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# Synthesis, reactivity, and molecular structure of $[\{N(CH_2CH_2O)_3Si-C_6H_5\}W(CO)_3]$

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## Abstract

Reaction of phenylsilatrane with  $W(CO)_6$  gives the compound  $[C_6H_5Si(OCH_2CH_2)_3N]W(CO)_3$  (**1**) in high yield. Compound **1** has been characterized by elemental analysis, IR,  $^1H$  NMR, and X-ray diffraction methods. Compound **1** crystallizes in the orthorhombic space group *Pbca*, with  $a = 22.258(5)$  Å,  $b = 12.237(1)$  Å,  $c = 12.313(3)$  Å, and  $Z = 8$ . Metallation of **1** by *n*-butyllithium in THF and subsequent treatment of the lithium derivatives with electrophile have been performed.

## 1. Introduction

Recently we reported the synthesis, reactivity, and molecular structure of (phenylsilatrane) $Cr(CO)_3$  [**1**]. The chromium complex undergoes photochemical substitution with monodentate phosphines and phosphites, and with a bidentate ligand, such as diphos. However, the chromium complex does not react with carbanion. The low electrophilicity of the chromium complex might result from the electron-donating ability of the silatranyl group. In pursuing the chemistry of the  $\pi$ -coordinated arene-silatranyl complex, we decided to make a tungsten derivative of phenylsilatrane and to study the reactivity of the tungsten complex. In this report, we present the preparation, reactivity, and molecular structure of (phenylsilatrane) $W(CO)_3$  (**1**).

## 2. Experimental

### 2.1. General

All solvents were purified by standard methods and all syntheses were done under nitrogen. Reagent grade chemicals were used without further purification.

Elemental analyses were performed at the Korea Basic Science Centre.  $^1H$  NMR spectra were measured on a Varian XL-200. Infrared spectra were recorded on a Perkin-Elmer 782 spectrometer.

### 2.2. Synthesis of $[\{N(CH_2CH_2O)_3Si-C_6H_5\}W(CO)_3]$ (**1**)

Phenylsilatrane (1.26 g, 5 mmol) was added to  $W(CO)_6$  (2.11 g, 6 mmol) in decalin (100 ml). The mixture was heated at reflux for 2 h. After cooling to 0°C, the reaction mixture was filtered. The precipitates were washed in hexane and redissolved in methylene chloride. After evaporation of the solvent, the yellow crystalline solids were obtained in 66% (1.70 g) yield. M.p. 201°C (dec.). IR (NaCl):  $\nu(CO)$  1930, 1820  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  2.91 (t,  $J = 5.8$  Hz,  $NCH_2$ ), 3.86 (t,  $J = 5.8$  Hz,  $OCH_2$ ), 5.36–5.68 (m, Ph) ppm. Anal: Found: C, 34.70; H, 3.30; N, 2.70.  $C_{15}H_{17}NO_6SiW$  calc.: C, 33.82; H, 3.11; N, 2.70%.

### 2.3. Collection and refinement of X-ray data for **1**

X-ray data were collected on an Enraf-Nonius CAD4 diffractometer using  $Mo K\alpha$  radiation at room temperature. Cell parameters and an orientation matrix for data collection were obtained from least squares refinement, using the setting angles of 25 reflections in the range  $23.5 < 2\theta < 27.7$ . The crystallographic data are summarized in Table 1. The intensities of 3 standard reflections, recorded every 3 h of X-ray exposure,

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TABLE 1. Crystallographic data for 1

Formula	$C_{15}H_{17}NO_6SiW$
F.W.	519.24
Space group	<i>Pbca</i> (No. 61)
<i>a</i> , Å	22.258(5)
<i>b</i> , Å	12.237(1)
<i>c</i> , Å	12.313(3)
Vol., Å <sup>3</sup>	3354(1)
<i>Z</i>	8
Temp., °C	25
<i>d</i> <sub>calcd</sub> , g cm <sup>-3</sup>	2.057
$\lambda$ (Mo $K\alpha_1$ ), Å	0.70926
Monochromator	graphite
Linear abs. coeff., cm <sup>-1</sup>	71.4
2 $\theta$ limits, deg	3 < 2 $\theta$ < 50
No. of unique data	3336
No. of unique data with $F_o^2 > 3\sigma(F_o^2)$	1923
No. of variables	217
<i>R</i> <sup>a</sup>	0.061
<i>R</i> <sub>w</sub> <sup>b</sup>	0.078

