Tri(η-cyclopentadienyl)uranium(IV) Silyl and Siloxide Compounds. Crystal Structure of $[U(\eta^5\text{-}C_5H_5)_3(OSiPh_3)]$. Insertion of Isocyanide into a Uranium–Silicon Bond†

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The complex $[U(\eta^5\text{-}C_5H_5)_3(SiPh_3)]$ (**1**) has been synthesized from $[U(\eta^5\text{-}C_5H_5)_3Cl]$ and $Li(SiPh_3)$ and fully characterized. The direct U–Si bond in (**1**) is quite reactive towards proton acidic molecules, moreover it reacts with 2,6-dimethylphenyl isocyanide to give the insertion product $[U(\eta^5\text{-}C_5H_5)_3\{C(NC_6H_3Me_2\text{-}2,6)SiPh_3\}]$ (**3**), the ^1H n.m.r. and i.r. data for which show that the isocyanide ligand is η^2-co-ordinated to the uranium atom. The synthesis of $[U(\eta^5\text{-}C_5H_5)_3(OSiPh_3)]$ (**2**) by reaction of $[U(\eta^5\text{-}C_5H_5)_3(NEt_2)]$ with $SiPh_3(OH)$ and its *X*-ray structural determination are also reported. Compound (**2**) crystallizes from diethyl ether in the monoclinic space group $P2_1/n$ with a = 15.368(5), b = 17.333(5), c = 10.778(5) Å, and β = 106.27(3)° for Z = 4. The main features are the almost linear U–O–Si bond angle of 172.6(6)° and the short U–O distance of 2.135(8) Å.

A large number of compounds containing metal–silicon bonds have been known from many years both for *d*-transition metals and non-transition metals;[1] in this respect, silicon reflects the properties of the first representative of the Group 14 elements, *i.e.* carbon. Interest is still thriving and expanding in this chemistry although it is less varied than metal–carbon chemistry as far as reactivity patterns and bonding modes are concerned. However compounds containing a direct actinide–silicon bond are completely unknown so far. Thus it appeared worthwhile to carry out an investigation aimed at verifying the probability of the existence of a U–Si bond as part of our research program concerning the synthesis and characterization of compounds containing direct U–E bonds (E = Group 14, 15, or 16 element). We have recently described the compounds $[U(\eta^5\text{-}C_5H_5)_3(GePh_3)]$,[2] $[U(\eta^5\text{-}C_5H_5)_3(SnPh_3)]$,[3] and $[U(\eta^5\text{-}C_5H_5)_3(PPh_2)]$.[4] Here we report on the synthetic approach to $[U(\eta^5\text{-}C_5H_5)_3(SiPh_3)]$ and $[U(\eta^5\text{-}C_5H_5)_3(OSiPh_3)]$ as well as on the 2,6-dimethylphenyl isocyanide insertion into the U–Si bond leading to the formation of tris(η-cyclopentadienyl)[η^2-(2,6-dimethylphenylimino)(triphenylsilyl)methyl]uranium(IV).

Experimental

All manipulations concerning the organouranium compounds were conducted in dry-boxes under an inert atmosphere of nitrogen. The operations (purification of starting materials and of solvents, spectra recording, *etc.*) were carried out as reported previously.[5] Commercially available tetraphenylsilane, triphenylsilane, and hydroxytriphenylsilane were used as supplied.

