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A facile synthesis of rhodium(III) porphyrin–silyls

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Abstract

Rhodium(III) porphyrin–silyls [$Me_3SiRhT(p\text{-}X)PP$ ($X = H$, Me)] were synthesized from the reactions of the rhodium(I) porphyrin anions, generated from the reduction of the rhodium(III) porphyrin chlorides with the sodium amalgam in toluene, with degassed Me_3SiCl at room temperature. A single crystal structure of (5,10,15,20-tetraphenylporphyrinato)(trimethylsilyl)rhodium(III) (**1**) showed that the Rh–Si bond length is equal to 2.305 Å. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Rhodium; Porpyhrin–silyls; Structures

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1. Introduction

The studies of intermediates as well as the measurements of the bond dissociation energies are important in understanding chemical reactions [1]. Transition metal silyl complexes have been proposed to be vital in catalytic processes such as hydrosilylation [2], silane polymerization [3] and silylformylation [4]. Transition metal catalyzed hydrosilylation of olefins is of paramount importance for the formation of silicon carbon bonds. Rhodium(I) complexes such as $RhCl(PPh_3)_3$, $HRh(CO)(PPh_3)$, $[Rh(CO)_2Cl]_2$, $[Rh(C_2H_4)_2Cl]_2$, $Rh(acac)(CO)_2$ etc., have been demonstrated to be powerful catalysts in the hydrosilylation of olefins [5]. Rhodium–cobalt clusters like $Co_2Rh_2(CO)_{12}$, $Rh_4(CO)_{12}$ and $(^tBuNC)RhCo(CO)_4$ catalyze the silylformylation of hydrosilanes and 1-hexyne at 10 atm of CO to give (*Z*)-1-silyl-2-formyl-1-hexenes [4].

The involvement of metal–silyl intermediates are proposed. However, the detection of intermediates is hampered by the fact high catalytic rates [6] and the sometimes heterogenous nature of the systems [7]. Furthermore, the isolation of stable compounds in the reaction mixtures may not always be the active intermediates. Since the fundamental requirement for the design of an appropriate catalyst is not well understood and may be due to the somewhat primitive state of our understanding of the chemistry of the transition metal–silyl bond [8], the synthesis of rhodium silyls has mainly been achieved through the oxidation of silanes into low valent rhodium metal centers [3]. We are motivated to study the properties of the rhodium–silyl porphyrin complexes and now report the facile synthesis of rhodium porphyrin silyls from the reductive silylation of rhodium porphyrin chlorides.

2. Result and discussion

Rhodium(III) porphyrin–silyls were prepared from the reaction of nucleophilic rhodium porphryin anions with trimethylsilyl chloride in toluene. Since the reaction of Me_3SiLi–HMPA with cobalt porphyrin chlorides did not yield the cobalt porphyrin silyls but the cobalt porphyrin phosphoryl complex [9], the use of silyl lithium would not be expected to be fruitful. The

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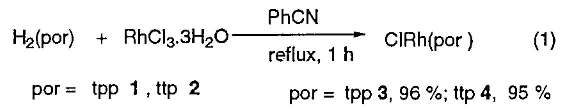
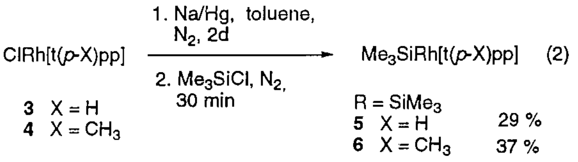
reaction of Rh^I porphyrin anion in THF, a polar solvent, with Me_3SiCl was not suitable since THF is known to be polymerized by Me_3SiCl [10]. The nucleophilic rhodium(I) porphyrin anion $[Rh^I(por)]$, was generated successfully from the reduction of the rhodium(III) porphyrin chlorides **3** and **4** by sodium amalgam in toluene for 2 days [11] and reacted with Me_3SiCl at room temperature (r.t.) to produce the corresponding rhodium(III) porphyrin–silyls [$Me_3SiRh(tpp)$ **5** and $Me_3SiRh(tpp)$ **6**] in 29 and 37% yield, respectively (Eq. 1).