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}; w = 4F_o^2 / \sigma^2(F_o^2); \sigma(F_o^2) = [\sigma(I) + (pI)^2]^{1/2}$$

showed no systematic changes. All the calculations were carried out with the Enraf-Nonius MOLEN package. The intensity data were corrected for Lorentz and polarization effects and empirical absorption corrections were also applied. The structures were solved by a combination of Patterson and difference Fourier methods and refined by full-matrix least-squares methods. All the nonhydrogen atoms were refined anisotropically. The positions of hydrogen atoms were idealized ( $d(C-H) = 0.95$  Å) and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotropic thermal parameter of 1.2 times that of attached atom. The final cycle of refinement led to the *R* indices listed in Table 1. The atomic scattering factors were taken from *International Tables* [2] for the non-hydrogen atoms and from the literature [3] for hydrogen. The final positional and equivalent isotropic thermal parameters are listed in Table 2. Complete lists of thermal parameters and structure factors are available from the authors.

#### 2.4. Metallation of 1 and electrophilic trapping of the complexed lithiated intermediate

The procedure was typically as follows. To the solution of 1 (0.156 g, 0.3 mmol) in THF (50 ml) at  $-78^\circ\text{C}$  was added <sup>n</sup>BuLi (1.5 mmol, 1.4 M solution in n-hexane). The reaction mixture was stirred for 1 h at  $-78^\circ\text{C}$ . Then the reaction mixture was allowed to warm to  $-30^\circ\text{C}$ . Trimethylchlorosilane (0.4 ml, 3.2 mmol) was added to the complexed lithiated intermediate. Then the reaction mixture was allowed to warm to

room temperature and stirred for another 1 h. The reaction mixture was poured into water and extracted with diethyl ether (30 ml  $\times$  3). The ether extracts were dried over anhydrous MgSO<sub>4</sub> and evaporated to dryness to obtain the crude product. The product was purified by column chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub>. (Yield: 52 mg, 29%). The ratio of *meta*- : *para*-substituted product was determined by the integration of <sup>1</sup>H NMR peaks. M.p. 142°C (dec.). IR (NaCl):  $\nu(\text{CO})$  1940, 1850 cm<sup>-1</sup>. Anal. Found: C, 36.21; H, 4.87; N, 2.19. C<sub>18</sub>H<sub>25</sub>NO<sub>6</sub>Si<sub>2</sub>W calc.: C, 36.56; H, 4.26; N, 2.37%. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>). *Meta*-substituted product:  $\delta$  0.24 (s, SiMe<sub>3</sub>), 3.02 (t, *J* = 6.1 Hz,

TABLE 2. Positional parameters and equivalent isotropic thermal parameters for 1

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> ) <sup>a</sup>
W	0.31034(4)	0.22086(7)	0.14940(7)	2.01(1)
Si	0.4848(3)	0.2418(5)	0.2138(5)	1.9(1)
O1	0.3609(9)	0.003(2)	0.056(2)	5.6(5)
O2	0.1995(8)	0.172(2)	-0.002(2)	5.4(5)
O3	0.2476(9)	0.095(2)	0.340(2)	5.2(4)
O4	0.4869(6)	0.162(1)	0.106(1)	2.4(3)
O5	0.5163(7)	0.367(1)	0.206(1)	3.0(3)
O6	0.4711(7)	0.187(1)	0.335(1)	2.7(3)
N	0.5738(8)	0.189(1)	0.236(1)	2.1(3)
C1	0.343(1)	0.085(2)	0.089(2)	3.2(5)
C2	0.242(1)	0.191(2)	0.055(2)	3.6(5)
C3	0.270(1)	0.140(2)	0.271(2)	2.7(5)
C4	0.406(1)	0.297(2)	0.190(2)	2.4(4)
C5	0.3666(9)	0.323(2)	0.276(2)	2.2(4)
C6	0.311(1)	0.378(2)	0.263(2)	3.0(5)
C7	0.301(1)	0.414(2)	0.151(3)	3.6(5)
C8	0.337(1)	0.388(2)	0.057(2)	3.9(6)
C9	0.388(1)	0.332(2)	0.082(2)	3.3(5)
C10	0.537(1)	0.090(2)	0.086(2)	3.5(5)
C11	0.592(1)	0.141(2)	0.131(2)	3.1(5)
C12	0.579(1)	0.384(2)	0.203(2)	3.8(6)
C13	0.609(1)	0.288(2)	0.262(2)	4.1(6)
C14	0.517(1)	0.144(2)	0.400(2)	3.4(5)
C15	0.568(1)	0.107(2)	0.331(2)	3.9(6)
H1	0.378	0.302	0.347	2.6 *
H2	0.283	0.390	0.320	3.6 *
H3	0.268	0.460	0.139	4.3 *
H4	0.326	0.408	-0.015	4.6 *
H5	0.414	0.313	0.023	3.9 *
H6	0.542	0.080	0.010	4.2 *
H7	0.530	0.021	0.119	4.2 *
H8	0.622	0.087	0.142	3.7 *
H9	0.607	0.196	0.084	3.7 *
H10	0.588	0.451	0.239	4.5 *
H11	0.592	0.388	0.130	4.5 *
H12	0.649	0.280	0.238	4.9 *
H13	0.608	0.300	0.338	4.9 *
H14	0.501	0.083	0.439	4.0 *
H15	0.530	0.198	0.449	4.0 *
H16	0.604	0.107	0.372	4.7 *
H17	0.561	0.036	0.303	4.7 *