Synthesis of $[U(\eta^5\text{-}C_5H_5)_3(SiPh_3)]$ (**1**).—The compound $[U(\eta^5\text{-}C_5H_5)_3Cl]$ (468 mg, 1 mmol) dissolved in tetrahydrofuran (thf) was stirred with $Li(SiPh_3)$ (1 mmol) at low temperature (–30 °C) for 30 min and the initial brown solution immediately became green. The solvent was removed under vacuum, keeping the solution at –30 °C; the residue was dissolved in toluene and the LiCl separated by filtration; the toluene was removed and the residue washed several times with n-hexane. The mode of preparation of $Li(SiPh_3)$ is crucial for the successful synthesis of (**1**). Compound (**1**) was obtained in good yields only when $Li(SiPh_3)$ was freshly prepared by reaction of metallic Li with $SiPh_4$. In particular, Li, cut into small pieces, was added in excess to $SiPh_4$ (2 mmol, 672 mg) in thf. After stirring overnight at room temperature, the solution was filtered from unreacted Li, thf removed under vacuum, and the residue washed with n-hexane to remove LiPh, dried, and used immediately (Found: C, 57.0; H, 4.35; U, 34.0. Calc. for $C_{33}H_{30}SiU$: C, 57.2; H, 4.35; U, 34.35%). I.r.: $\nu_{max.}$ at 1 110m, 1 080m, 1 010s, 780vs, 740m, 720m, 700vs, and 500m cm^{-1}. ^1H N.m.r. (C_6D_6, 27 °C): δ –9.65 (6 H, d, *o*-H of phenyl), –3.69 (15 H, s, C_5H_5), 3.86 (3 H, t, *p*-H of phenyl), and 4.35 (6 H, t, m-H of phenyl). Near-i.r.–visible (toluene): $\lambda_{max.}$ at 1 320, 1 120, 1 050, 1 020, 1 000, 710 (sh), and 650 nm. Mass spectrum: m/z = 626 $[U(\eta^5\text{-}C_5H_5)_2(SiPh_3)]^+$, 433 $[U(\eta^5\text{-}C_5H_5)_3]^+$, 368 $[U(\eta^5\text{-}C_5H_5)_2]^+$, 259 $[SiPh_3]^+$, and 182 $[SiPh_2)]^+$; parent ion not detected. Attempts to prepare (**1**) by protolysis reactions between $[U(\eta^5\text{-}C_5H_5)_3(NEt_2)]$ and $SiPh_3H$ failed.

Synthesis of $[U(\eta^5\text{-}C_5H_5)_3(OSiPh_3)]$ (**2**).—The compound $SiPh_3(OH)$ (1 mmol, 353 mg) was added to $[U(\eta^5\text{-}C_5H_5)_3(NEt_2)]$ (1 mmol, 505 mg) in thf at room temperature. After stirring for 5 h the solution became yellow-green, thf was removed under vacuum, and the yellow powder obtained washed with n-hexane and analysed (yield >90%) (Found: C, 55.9; H, 4.25; Si, 4.00; U, 33.5. Calc. for $C_{33}H_{30}OSiU$: C, 55.9; H, 4.30; Si, 3.95; U, 33.6%). I.r.: $\nu_{max.}$ at 1 595w, 1 435s, 1 120vs, 935s, 785s, 710vs, and 520vs cm^{-1}. ^1H N.m.r. (C_6D_6, 27 °C); δ –9.42 (15 H, s, C_5H_5), 3.82 (6 H, d, *o*-H of phenyl), and 6.68 (9 H, *m*- and *p*-H of phenyl). Near-i.r.–visible (toluene): $\lambda_{max.}$ at 1 350, 1 280, 1 190s, 1 160 (sh), 1 050, 1 010, 980, 900, 800, 755, 700, and 605 nm. Mass spectrum: m/z = 708 (M^+); other characteristic ions at 643 $[U(\eta^5\text{-}C_5H_5)_2(OSiPh_3)]^+$, 578 $[U(\eta^5\text{-}$

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Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Atomic co-ordinates of complex (**2**)

Atom	X/a	Y/b	Z/c
U	0.067 82(4)	0.787 56(3)	−0.104 57(5)
Si	0.042 1(3)	0.794 7(2)	0.230 4(3)
O(1)	0.045 4(7)	0.793 2(7)	0.082 0(8)
C(2)	−0.063 4(6)	0.890 9(6)	0.347 3(8)
C(3)	−0.140 0(6)	0.933 1(6)	0.350 5(8)
C(4)	−0.216 6(6)	0.932 6(6)	0.244 0(8)
C(5)	−0.216 6(6)	0.889 9(6)	0.134 4(8)
C(6)	−0.140 0(6)	0.847 6(6)	0.131 2(8)
C(1)	−0.063 4(6)	0.848 1(6)	0.237 6(8)
C(8)	0.159 5(7)	0.923 3(5)	0.311 2(9)
C(9)	0.232 8(7)	0.963 8(5)	0.389 9(9)
C(10)	0.289 7(7)	0.928 3(5)	0.498 9(9)
C(11)	0.273 4(7)	0.852 4(5)	0.529 1(9)
C(12)	0.200 1(7)	0.812 0(5)	0.450 3(9)
C(7)	0.143 1(7)	0.847 4(5)	0.341 4(9)
C(14)	0.103 8(7)	0.639 3(7)	0.267 5(11)
C(15)	0.098 7(7)	0.561 7(7)	0.298 8(11)
C(16)	0.029 8(7)	0.536 3(7)	0.350 0(11)
C(17)	−0.034 0(7)	0.588 6(7)	0.369 8(11)
C(18)	−0.028 9(7)	0.666 3(7)	0.338 4(11)
C(13)	0.040 0(7)	0.691 6(7)	0.287 3(11)
C(100)	−0.030 5(7)	0.896 2(6)	−0.215 6(10)
C(200)	0.014 1(7)	0.654 7(6)	−0.180 1(10)
C(300)	0.233 8(7)	0.810 5(6)	−0.053 6(10)
C(19)	0.028 7(7)	0.941 6(6)	−0.166 4(10)
C(20)	−0.041 3(7)	0.916 4(6)	−0.113 7(10)
C(21)	−0.096 4(7)	0.863 2(6)	−0.201 8(10)
C(22)	−0.060 3(7)	0.855 6(6)	−0.309 0(10)
C(23)	0.016 9(7)	0.904 1(6)	−0.287 1(10)
C(24)	0.006 8(11)	0.639 3(7)	−0.074 2(10)
C(25)	−0.062 1(11)	0.670 7(7)	−0.178 5(10)
C(26)	−0.025 7(11)	0.680 0(7)	−0.285 1(10)
C(27)	0.065 6(11)	0.654 3(7)	−0.246 6(10)
C(28)	0.085 7(11)	0.629 1(7)	−0.116 2(10)
C(29)	0.235 4(9)	0.775 0(10)	−0.149 3(16)
C(30)	0.246 5(9)	0.743 3(10)	−0.024 3(16)
C(31)	0.240 0(9)	0.804 5(10)	0.060 1(16)
C(32)	0.225 0(9)	0.874 0(10)	−0.012 5(16)
C(33)	0.222 2(9)	0.855 7(10)	−0.142 0(16)

