh₃ not observed; ²⁹Si NMR (79.5 MHz, CDCl₃) –65.00 (t, OsSi, ²J_{CP} = 16.3 Hz); ³¹P NMR (162.0 MHz, CDCl₃) 25.83 (s, PPh₃). Anal. Calcd for C₄₃H₄₂ClNO₄OsP₂Si: C, 54.22; H, 4.44; N, 1.47. Found: C, 54.99; H, 4.77; N, 1.42. [Os(Si{OCH₂CH₂}₃NMe)Cl(CO)-(PPh₃)₂]CF₃SO₃ (**2a**): Os(Si{OCH₂CH₂}₃N)Cl(CO)(PPh₃)₂ (200 mg, 0.210 mmol) was added to a Schlenk tube containing dry dichloromethane (25 mL). Methyl triflate (48 μL, 0.42 mmol) was added to the solution, whereupon the color changed from bright yellow to a slightly lighter yellow. Ethanol (10 mL) was added slowly, and the yellow product which formed was collected and recrystallized from dichloromethane:ethanol (25:5 mL) to give pure **2a** (179 mg, 76%): mp 209–212 °C; *m/z* 968.1853, C₄₅H₄₅ClNO₄OsP₂Si requires 968.1897; IR 1924 ν(CO), 1279, 1259, 1225, 1157, 1063, 982, 934, 911, 849, 832, 799, 708, 639 cm⁻¹; ¹H NMR (400.1 MHz, CDCl₃, TMS = 0.00) 3.30 (s, 3H, CH₃) 3.45 (bs, 6H, CH₂N), 3.75 (bs, 6H, OCH₂), 7.39–7.58 (m, 30H, PPh₃); ¹³C NMR (100.6 MHz, CDCl₃, TMS = 0.00) 58.12 (s, CH₂N), 63.95 (s, CH₃), 66.66 (s, OCH₂), 128.22 (t, PPh₃ *ortho*-C, ^{2,4}J_{CP} = 10.1 Hz), 130.33 (s, PPh₃ *para*-C), 134.35 (t, PPh₃ *meta*-C, ^{3,5}J_{CP} = 11.1 Hz), 131.41 (t, PPh₃ *ipso*-C, ^{1,3}J_{CP} = 52.6 Hz); ²⁹Si NMR (79.5 MHz, CDCl₃) –49.44 (t, OsSi, ²J_{CP} = 12.3 Hz); ³¹P NMR (162.0 MHz, CDCl₃) 33.61 (s, PPh₃). Anal. Calcd for C₄₅H₄₅ClF₃NO₇OsP₂SSi: C, 47.15; H,

4.00; N, 1.21. Found: C, 47.12; H, 3.91; N, 1.24. Os(η²-C(Si)Si{OCH₂CH₂}₃N)Cl(CO)(PPh₃)₂ (**4**): Os(Si{OCH₂CH₂}₃N)Cl(CS)(PPh₃)₂ (200 mg, 0.207 mmol) was dissolved in CHCl₃ (25 mL), and the resulting solution placed in a Fischer–Porter bottle. The bottle was then pressurized with CO (4 atm) for 5 min, whereupon the tan-yellow solution became colorless. At this point, the CO pressure was decreased to 1 atm and the solution was heated to 40 °C for 20 min. The resulting orange solution was then reduced in volume on a rotary evaporator, and ethanol was added. The orange crystals that formed were collected and recrystallized from dichloromethane:ethanol to yield pure **4** (130 mg, 63%): mp 253–254 °C; *m/z* 997.1406, C₄₄H₄₂ClNO₄OsP₂SSi requires 997.1383; IR 1877 ν(CO), 1588, 1402, 1384, 1267, 1119, 1019, 938, 912, 794, 747, 724, 638, 592 cm⁻¹; ¹H NMR (400.1 MHz, CD₂Cl₂, TMS = 0.00) 2.71 (t, 6H, CH₂N, ³J_{HH} = 5.8 Hz) 3.49 (t, 6H, OCH₂, ³J_{HH} = 5.9 Hz) 7.18–7.68 (m, 30H, PPh₃); ¹³C NMR (100.6 MHz, CD₂Cl₂, TMS = 0.00) 50.37 (s, CH₂N), 56.63 (s, OCH₂), 127.27 (t, PPh₃ *ortho*-C, ^{2,4}J_{CP} = 10.1 Hz), 129.54 (s, PPh₃ *para*-C), 132.14 (t, PPh₃ *ipso*-C, ^{1,3}J_{CP} = 51.3 Hz), 134.77 (t, PPh₃ *meta*-C, ^{3,5}J_{CP} = 10.1 Hz); ²⁹Si NMR (79.5 MHz, CD₂Cl₂) –87.41 (s, CSi); ³¹P NMR (162.0 MHz, CD₂Cl₂) 4.25 (s, PPh₃). Anal. Calcd for C₅₀H₄₂N₃OsO₂P₃: C, 53.03; H, 4.25; N, 1.41. Found: C, 53.18; H, 4.28; N, 1.21.