<sup>a</sup>  $B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i a_j$ . Starred atoms were refined isotropically.

NCH<sub>2</sub>, 6H), 3.78 (t,  $J = 6.1$  Hz, OCH<sub>2</sub>, 6H), 5.42 (t,  $J = 6.3$  Hz, Ph, 1H), 5.68 (dt,  $J = 6.3$  Hz, 0.98 Hz, Ph, 1H), 5.84 (br s, Ph, 1H), 5.91 (dt,  $J = 6.3$  Hz, 0.98 Hz, Ph, 1H) ppm. *Para*-substituted product:  $\delta$  0.24 (s, SiMe<sub>3</sub>, 9H), 3.04 (t,  $J = 6.1$  Hz, NCH<sub>2</sub>, 6H), 3.80 (t,  $J = 6.1$  Hz, OCH<sub>2</sub>, 6H), 5.61 (s, Ph, 4H) ppm.

When the metallation was performed at  $-78^\circ\text{C}$  and the trapping with trimethylchlorosilane at  $-10^\circ\text{C}$ , a mixture of *meta*-, *para*-substituted, and 3,5-disubstituted products was obtained. The 3,5-disubstituted product was isolated in 2% yield from the mixture. The yield of a mixture of *meta*- and *para*-substituted products was 42% and the ratio of *meta*- to *para*-substituted product was 57:43.

3,5-disubstituted product: M.p.  $197^\circ\text{C}$  (dec.). IR (NaCl):  $\nu(\text{CO})$  1932, 1850  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (CDCl<sub>3</sub>)  $\delta$  0.25(s, Me), 0.29 (s, Me), 3.03 (t,  $J = 6.1$  Hz, NCH<sub>2</sub>), 3.81 (t,  $J = 6.1$  Hz, OCH<sub>2</sub>), 5.55 (s, Ph, 2H), 6.02 (s, Ph, 1H). EI-MS:  $m/z$  736 (M<sup>+</sup>), 663 (M<sup>+</sup> - SiMe<sub>3</sub>), 635 (M<sup>+</sup> - SiMe<sub>3</sub> - CO), 607 (M<sup>+</sup> - SiMe<sub>3</sub> - 2CO), 579 (M<sup>+</sup> - SiMe<sub>3</sub> - 3CO), 552 (M<sup>+</sup> - 2SiMe<sub>3</sub> - CO), 174 (Si(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N).