$C_5H_5)(OSiPh_3)]^+$, 566 $[U(\eta^5\text{-}C_5H_5)_2(OSiPh_2)]^+$, 512 $[U(OSiPh_3)]^+$, and 319 $[U(\eta^5\text{-}C_5H_5)O]^+$.

Synthesis of $[U(\eta^5\text{-}C_5H_5)_3\{C(NC_6H_3Me_2\text{-}2,6)SiPh_3\}]$ (**3**).—The compounds (**1**) (1 mmol, 692 mg) and $CNC_6H_3Me_2$-2,6 (1 mmol, 131 mg) were stirred in toluene at room temperature. After 3 h the brown reaction mixture was evaporated to dryness giving quantitatively a brown-beige powder (Found: C, 61.2; H, 4.85; N, 1.75; Si, 3.5; U, 28.85. Calc. for $C_{42}H_{39}NSiU$: C, 61.2; H, 4.7; N, 1.7; Si, 3.4; U, 28.9%). I.r.: $\nu_{max.}$ at 1 530m, 1 160m, 1 110s, 1 010s, 770vs, 740m, 700vs, 640m, 600m, 510s, and 490m cm^{-1}. ^1H N.m.r. (C_6D_6, 27 °C): δ −29.1 (6 H, s, CH_3), −11.8 (15 H, br s, C_5H_5), 0.7 (1 H, t, *p*-H of xylyl), 1.6 (2 H, d, *m*-H of xylyl), 10.0 (3 H, t, *p*-H of phenyl), 11.9 (6 H, t, *m*-H of phenyl), and 25.8 (6 H, d, *o*-H of phenyl). Near-i.r.–visible (toluene): $\lambda_{max.}$ at 1 350, 1 160, 1 120, and 910 nm. Mass spectrum: parent ion was not detected; most intense peaks m/z = 259 $[SiPh_3]^+$ and 433 $[U(\eta^5\text{-}C_5H_5)_3]^+$; other intense peaks 626 $[U(\eta^5\text{-}C_5H_5)_2(SiPh_3)]^+$, 368 $[U(\eta^5\text{-}C_5H_5)_2]^+$, 303 $[U(\eta^5\text{-}C_5H_5)]^+$, 182 $[SiPh_2]^+$, and 105 $[C_6H_3Me_2\text{-}2,6]^+$.

Crystal-structure Determination of $[U(\eta^5\text{-}C_5H_5)_3(OSiPh_3)]$.—Yellow crystals suitable for *X*-ray structural determination were obtained by slowly evaporating an Et_2O solution of compound (**2**). They were mounted and sealed in a dry-box filled with purified nitrogen.