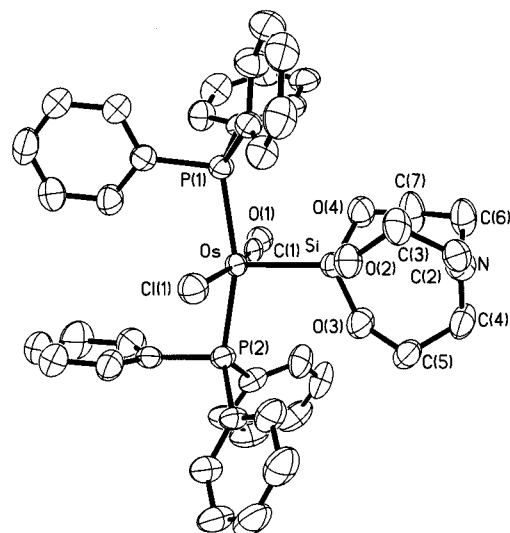


Figure 1. ORTEP drawing of **1a** with 50% thermal ellipsoids. Selected bond lengths (Å): Os–Si, 2.326(2); N–Si, 3.000(7).

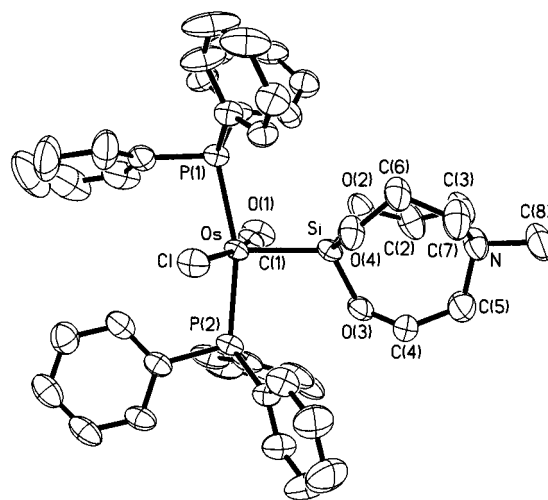


Figure 2. ORTEP drawing of **2a** with 50% thermal ellipsoids. Selected bond lengths (Å): Os–Si, 2.297(2); N–Si, 3.564(7).

deed, this was found to be the case, and on treatment of **1a** with either methyl triflate or methyl iodide, the nitrogen atom is smoothly quaternized and the corresponding cationic, *N*-methyl complexes [Os(Si{OCH₂CH₂}₃NMe)Cl(CO)(PPh₃)₂]X (**2a**, X = CF₃SO₃; **2b**, X = I),⁹ are formed (see Scheme 1). In the ¹H NMR spectrum of **2a**, the methyl group is assigned to the singlet signal at 3.30 ppm. The resonance of the silicon atom in the ²⁹Si NMR spectrum of **2a** appears at –49.44 ppm, 15.56 ppm further downfield than that in the parent compound, **1a**.

An X-ray crystal structure determination of **2a** has been completed, and the molecular structure is depicted in Figure 2.¹⁵ The triflate anion is not coordinated to the metal center, and the arrangement of the five ligands about the osmium center is similar to that found for **1a**. As would be expected, the quaternization of the silatrane nitrogen causes a large change in the silatrane cage geometry. The N–Si distance is increased to 3.564(7) Å (cf. 3.000(7) Å in **1a**), and the angles subtended at the quaternary nitrogen atom by the carbon atoms of the silatrane cage are decreased (average values 113.9° vs 120.0° for **1a**). In addition, the O–Si–O

angles are contracted, on average, by 4.6° compared with the corresponding angles in **1a**.

The Os–Si distance of 2.297(2) Å in **2a** is significantly shorter than that found in the neutral precursor compound (2.326(2) Å). Among the factors that may be responsible for the decrease in this bond length are the loss of any residual N–Si bonding interaction upon quaternization of the nitrogen atom, an increase in *s*-character of the Os–Si bond brought about by the decreased O–Si–O angles in **2a**, and electrostatic effects.

Electrophilic attack at the silatranyl nitrogen atom of **1a** is not restricted to methylation. On treatment of **1a** with triflic acid, protonation occurs at nitrogen and the cationic compound [Os(Si{OCH₂CH₂})₃NH]Cl(CO)(PPh₃)₂CF₃SO₃ (**3**)⁹ is formed. The N–H signal appears in the ¹H NMR spectrum at 10.41 ppm and rapidly exchanges on addition of D₂O. Compelling evidence that protonation has occurred at the silatranyl nitrogen rather than at one of the equatorial oxygens comes from the ²⁹Si NMR spectrum of **3**. The chemical shift of the silicon atom in **3** (–51.75 ppm) is almost the same as that in the cationic compound **2a** (–49.44 ppm), where the silatranyl ligand is methylated at nitrogen, but very different from the higher-field value recorded for **1a** (–65.00 ppm), where the silicon atom is pseudopentacoordinate through weak interaction with the nitrogen atom.¹⁶