#### 2.5. Metallation and electrophilic trapping with TBDM-*SiCl* (TBDM*SiCl* = *tert*-butyldimethylsilyl chloride)

Under conditions identical with those above, a mixture of *meta*- and *para*-substituted product was obtained in 22% yield. M.p.  $152^\circ\text{C}$  (dec.). IR (NaCl):  $\nu(\text{CO})$  1945, 1850  $\text{cm}^{-1}$ . Anal. Found: C, 40.06; H, 4.96; N, 2.15. C<sub>21</sub>H<sub>31</sub>NO<sub>6</sub>Si<sub>2</sub>W calc.: C, 39.82; H, 4.93; N, 2.21%.  $^1\text{H}$  NMR (acetone-*d*<sub>6</sub>). *Meta*-substituted product:  $\delta$  0.21 (s, SiMe<sub>3</sub>), 0.94 (s, <sup>1</sup>Bu), 3.02 (t,  $J = 5.9$  Hz, NCH<sub>2</sub>, 6H), 3.78 (t,  $J = 5.9$  Hz, OCH<sub>2</sub>, 6H), 5.43 (td,  $J = 6.1$  Hz, 0.5 Hz, Ph, 1H), 5.64 (dt,  $J = 6.1$  Hz, 0.98 Hz, Ph, 1H), 5.81 (m, Ph, 1H), 5.95 (dt,  $J = 6.1$  Hz, 0.98 Hz, Ph, 1H) ppm. *Para*-substituted product:  $\delta$  0.21 (s, SiMe<sub>3</sub>), 0.94 (s, <sup>1</sup>Bu), 3.05 (t,  $J = 5.9$  Hz, NCH<sub>2</sub>), 3.80 (t,  $J = 5.9$  Hz, OCH<sub>2</sub>), 5.61 (s, Ph, 4H) ppm.

#### 2.6. Metallation and electrophilic trapping with Et<sub>3</sub>SnCl

Under conditions identical with those above, a mixture of *meta*- and *para*-substituted products was obtained in 26% yield. M.p.  $180^\circ\text{C}$  (dec.). IR (NaCl):  $\nu(\text{CO})$  1940, 1845  $\text{cm}^{-1}$ . Anal. Found: C, 34.33; H, 4.64; N, 1.38. C<sub>21</sub>H<sub>31</sub>NO<sub>6</sub>SiSnW calc.: C, 34.83; H, 4.08; N, 1.93%.  $^1\text{H}$  NMR (CDCl<sub>3</sub>). *meta*-substituted product:  $\delta$  1.06 (t,  $J = 7.5$  Hz, CH<sub>3</sub>), 1.25 (q,  $J = 7.5$  Hz, CH<sub>2</sub>), 2.90 (t,  $J = 5.9$  Hz, NCH<sub>2</sub>), 3.85 (t,  $J = 5.9$  Hz, OCH<sub>2</sub>), 5.25 (t,  $J = 6.3$  Hz, Ph, 1H), 5.37 (d,  $J = 6.3$  Hz, Ph, 1H), 5.68 (s, Ph, 1H), 5.84 (d,  $J = 6.3$  Hz, 1H) ppm. *Para*-substituted product:  $\delta$  1.06 (t,  $J = 7.5$  Hz, CH<sub>3</sub>), 1.25 (q,  $J = 7.5$  Hz, CH<sub>2</sub>), 2.93 (t,  $J = 5.9$  Hz, NCH<sub>2</sub>), 3.87 (t,  $J = 5.9$  Hz, OCH<sub>2</sub>), 5.33 (d,  $J = 6.3$  Hz, Ph, 2H), 5.57 (d,  $J = 6.3$  Hz, Ph, 2H) ppm.

#### 2.7. Metallation and electrophilic trapping with Pr<sub>3</sub>SnCl

Under conditions identical with those above, a mixture of *meta*- and *para*-substituted products was obtained in 24% yield. M.p.  $138^\circ\text{C}$  dec. IR (NaCl):  $\nu(\text{CO})$  1942, 1855  $\text{cm}^{-1}$ . Anal. Found: C, 37.13; H, 5.00; N, 1.74. C<sub>24</sub>H<sub>37</sub>NO<sub>6</sub>SiSnW calc.: C, 37.62; H, 4.87; N, 1.83%.  $^1\text{H}$  NMR (CDCl<sub>3</sub>). *Meta*-substituted product:  $\delta$  0.99 (m, CH<sub>3</sub>), 1.60 (m, CH<sub>2</sub>), 2.91 (t,  $J = 5.9$  Hz, NCH<sub>2</sub>), 3.84 (t,  $J = 5.9$  Hz, OCH<sub>2</sub>), 5.26 (t,  $J = 6.1$  Hz, Ph, 1H), 5.37 (d,  $J = 6.1$  Hz, Ph, 1H), 5.70 (s, Ph, 1H), 5.83 (d,  $J = 6.1$  Hz, Ph, 1H) ppm. *Para*-substituted product:  $\delta$  0.99 (m, CH<sub>3</sub>), 1.60 (m, CH<sub>2</sub>), 2.93 (t,  $J = 5.9$  Hz, NCH<sub>2</sub>), 3.86 (t,  $J = 5.9$  Hz, OCH<sub>2</sub>), 5.34 (d,  $J = 5.6$  Hz, Ph, 2H), 5.57 (d,  $J = 5.6$  Hz, Ph, 2H) ppm.