Table 2. Bond distances (Å) and angles (°) for $[U(\eta^5\text{-}C_5H_5)_3(OSiPh_3)]$*

U–O	2.135(8)	Si–O	1.62(1)
U · · · Cp(1)	2.50(1)	Si–C(1)	1.89(1)
U · · · Cp(2)	2.50(1)	Si–C(7)	1.91(1)
U · · · Cp(3)	2.49(1)	Si–C(13)	1.89(1)
Cp(1) · · · U–O	100.4(4)	U–O–Si	172.6(6)
Cp(2) · · · U–O	102.9(4)	O–Si–C(1)	108.4(5)
Cp(3) · · · U–O	102.2(4)	O–Si–C(7)	112.5(6)
Cp(1) · · · U · · · Cp(2)	115.9(4)	O–Si–C(13)	107.3(5)
Cp(2) · · · U · · · Cp(3)	116.3(4)	C(1)–Si–C(13)	110.9(5)
		C(7)–Si–C(13)	109.5(5)

* In this table Cp(1), Cp(2), and Cp(3) represent the centroids of the cyclopentadienyl rings.

A crystal of maximum dimensions 0.2 mm was selected. Data collection was made on a Philips diffractometer with monochromatized Mo-K_α radiation. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings.

Crystal data. $C_{33}H_{30}OSiU$, M = 799, monoclinic, space group $P2_1/n$, a = 15.368(5), b = 17.333(5), c = 10.778(5) Å, β = 106.27(3)°, U = 2 756 Å^3, Z = 4, D_c = 1.92 g cm^{-3}, λ(Mo-K_α) = 0.7107 Å, μ(Mo-K_α) = 82.7 cm^{-1}.

Intensities were measured by the θ–2θ method, with a scan speed of 2° min^{-1} between 2 and 25° (θ) and with a range of $\pm 0.65°$ for each reflection, yielding 4 854 reflections, 3 359 of which were significantly above background $[I > 3\sigma(I)]$. The data were corrected for Lorentz polarization factors and for absorption.[6] Two standard reflections measured periodically had constant intensities within counting statistics. Solution of the structure was achieved with standard Patterson and Fourier methods alternated with cycles of least-squares refinement of the atomic parameters.

Ring carbon atoms were treated as rigid bodies with fixed C–C and C–H bond distances (C–C 1.395 Å for phenyl and 1.420 Å for cyclopentadienyl groups, C–H 1.08 Å). A fixed thermal parameter of 0.07 Å^2 was assigned to H atoms. Anisotropy was introduced for all non-hydrogen atoms. Refinement of scale factor, positional, and thermal parameters converged to a final agreement index R of 0.054, when the largest parameter shift for the refined parameters was 0.5σ. The full-matrix refinement minimized the function $\Sigma w(\Delta F)^2$ with w = 1. No significant residual of electronic density was observed in the final Fourier difference map. Scattering factors for neutral atoms were taken from ref. 7. The scattering factors for U and Si were corrected for anomalous dispersion.[8] Calculations were done using the SHELX program system.[9] Final atomic parameters are listed in Table 1, bond distances and angles are in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Results and Discussion

The compound $[U(\eta^5\text{-}C_5H_5)_3(SiPh_3)]$ (**1**) can be synthesized by metathesis as in equation (1). However the following points

$$[U(\eta^5\text{-}C_5H_5)_3Cl] + Li(SiPh_3) \longrightarrow [U(\eta^5\text{-}C_5H_5)_3(SiPh_3)] + LiCl \quad (1)$$

should be noted. (*i*) Only $Li(SiPh_3)$ prepared from $SiPh_4$ and metallic lithium gave satisfactory results. Other silylating agents such as $Li(SiPh_3)$ prepared from $SiPh_3Cl$ and lithium, or