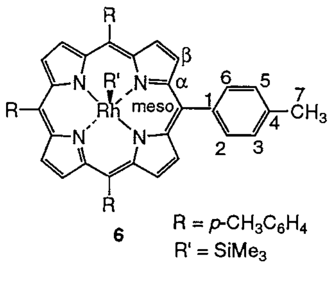




Complexes **5** and **6** exhibit characteristic ^1H and ^{13}C resonances. In the ^1H-NMR, these two complexes **5** and **6** showed high field singlets at -3.82 and -3.81 ppm, respectively with each corresponding to nine protons which are consistent with the presence of timethylsilyl groups. The upfield shift to -3.81 ppm is due to the porphyrin ring current effect on the Me_3Si group. The ^{13}C-NMR spectra of complexes **5** and **6** showed high field signals at -1.72 and -1.74 ppm, respectively corresponding to the trimethylsilyl carbons. An interesting aspect in the ^{13}C-NMR spectra for **6** was that all the tolyl carbons are non-equivalent with four singlets for the C_2–C_6 and C_3–C_5 positions (Fig. 1). The chemical shift difference of C_2–C_6 and C_3–C_5 carbons was due to the orthogonal nature of the 18 π porphyrin macrocycle and the tolyl group in this five coordinated rhodium complex.

The gate-decouped ^{13}C-NMR spectrum of complex **6** aids us in assigning all the carbons of the porphyrin ring and the Me_3Si group. The chemical shifts and ^{13}C–^1H coupling constants are summarized in Table 1.

The ^{29}Si-NMR spectra of complexes 5 and **6** showed an upfield singlet at -116.75 and -116.81 ppm and the line widths at half maximum were 1590 and 2226 Hz, respectively. The upfield shifted signal was due to the porphyrin ring current effect and the magnitude was comparable to the literature value of $Et_3SiRh(OEP)$ [12].



6

Fig. 1. General structural formula of porphyrin–silyl comlpexes.

Table 1
Chemical shifts and ^{13}C–^1H coupling constants of complex **6**

Carbon	Chemical shift, δ/ppm	J_{C-H} (Hz)
1	123.38	
2	128.67	141.4
3	134.55	159.3
4	137.84	
5	134.20	164.9
6	127.96	141.4
7	22.22	127.1
Meso	144.20	
α	139.94	
β	131.83	141.4
Me_3Si carbon	-1.09	120.5

The structure of **5** was confirmed by a single crystal X-ray diffraction study (Fig. 2). Crystals were grown from a chloroform-dichloromethane-hexane solution. Details of data collection and processing parameters was given in Table 2. The coordination sphere of the rhodium atom shows a square pyramidal geometry with four porphyrinato nitrogen atoms occupying the basal sites and the silicon atom of trimethylsilyl group residing at the axial site. The mean bond length of the Rh–N bonds is 2.016 Å which agrees with the five-coordinated organorhodium(III) porphyrin [13]. The Rh–Si length is 2.035 Å which is similar to the triethylsilyl rhodium porphyrin–silyl bond lengths [13]. The porphyrin ring is close to planar with a mean deviation of 0.0756 Å from the basal plane for the four nitrogens, whereas the nitrogen atoms deviate alternatively above and below the plane by 0.0232 Å (Table 3).

Recently, a non-concerted radical example of the reaction of a rhodium porphyrin dimer with a silane to yield rhodium(III) porphyrin-silyls has been documented [12]. However, the relatively inaccessible rhodium porphryin dimer starting material is required [13]. In summary, rhodium(III) porphyrin–silyls have been synthesized from the reaction of rhodium porphryin anion and Me_3SiCl.

3. Experimental

UV–vis spectra were recorded on a Hitachi U-3300 spectrophotometer using CH_2Cl_2 as the solvent. ^1H-NMR spectra were recorded on a Bruker WM 250 (250 MHz) spectrometer. Chemical shifts (δ) were reported with reference to the residual $CHCl_3$ (δ 7.24 ppm) in $CDCl_3$ and the coupling constant (J) was reported in

Hertz (Hz). ^{13}C-NMR spectra were obtained on either a Bruker WM 250 (62.9 MHz) or Bruker AMX 500 (125 MHz) spectrometer and referenced to the residual $CHCl_3$ (δ 77.00 ppm) in $CDCl_3$. ^{29}Si-NMR spectra was taken on a Bruker AMX 500 (99 MHz) spectrometer and the chemical shift (δ) was referenced to the external standard TMS (0.00 ppm). ^{31}P-NMR spectra was recorded on a Bruker AMX 500 (202 MHz) spectrometer and the chemical shift (δ) was referenced to the external standard H_3PO_4 (0.00 ppm). FAB MS spectra were recorded on a Joel JMS-HX 110 Mass Spectrometer using *m*-nitrobenzyl alcohol (NBA) as the matrix at National Tsing-Hua University, Taiwan. Elemental Analysis were performed by Medac, Department of Chemistry, Brunel University, United Kingdom.

Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. THF and toluene were distilled from the sodium benzophenone ketyl and sodium, respectively. HMPA was distilled from CaH_2. The complex Me_3SiCl was distilled from CaH_2, stored in a Telfon stoppered round-bottomed flask and was degassed by the freeze-pump-thaw method (three cycles) immediately prior to use. Silica gel (70–230 mesh) was used for column chromatography. Thin layer chromatography (TLC) was performed on Merck percoated silica 60F254 plates.