#### 2.8. Metallation and electrophilic trapping with <sup>n</sup>Bu<sub>3</sub>SnCl

Under conditions identical with those above, a mixture of *meta*- and *para*-substituted products was obtained in 39% yield. M.p.  $141^\circ\text{C}$  dec. IR (NaCl):  $\nu(\text{CO})$  1942, 1860, 1843  $\text{cm}^{-1}$ . Anal. Found: C, 40.44; H, 5.85; N, 1.62. C<sub>27</sub>H<sub>43</sub>NO<sub>6</sub>SiSnW calc.: C, 40.12; H, 5.36; N, 1.73%.  $^1\text{H}$  NMR (CDCl<sub>3</sub>). *meta*-substituted product:  $\delta$  0.93 (m, Bu), 1.10 (m, Bu), 1.37 (m, Bu), 1.61 (m, Bu), 3.01 (t,  $J = 6.1$  Hz, NCH<sub>2</sub>), 3.78 (t,  $J = 6.1$  Hz, OCH<sub>2</sub>), 5.42 (t,  $J = 6.2$  Hz, Ph, 1H), 5.54 (d,  $J = 6.2$  Hz, Ph, 1H), 5.78 (s, Ph, 1H), 5.85 (d,  $J = 6.2$  Hz, 1H) ppm. *Para*-substituted product:  $\delta$  0.93 (m, Bu), 1.10 (m, Bu), 1.37 (m, Bu), 1.61 (m, Bu), 3.03 (t,  $J = 6.1$  Hz, NCH<sub>2</sub>), 3.79 (t,  $J = 6.1$  Hz, OCH<sub>2</sub>), 5.51 (d,  $J = 6.6$  Hz, Ph, 2H), 5.62 (d,  $J = 6.6$  Hz, Ph, 2H) ppm.

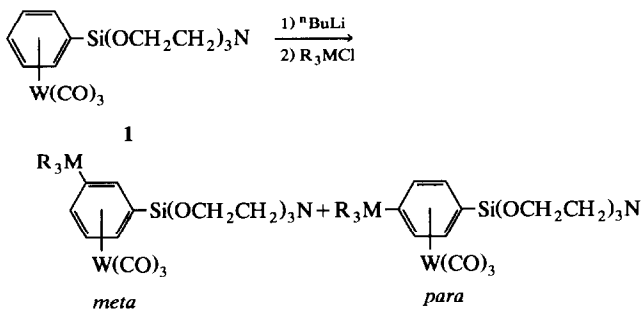
### 3. Results and discussion

Although [W(CO)<sub>3</sub>(C<sub>6</sub>H<sub>6</sub>)] was first reported [4] in 1958, subsequent development of (arene)tungsten chemistry has been relatively slow. Only limited studies of their reactions have been carried out. Recently, Kreiter [5] reported that the abstraction of the ring proton from tricarbonyl(arene)tungsten complexes by methyl lithium competes with the nucleophilic addition of methyl group to the arene ring or with the formation of a carbenoid complex depending on the reaction conditions. However, we thought that the reaction with <sup>n</sup>BuLi at low temperature would result in direct lithiation of the arene ring.

The tungsten derivative of phenylsilatrane, [(C<sub>6</sub>H<sub>5</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N)W(CO)<sub>3</sub>] (1), was synthesized by refluxing the decalin solution of phenylsilatrane and W(CO)<sub>6</sub>. The crystal suitable for X-ray study was obtained by slow precipitation of compound 1 from CH<sub>2</sub>Cl<sub>2</sub>/hexane.