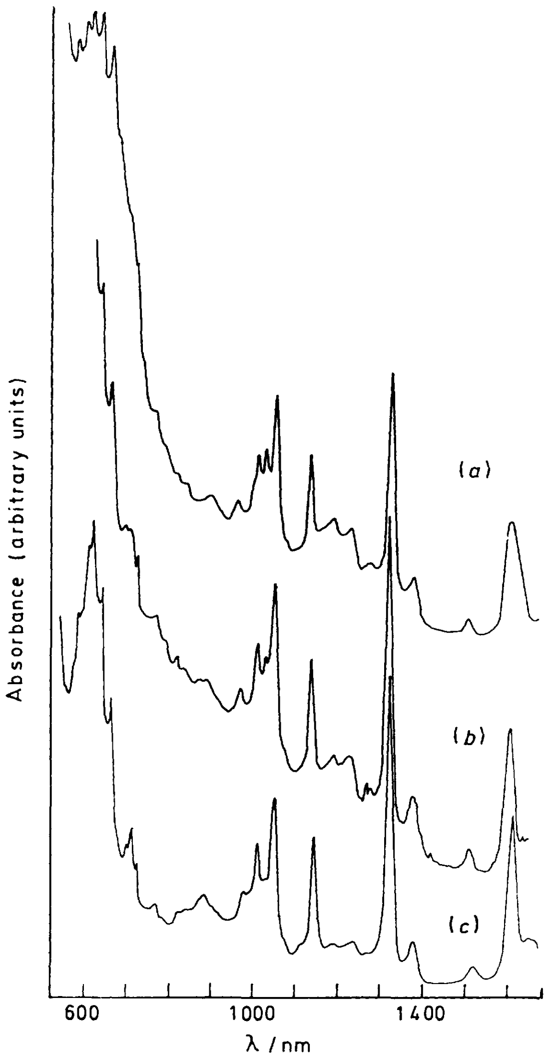


Figure 1. Near-i.r.–visible absorption spectra in toluene of the complexes $[U(\eta^5\text{-}C_5H_5)_3(SiPh_3)]$ (*a*), $[U(\eta^5\text{-}C_5H_5)_3(GePh_3)]$ (*b*), and $[U(\eta^5\text{-}C_5H_5)_3(SnPh_3)]$ (*c*)

$K(SiPh_3)$ prepared from $SiPh_3H$ with KH or K, when treated with $[U(\eta^5\text{-}C_5H_5)_3Cl]$ gave a mixture of products difficult to separate {among which the known compounds $[U(\eta^5\text{-}C_5H_5)_3Ph]$[10] and $[U(\eta^5\text{-}C_5H_5)_3(OPh)]$[11] were detected by ^1H n.m.r. spectroscopy}. (*ii*) The reaction must be carried out at low temperature. At room temperature in a oxygenated solvent such as thf, the main product is $[U(\eta^5\text{-}C_5H_5)_3(OSiPh_3)]$ (see below). (*iii*) The compound $[U(\eta^5\text{-}C_5H_5)_3(NEt_2)]$ does not react with $SiPh_3H$ to give (**1**), although protolysis of the U–N bond has been exploited in the synthesis of $[U(\eta^5\text{-}C_5H_5)_3(SnPh_3)]$ and $[U(\eta^5\text{-}C_5H_5)_3(PPh_2)]$ by $SnPh_3H$ and PPh_2H respectively.

Similar complications in the synthesis of organometallic compounds containing direct bonds between silicon and *d* transition metals have been extensively reported.[12]

Compound (**1**) is brown-green, thermally stable, but extremely oxygen and moisture sensitive. It is insoluble in n-hexane, soluble in benzene, toluene, and thf, less so in Et_2O giving deep green solutions. Unfortunately we did not succeed in obtaining crystals suitable for structural determination. The i.r. spectrum (range 1 200—400 cm^{-1}) of (**1**) shows absorptions typical of the organic groups (Ph and C_5H_5). The near-i.r.–visible (1 600—700 nm) spectrum in toluene solution presents a series of rather narrow peaks almost identical to those of $[U(\eta^5\text{-}C_5H_5)_3(SnPh_3)]$ and $[U(\eta^5\text{-}C_5H_5)_3(GePh_3)]$ in position and intensity (Figure 1). This probably indicates that the co-ordination around the uranium is the same in the three compounds.