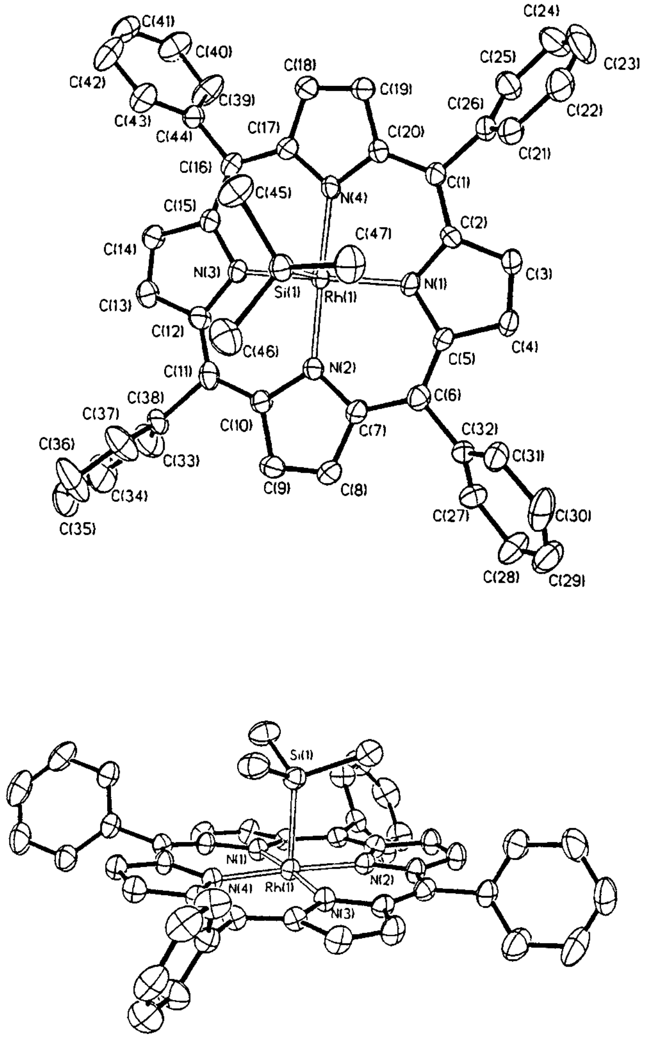


Fig. 2. ORTEP drawing of (5,10,15,20-tetraphenylporphyrinato)(trimethylsilyl) rhodium(III) (**5**), (a) and edge view, (b) hydrogens have been omitted for clarity.

Table 2
Crystal data for $Rh(tpp)SiMe_3$ 5

Empirical formula	$(C_{47}H_{37}N_4RhSi)$ $(1/2CHCl_3)$
Crystal system	Triclinic
Space group	$P1$ (no. 2)
Formula weight	848.5
a (Å)	12.723(3)
b (Å)	13.005(3)
c (Å)	15.091(3)
α (°)	100.46(1)
β (°)	102.52(1)
γ (°)	116.47(1)
Z	2
F(000)	870
V (Å^3)	2068.6(10)
$D_{calc.}$ (g/cm^3)	1.362
Crystal size (mm)	0.30 × 0.30 × 0.50
Radiation	M_o–K_α ($\lambda = 0.71073$ Å)
Monochromator	Highly oriented graphite crystal
μ (mm^{-1})	0.577
Number of unique reflections	7692
Number of reflections with $I > 10\sigma$	5425
Number of variables	531
R, $R_{w\ (\text{obs data})}$	0.056, 0.068
Goodness-of-fit	1.18
Largest and mean shift $H\Delta/\sigma$	0.101, 0.001
Res extrema in final diff map (e/Å^3)	1.05 to −0.91

$R = \Sigma|F_o - |F_o||/\Sigma|F_o|$, $wR = [\Sigma w^2(|F_o| - |F_c|^2/\Sigma w^2|F_o|^2]^{\frac{1}{2}}$.