1 has a very low electrophilicity as we expected. It does not react with any kind of carbanions. A photochemical substitution of carbonyl ligands by phospho-

TABLE 3. Electrophilic trapping of the lithio (phenylsilatrane) tungsten tricarbonyl complex



R <sub>3</sub> M	Temp. (°C)	Distribution of Product		Yield (%)
		<i>meta</i>	<i>para</i>	
Me <sub>3</sub> Si	-30	71	29	29
Me <sub>3</sub> Si	-10	57	43	42
<sup>t</sup> BuMe <sub>2</sub> Si	-78	56	44	22
Et <sub>3</sub> Sn	-30	60	40	26
Pr <sub>3</sub> Sn	-30	55	45	24
<sup>n</sup> Bu <sub>3</sub> Sn	-30	29	71	39

rus ligands does not occur. The low electrophilicity might come from a high electron-donating ability of silatranyl group [1]. Thus the  $\pi$ -coordinated arene ring should be electron-rich.

**1** was lithiated by reaction with <sup>n</sup>BuLi. The resulting lithio ( $\eta^6$ -phenylsilatrane) tungsten carbonyl complex reacted with electrophiles, such as, R<sub>3</sub>SiCl (R<sub>3</sub> = Me<sub>3</sub> and <sup>t</sup>BuMe<sub>2</sub>) and R<sub>3</sub>SnCl (R = Et, Pr, and <sup>n</sup>Bu). However, electrophilic trapping with carbon donors such as MeI, <sup>t</sup>BuCl, CO<sub>2</sub>, methyl acetate, RC(O)X (R = Me, Ph), and benzophenone were unsuccessful. Under optimum conditions (n-butyllithium, THF, -78°C, 1 h), the lithio complex was formed with high efficiency. Under these conditions, the arene-tungsten bond is maintained. After electrophilic trapping, *meta*- and *para*-substituted arene silatranyl tungsten compounds were isolated in rather low yields (Table 3). The low yield is due to the demetallation of product during work-up. The selectivity also proved to be rather low. The yield and ratio of the isomers depend on the reaction conditions and the electrophile. For the trapping with trimethylchlorosilane, the temperature of electrophilic trapping is important to the yield and ratio of isomers. If electrophile was added at -78°C, then a mixture of *meta*- and *para*-substituted product was obtained in the ratio of 7:3 (total yield: 29%). If electrophile was added at -10°C, then a mixture of *meta*- and *para*-substituted product was obtained in the ratio of 6:4 (total yield: 42%) and a double substituted compound was obtained in 2% yield. For the trapping with R<sub>3</sub>SnCl, the *para*-substituted product

increases at expense of the *meta*-substituted product as the steric bulk of the electrophile increases.

Usually, regioselective *ortho* lithiation of arenes directed by a heteroatom substituent has been found for tricarbonyl(arene) chromium compounds [6]. Sometimes, the *ortho*-metallation is effectively prevented by a bulky blocking group on the heteroatoms and *meta* or *para* positions are expected to be metallated by an alkyl lithium treatment [7]. Some reports discussed the relationship between the regioselectivity and the relative configuration of the chromium tricarbonyl group to the benzene ring. Alkylation abstracts a hydrogen from the aromatic carbon eclipsed to the carbonyl ligand [8]. For **1**, no *ortho*-substituted products were obtained in such cases. The regioselectivity would be rationalized, at least in part, by taking account of the bulk of the silatrane moiety and the configuration of the tungsten tricarbonyl group.

Since this process results in a stable tricarbonyl (phenylsilatrane) tungsten complex, further functionalization by metallation/electrophilic trapping would be possible.

### 3.1. Molecular structure of **1**

The molecular geometry and labelling scheme for complex **1** is shown in Fig. 1. The bond distances and angles are in Table 4. **1** possesses the usual skeleton containing a five coordinate silicon atom. The N-Si-C(4) angle is 176.6(4)°, and the Si atom is displaced 0.15 Å from the centre of the plane defined by O4, O5, and O6, towards the C(4) atom. The stereochemistry of the Si atom is distorted trigonal bipyramidal. Introduction of W(CO)<sub>3</sub> into the phenylsilatrane does not affect the silatrane geometry very much. However, the N-Si bond is shortened to 2.102(18) Å and Si-C(phenyl) is lengthened to 1.902(7) Å [9].