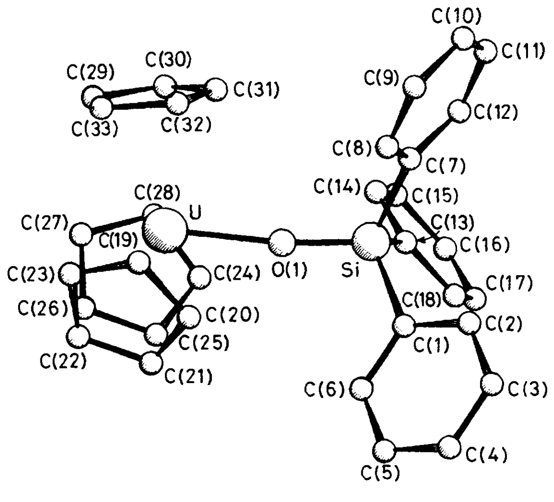


Figure 2. Molecular structure of $[U(\eta^5\text{-}C_5H_5)_3(OSiPh_3)]$

The ^1H n.m.r. spectrum of compound (**1**) shows a set of signals well shifted due to the paramagnetism of the uranium $5f^2$ ion, as generally found for similar organometallic uranium derivatives.[2] In particular, it shows a singlet due to C_5H_5 protons in the same position (−3.7 p.p.m.) as previously found for $[U(\eta^5\text{-}C_5H_5)_3(GePh_3)]$[2] and $[U(\eta^5\text{-}C_5H_5)_3(SnPh_3)]$[3] and generally for $[U(\eta^5\text{-}C_5H_5)_3X]$ systems in which a single U–X[3,13] bond occurs. In contrast to the C_5H_5 protons, it is noteworthy that the *o*-phenyl proton signals have a shift downfield on passing from Sn to Ge and Si. Moreover the signals of the *m*- and *p*-phenyl protons become sharper and can easily be assigned. In our experiments they appear as broad multiplets at 4.3 p.p.m. for $[U(\eta^5\text{-}C_5H_5)_3(SnPh_3)]$ and at 4.1 p.p.m. for $[U(\eta^5\text{-}C_5H_5)_3(GePh_3)]$, whereas in the present case they are split into triplets at 3.86 (*p*-H) and 4.35 p.p.m. (*m*-H of phenyl) for (**1**). This behaviour is probably due to a shorter U–Si bond with respect to the other U–M bonds and to the subsequent change in geometric parameters which define chemical shift.

As has been mentioned, the synthesis of compound (**1**) must be carried out at low temperature, since at room temperature the reaction between $[U(\eta^5\text{-}C_5H_5)_3Cl]$ and $Li(SiPh_3)$ leads to the formation of a mixture of products. When a solution of (**1**) is warmed or reaction (1) is carried out at room temperature a yellow substance is obtained as the main product, which shows ^1H n.m.r. signals and an i.r. spectrum analogous to those of (**1**) except for the presence of an absorption band at 935 cm^{-1}, in a position where the bands corresponding to $M\text{–}OSiR_3$ stretching vibrations (*e.g.* $Zr\text{–}OSiR_3$) have been found.[12a] In order to confirm the hypothesis that this yellow compound is the siloxide $[U(\eta^5\text{-}C_5H_5)_3(OSiPh_3)]$ (**2**) {the ^1H n.m.r. signal of the C_5H_5 protons at −9.42 p.p.m. occurs in a position typical of $[U(\eta^5\text{-}C_5H_5)_3(OR)]$}[11] formed by oxygen uptake by (**1**) probably from the tetrahydrofuran solvent, we prepared (**2**) by an alternative route (2). The yield is quantitative and the identity of the

$$[U(\eta^5\text{-}C_5H_5)_3(NEt_2)] + SiPh_3(OH) \longrightarrow [U(\eta^5\text{-}C_5H_5)_3(OSiPh_3)] + NEt_2H \quad (2)$$

two compounds was confirmed by the ^1H n.m.r. and near-i.r.–visible spectra. In addition, slow evaporation of a diethyl ether solution of (**2**) gave crystals suitable for its structural determination. The crystal structure of (**2**) is shown in Figure 2.

The co-ordination around uranium can be considered as distorted tetrahedral if the centroids (Cp) of the cyclopentadienyl rings and the oxygen atom are taken as the vertices,[14] the distortion consisting in a movement of U towards the plane of the three centroids. The mean values of the Cp–U–Cp angles are significantly larger (116°) while U–O–Cp are smaller (102°) than the ideal values, even though both these values are not unusual for $[U(\eta^5\text{-}C_5H_5)_3X]$ derivatives. Although the molecule as a whole is asymmetric, a mirror plane can be identified comprising the U, O, and Si atoms as well as the centroid Cp(3) and the C(31) atom of the same cyclopentadienyl ring which bisects the molecule, and forms with the Cp(1) and Cp(2) ring planes dihedral angles of 35 and 29° respectively, while the plane involving Cp(3) is essentially perpendicular to that plane (93°). Interestingly, for the U–O–Si system two features must be underlined: the short U–O bond length (2.14 Å) and the almost linear U–O–Si bond angle (173°). This geometrical combination is quite common for U–O–C systems [mainly alkoxide and aroxide, but also $U\leftarrow:O{=}C(NMe_2)_2$ complexes] and has been considered a clear manifestation of the formation of $O^{\pi}\longrightarrow U$ dative bonds possibly from both oxygen lone-pair orbitals through hybridization.[15] Although in uranium chemistry no similar compounds have been reported so far, siloxide derivatives are known for *d* transition metals. All cases where M–O–Si linearity and short M–O bonds have been observed in strict similarity with the M–O–C bond angles and the M–O bonds of their corresponding alkoxides have been explained on the basis of a *sp* oxygen hybridization;[16] thus it is reasonable to suppose that the same effect is responsible for the geometry of the present uranium–siloxide bond. On the other hand, the O–Si and Si–C bonds and O–Si–C bond angles are in the range found with other siloxide derivatives and correspond to a tetrahedral geometry around the silicon atom.