Alkylation or protonation of a silatrane nitrogen atom has not been reported before. Normally, the preferred sites for electrophilic attack are the equatorial oxygen atoms¹⁷ or the axial oxygen in alkoxy-substituted silatrane.¹⁸ There has been a single report of the alkylation of the axial nitrogen in a substituted *azasilatrane*.¹⁶

The five-coordinate thiocarbonyl, silatranyl compound Os(Si{OCH₂CH₂})₃NCl(CS)(PPh₃)₂ (**1b**)⁹ can be prepared by a similar route to that which gives **1a**. On treatment of **1b** with CO, the silatranyl and thiocarbonyl ligands undergo a migratory insertion reaction and the η²-silathioacyl-containing compound Os(η²-C{S}Si-

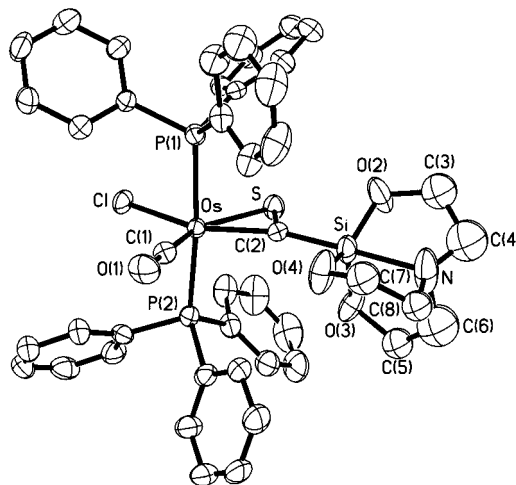


Figure 3. ORTEP drawing of **4** with 50% thermal ellipsoids. Selected bond lengths (Å): N–Si, 2.086(6); Os–C(2), 1.987(5); Os–S, 2.484(1); S–C(2), 1.664(5).

{OCH₂CH₂})₃N]Cl(CO)(PPh₃)₂ (**4**)⁹ is formed (see Scheme 1). The X-ray structure of **4** has been determined, and the molecular structure is depicted in Figure 3.¹⁹ The most notable feature is that the N–Si distance has decreased in this molecule to 2.086(6) Å, a value that is at the short end of reported silatrane N–Si distances.^{11,20} The remaining structural parameters are similar to those found in the related ruthenium compound Ru(η²-C{S}SiMe₂OEt)Cl(CO)(PPh₃)₂.²¹ The observation that a short N–Si distance is reestablished when the silatranyl group undergoes a migratory insertion reaction in which the direct bond to the metal is broken reinforces the notion that it is the special nature of the bond to the electron-releasing osmium center⁸ that is responsible for the very long N–Si distance in **1a**.

Acknowledgment. We are grateful for support from the Marsden Fund for this work and to The University of Auckland for grants-in-aid and the award of a postgraduate scholarship to S.D.W.

Supporting Information Available: Text giving experimental procedures and characterization data for all new compounds as well as tables of data collection parameters, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates (25 pages). Ordering information is given on any current masthead page.

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(10) Crystal data for **1a** at 203 K with Mo Kα radiation (Siemens SMART CCD diffractometer): C₄₃H₄₂ClNO₄OsP₂Si, fw = 952.46, *a* = 9.6775(1) Å, *b* = 12.1180(1) Å, *c* = 18.1361(1) Å, α = 94.532(1)°, β = 100.817(1)°, γ = 105.204°, triclinic, *P*1, *Z* = 2, *V* = 1997.41(3) Å³, *D*_c = 1.584 g cm⁻³, *R* = 0.0389 for 6545 observed (*I* > 2σ(*I*)) reflections; weighted *R*² = 0.0960.

(11) A search of the Cambridge Structural Database gave the following results for the N–Si distances in 72 silatrane structures: Mean, 2.138; SD, 0.064 Å.

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(15) Crystal data for **2a** at 203 K with Mo Kα radiation (Siemens SMART CCD diffractometer): C₄₅H₄₅ClF₃NO₇OsP₂SSi, fw = 1116.56, *a* = 10.4535(2) Å, *b* = 17.5941(2) Å, *c* = 25.3620(1) Å, β = 96.250(2)°, monoclinic, *P*2₁/*c*, *Z* = 4, *V* = 4636.84 Å³, *D*_c = 1.599 g cm⁻³, *R* = 0.0525 for 7338 observed (*I* > 2σ(*I*)) reflections; weighted *R*² = 0.1265.

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(19) Crystal data for **4** at 203 K with Mo Kα radiation (Siemens SMART CCD diffractometer): C₄₄H₄₂ClNO₄OsP₂SSi, *a* = 12.4896(4) Å, *b* = 14.3772(4) Å, *c* = 23.8280(7) Å, β = 103.867(1)°, monoclinic, *P*2₁/*n*, *Z* = 4, *V* = 4154.0(2) Å³, *D*_c = 1.593 g cm⁻³, *R* = 0.0392 for 7418 observed (*I* > 2σ(*I*)) reflections; weighted *R*² = 0.0795.

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