When we consider complex **1** as a derivative of tungsten tricarbonyl, **1** is seen to possess a piano-stool

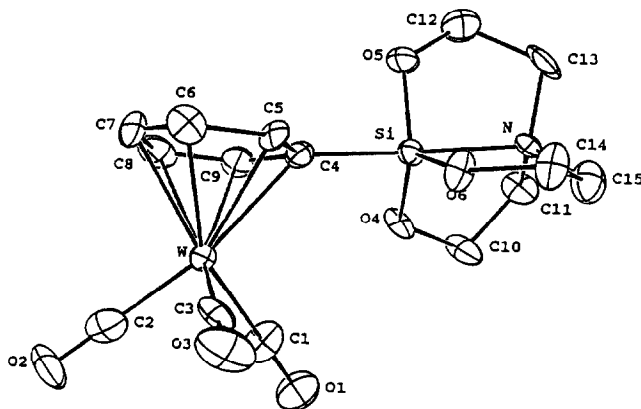
Fig. 1. ORTEP drawing of **1** with the atom labelling scheme.

TABLE 4. Bond distances (Å) and bond angles (°) for **1**<sup>a</sup>

W–C(1)	1.961(9)	W–C(2)	1.949(9)
W–C(3)	2.007(9)	W–C(4)	2.377(9)
W–C(5)	2.358(14)	W–C(6)	2.378(9)
W–C(7)	2.373(9)	W–C(8)	2.414(9)
W–C(9)	2.351(9)	Si–O(4)	1.649(6)
Si–O(5)	1.688(9)	Si–O(6)	1.664(7)
Si–N	2.102(18)	Si–C(4)	1.902(7)
O(1)–C(1)	1.154(8)	O(2)–C(2)	1.201(14)
O(3)–C(3)	1.129(9)	O(4)–C(10)	1.442(11)
O(5)–C(12)	1.411(16)	O(6)–C(14)	1.400(12)
N–C(11)	1.477(6)	N–C(13)	1.478(10)
N–C(15)	1.547(3)	C(4)–C(5)	1.411(13)
C(4)–C(9)	1.453(3)	C(5)–C(6)	1.418(18)
C(6)–C(7)	1.465(4)	C(7)–C(8)	1.443(4)
C(8)–C(9)	1.361(3)	C(10)–C(11)	1.482(3)
C(12)–C(13)	1.534(3)	C(14)–C(15)	1.488(3)
Si–C(4)–W	136.0(3)	O(1)–C(1)–W	177.1(6)
O(2)–C(2)–W	178.3(3)	O(3)–C(3)–W	178.1(2)
O(5)–Si–O(4)	118.7(5)	O(6)–Si–O(4)	119.2(4)
O(6)–Si–O(5)	119.5(4)	N–Si–O(4)	84.0(5)
N–Si–O(5)	84.0(6)	N–Si–O(6)	86.1(6)
C(2)–W–C(1)	84.5(4)	C(3)–W–C(1)	91.8(4)
C(3)–W–C(2)	90.2(4)	C(4)–W–C(1)	94.6(4)
C(4)–W–C(2)	153.9(5)	C(4)–W–C(3)	115.9(4)
C(4)–Si–O(4)	96.5(5)	C(4)–Si–O(5)	93.0(6)
C(4)–Si–O(6)	96.4(6)	C(4)–Si–N	176.6(4)
C(4)–C(5)–W	73.4(3)	C(4)–C(9)–W	73.1(2)
C(5)–W–C(1)	120.2(6)	C(5)–W–C(2)	155.2(6)
C(5)–W–C(3)	90.3(4)	C(5)–W–C(4)	34.7(4)
C(5)–C(4)–W	71.9(6)	C(5)–C(4)–Si	122.5(6)
C(5)–C(6)–W	71.8(3)	C(6)–W–C(1)	155.0(5)
C(6)–W–C(2)	120.5(4)	C(6)–W–C(3)	87.9(3)
C(6)–W–C(4)	63.5(2)	C(6)–W–C(5)	34.8(4)
C(6)–C(5)–W	73.4(7)	C(6)–C(5)–C(4)	124.4(4)
C(6)–C(7)–W	72.2(3)	C(7)–W–C(1)	151.6(5)
C(7)–W–C(2)	97.1(4)	C(7)–W–C(3)	116.5(4)
C(7)–W–C(4)	71.7(3)	C(7)–W–C(5)	60.9(3)
C(7)–W–C(6)	35.9(2)	C(7)–C(6)–W	71.9(2)
C(7)–C(6)–C(5)	112.4(3)	C(7)–C(8)–W	70.9(2)
C(8)–W–C(1)	116.6(4)	C(8)–W–C(2)	94.0(3)
C(8)–W–C(3)	151.6(4)	C(8)–W–C(4)	63.1(2)
C(8)–W–C(5)	74.5(3)	C(8)–W–C(6)	65.8(2)
C(8)–W–C(7)	35.1(2)	C(8)–C(7)–W	74.0(3)
C(8)–C(7)–C(6)	127.2(2)	C(8)–C(9)–W	76.0(3)
C(8)–C(9)–C(4)	125.8(2)	C(9)–W–C(1)	94.8(4)
C(9)–W–C(2)	118.1(4)	C(9)–W–C(3)	151.3(5)
C(9)–W–C(4)	35.8(2)	C(9)–W–C(5)	62.4(4)
C(9)–W–C(6)	74.7(3)	C(9)–W–C(7)	59.4(2)
C(9)–W–C(8)	33.2(1)	C(9)–C(4)–W	71.1(2)
C(9)–C(4)–Si	120.0(3)	C(9)–C(4)–C(5)	116.7(5)
C(9)–C(8)–W	70.8(3)	C(9)–C(8)–C(7)	113.1(2)
C(10)–O(4)–Si	121.4(7)	C(10)–C(11)–N	105.6(7)
C(11)–N–Si	105.5(6)	C(11)–C(10)–O(4)	108.5(4)
C(12)–O(5)–Si	123.1(6)	C(12)–C(13)–N	107.1(5)
C(13)–N–Si	106.0(5)	C(13)–N–C(11)	111.7(8)
C(13)–C(12)–O(5)	107.8(2)	C(14)–O(6)–Si	122.0(10)
C(14)–C(15)–N( )	107.3(5)	C(15)–N–Si	102.7(8)
C(15)–N–C(11)	115.3(3)	C(15)–N–C(13)	114.3(5)
C(15)–C(14)–O(6)	110.2(4)		