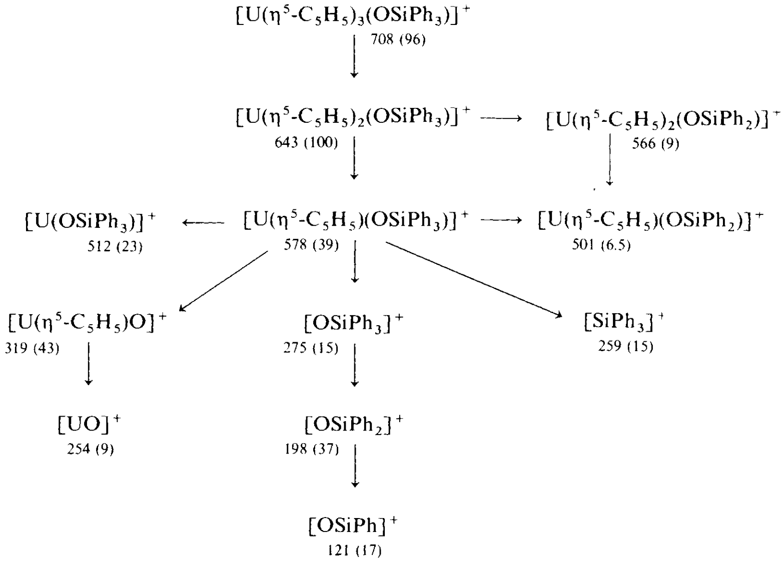
Reactions of Compound (**1**).—Compound (**1**) is very oxygen and moisture sensitive, but an interesting reaction is the hydrostannolytic cleavage of the U–Si bond by $SnPh_3H$ which smoothly and rapidly leads to the formation of the previously described $[U(\eta^5\text{-}C_5H_5)_3(SnPh_3)]$[3] [equation (3)]. Here the

$$[U(\eta^5\text{-}C_5H_5)_3(SiPh_3)] + SnPh_3H \longrightarrow [U(\eta^5\text{-}C_5H_5)_3(SnPh_3)] + SiPh_3H \quad (3)$$

driving force of the reaction is probably the greater acid strength of $SnPh_3H$ with respect to $SiPh_3H$ *cf.* also reaction (4).

$$[U(\eta^5\text{-}C_5H_5)_3(GePh_3)] + SnPh_3H \longrightarrow [U(\eta^5\text{-}C_5H_5)_3(SnPh_3)] + GePh_3H \quad (4)$$

Compound (**1**) reacts under mild conditions with 2,6-dimethylphenyl isocyanide giving the insertion compound (**3**), characterized by elemental analysis and spectroscopic methods. In the range 1 600—700 nm, a toluene solution of (**3**) gives a spectrum which looks very different from those of (**1**) and (**2**) in that broad and shifted absorptions (with lower absorption coefficients) are observed. In the range 3 000—400 cm^{-1} compound (**3**) shows absorption bands typical of the functional groups present in the molecule; in particular, the vibration at 1 530 cm^{-1} is strongly indicative of a iminosilyl ligand η^2-co-ordinated to the uranium atom (for a similar insertion into a Zr–Si bond there was a band at 1 558 cm^{-1} [17b]). This assignment is based on analogy with other isonitriles inserted into U–E (E = C,[18], N,[5], Ge,[2], or H[19]) bonds. The ^1H n.m.r. spectrum of (**3**) is strongly reminiscent of the analogous $[U(\eta^5\text{-}C_5H_5)_3\{C(GePh_3){=}NC_6H_3Me_2\text{-}2,6\}]$;[2] at room temperature the signal pattern (see Experimental section) gives further support to the proposed formulation. In addition the signal of the cyclopentadienyl protons is split into two singlets at low temperature suggesting that, analogously to $[U(\eta^5\text{-}C_5H_5)_3\{C(GePh_3){=}NC_6H_3Me_2\text{-}2,6\}]$ and other isonitrile insertion products, the strong interaction between U and the η^2-bonded ligand hampers rotation of the ligand itself around the axis connecting the U atom and the midpoint of the C=N bond. The barrier to rotation has been estimated at the coalescence temperature (−45 °C). The isotropic shifts of the C_5H_5 resonances were found to obey an approximate Curie relationship below the coalescence temperature and an extrapolation of a least-squares fit to these data yields $\Delta\delta$ 7 022 Hz and τ_C 6.41×10^{-5} at this temperature. The activation energy $\Delta G^{\ddagger}$ for the process was estimated to be 37 ± 3 kJ mol^{-1} so even if τ_C is lower with respect to the same process for the