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits.

structure in which the  $W(CO)_3$  group lies directly below the arene ring. The planarity of the phenyl ring is rather obscure. The maximum deviation of any of the 6 ring carbon atoms of this group from the plane is 0.04 Å. The perpendicular distance of the tungsten atom from the least squares plane is 1.90 Å. The C–C distances in arene ring carbons vary apparently randomly from 1.361(3) to 1.465(4) Å (av. 1.42 Å). No conclusive evidence of altering long and short bonds due to  $\pi$ -coordination is found. When the tripod of  $W(CO)_3$  is projected onto the plane of arene ring, the torsion angles C1–W–G–C4, C2–W–G–C8, and C3–W–G–C6 are respectively 33.1, 27.6, and 29.4° (when the W atom is projected on the plane containing C4, C7, and C9 atoms, G is the corresponding point). The staggered conformation of compound **1** appears to arise because of the steric bulk and electron-donating ability of the silatranyl group. The problem of the orientation of the carbonyl groups in tricarbonyl chromium arene complexes has been treated extensively [10]. According to the study of  $(C_6H_5X)Cr(CO)_3$  complexes, Albright [10] suggested that as the electron-donating group becomes bulkier, the  $Cr(CO)_3$  group is rotated away from the *syn*-eclipsed conformation towards the less encumbered *anti*-eclipsed form.  $[(C_6H_5CMe_3)Mn(CO)_3]ClO_4$  [11],  $[(C_6H_5Si(OCH_2CH_2)_3N)Cr(CO)_3]$  [1], and  $[(C_6H_5Si(OCH_2CH_2)_3N)Mn(CO)_2 P(OMe)_3]ClO_4$  [12] have been observed to have similar conformations, in which the carbonyl groups are rotated by 25°, 32.5° and 38.5°, respectively, from the *syn*-eclipsed form. The W–CO distances vary from 1.95 to 2.01 Å (av. 1.97 Å). These distances compare quite well with the corresponding distances in the  $[(1,3,5-C_6H_3(CH_3)_3)W(CO)_3]$  (av. W–C distance 1.95 Å) [13].

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