Scheme. Fragmentation pattern of $[U(\eta^5\text{-}C_5H_5)_3(OSiPh_3)]$

analogous $[U(\eta^5\text{-}C_5H_5)_3\{C(GePh_3)\text{=}NC_6H_3Me_2\text{-}2,6\}]$, the $\Delta G^\ddagger$ values are similar within experimental error.[2] Apart from the adventitious incorporation of oxygen into the transition metal–silicon bond to give the siloxide derivative, only few examples of insertion reactions into such a bond have been reported: reversible insertion of ethylene into a Fe–Si[17a] bond, of organic carbonyls into a Ta–Si bond, and of CO into Zr–Si[17b] and Ta–Si[17c] bonds with formation of η^2-siloacyl derivatives. The easy formation of compound (**3**) represents a further example of an insertion reaction which, in contrast to the above examples, is irreversible up to 100 °C as inferred by the ^1H n.m.r. spectrum; in the range 27—100 °C only the spectrum of (**3**) is observed.

Compounds (**1**)—(**3**) were studied mass spectrometrically; (**1**) and (**3**) do not show any molecular ions, however in both their complicated spectra the highest peak corresponds to $m/z = 626$. In our opinion it should be ascribed to the $[U(\eta^5\text{-}C_5H_5)(C_5H_4SiPh_3)]^+$ ion rather than to the $[U(\eta^5\text{-}C_5H_5)(C_5H_4)(SiPh_3)]^+$ ion as the transposition of the $SiPh_3$ group to the C_5H_5 ring is suggested by the presence of the $[C_5H_5SiPh]^+$ ion ($m/z = 324$) and parallels the analogous transposition of GeR_3 and SnR_3 groups detected in the mass spectra of other organometallic compounds.[20] Besides the uranium-containing fragments typical of these cyclopentadienyl compounds {for (**1**), $m/z = 433$ $[U(\eta^5\text{-}C_5H_5)_3]^+$, and 368 $[U(\eta^5\text{-}C_5H_5)_2]^+$; for (**3**), $m/z = 512$ $[UNSiPh_3]^+$, 447 $[U(\eta^5\text{-}C_5H_5)_3N]^+$, 433 $[U(\eta^5\text{-}C_5H_5)_3]^+$, 382 $[U(\eta^5\text{-}C_5H_5)_2N]^+$, 368 $[U(\eta^5\text{-}C_5H_5)_2]^+$, 317 $[U(\eta^5\text{-}C_5H_5)N]^+$, and 303 $[U(\eta^5\text{-}C_5H_5)]^+$} it is remarkable that (**3**) also shows ions originating from the ligand formed by the insertion of the xylyl isonitrile, *i.e.* m/z 391 $[HC(SiPh_3)\text{=}NC_6H_3Me_2\text{-}2,6]^+$ and 390 $[C(SiPh_3)\text{=}NC_6H_3Me_2\text{-}2,6]^+$. In comparison, the mass spectrum of compound (**2**) is quite simple and easy to rationalize as illustrated in the Scheme (abundance in parentheses). Here of note is the high abundance of the $[M]^+$ and $[M - C_5H_5]^+$ ions and the reluctance of the siloxide group to be split, which probably depends on the strong affinity of uranium(IV) for oxygenated ligands; in this way the absence of ions such as $[U(\eta^5\text{-}C_5H_5)_3]^+$ and $[U(\eta^5\text{-}C_5H_5)_2]^+$ which are ubiquitous in the mass spectra of $[U(\eta^5\text{-}C_5H_5)_3X]$ derivatives may be understood.

Conclusions

The results reported in this paper contribute further to the goal we undertook with the synthesis of $[U(\eta^5\text{-}C_5H_5)_3(SnPh_3)]$, that is to explore the possibility of extending the chemistry to compounds containing a direct bond between U and the Group 14 elements beyond carbon. Amongst the compounds of this series studied, (**1**) seems the more difficult to synthesize probably because of the strong affinity of silicon for oxygen, which is added to that of uranium. In particular the synthesis of compounds (**1**) and (**2**), *i.e.* of compounds containing U–Si and U–O–Si bonds respectively, seems of relevance in view of the presently growing interest in metal silicides[21] as well as in support materials based on the M–O–Si systems.

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