3.1. Rhodium(III) tetraphenylporphyrin chloride ClRh(tpp) (3) [14]

To a hot solution of H_2(tpp) **1** (0.30 g, 0.48 mmol) in PhCN (30 ml), $RhCl_3 \cdot 3H_2O$ (0.25 g, 0.95 mmol) was

Table 3
Bond lengths (Å) and angles (°) of **5**

Bond length (Å)			
Rh(1)–N(1)	2.025(5)	Rh(1)–N(2)	2.009(5)
Rh(1)–N(3)	2.014(5)	Rh(1)–N(4)	2.017(5)
Rh(1)–Si(1)	2.305(2)	Si(1)–C(45)	1.846(10)
Si(1)–C(46)	1.879(7)	Si(1)–C(47)	1.857(8)
Bond angle (°)			
Si(1)–Rh(1)–N(1)	94.7(1)	Si(1)–Rh(1)–N(2)	91.3(1)
N(1)–Rh(1)–N(2)	89.9(2)	Si(1)–Rh(1)–N(3)	91.1(1)
N(1)–Rh(1)–N(3)	174.2(2)	N(2)–Rh(1)–N(3)	90.0(2)
Si(1)–Rh(1)–N(4)	177.2(2)	N(3)–Rh(1)–N(4)	90.1(2)
Rh(1)–Si(1)–C(45)	111.4(3)	Rh(1)–Si(1)–C(46)	112.8(2)
C(45)–Si(1)–C(47)	107.8(4)	Rh(1)–Si(1)–C(47)	110.1(3)

added and the mixture refluxed for 1 h to give a red solution. After removal of the solvent by high vacuum, the crude product was chromatographed over silica gel using $CHCl_3$ as eluent to give **3** as a red solid (0.35 g, 0.47 mmol, 95%). $R_f = 0.60$ (1:1 hexane/CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 7.95 (m, 12H), 8.12 (d, 8H, $J = 4.3$ Hz), 8.96 (s, 8H).

*3.2. Rhodium(III) tetratolylporphyrin chloride ClRh(ttp) (**4**) [15]*

To a hot solution of H_2(ttp) **2** (0.30 g, 0.48 mmol) in PhCN (30 ml), $RhCl_3 \cdot 3H_2O$ (0.25 g, 0.95 mmol) was added and the mixture refluxed for 1 h to give a red solution. After removal of solvent by high vacuum, the crude product was chromatographed over silica gel using $CHCl_3$ as eluent to give **4** as a red solid (0.36 g, 0.45 mmol, 96%). $R_f = 0.78$ (1:1 hexane/CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 2.70 (s, 12H), 8.07 (d, 4H, $J = 7.5$ Hz), 8.20 (d, 4H, $J = 7.5$ Hz), 8.94 (s, 8H).

*3.3. 5,10,15,20-Tetratolylporphyrinato trimethylsilyl rhodium (III) Me_3SiRh(ttp) (**6**)*

The preparation of Me_3SiRh(ttp) **6** was described as a typical procedure. A solution of Rh(ttp)Cl **4** (0.100 g, 0.133 mmol) and Na/Hg (4%, 3 g) in freshly distilled toluene (50 ml) was degassed by the freeze-pump-thaw method (three cycles). The red solution was stirred at r.t. under N_2 for 3 days to give a greenish–brown solution. This solution was added into a degassed solution of Me_3SiCl (0.86 g, 7.98 mmol) via a cannular under N_2 at r.t. in the absence of light. The solution was stirred for 20 min and CH_2Cl_2 was added. The mixture was washed with water (2 × 50 ml) and dried ($MgSO_4$). The solvent was removed by high vacuum and the resulting residue was chromatographed over silca gel using CH_2Cl_2/hexane (1:4) as the eluent. The first fraction was collected, evaporated and dried to give an orange solid. It was recrystallized by CH_2Cl_2/hexane to give orange crystals (0.042 g, 37%). $R_f = 0.54$ (CH_2Cl_2:hexane = 1:2); ^{1}H-NMR ($CDCl_3$, 250 MHz) δ −3.81 (s, 9H), 2.68 (s, 12H), 7.50 (t, 8H, $J = 6.9$ Hz), 7.95 (d, 4H, $J = 7.6$ Hz), 8.04 (d, 4H, $J = 7.6$ Hz), 8.64 (s, 8H); ^{13}C-NMR ($CDCl_3$, 62.9 MHz) δ −1.74, 21.49, 122.74, 127.32, 127.41, 131.16, 135.58, 133.86, 137.17, 139.35, 143.48; Gate-decoupling ^{13}C-NMR ($CDCl_3$, 125.8 MHz) δ −1.09 (q, $J_{C-H} = 120.5$ Hz), 22.22 (q, $J_{C-H} = 127.1$ Hz), 123.38, 127.96 (d, $J_{C-H} = 141.4$ Hz), 128.67 (d, $J_{C-H} = 141.4$ Hz), 131.83 (d, $J_{C-H} = 176.9$ Hz), 134.20 (d, $J_{C-H} = 164.9$ Hz), 134.55 (d, $J_{C-H} = 159.3$ Hz), 137.84, 139.94, 144.12; ^{29}Si-NMR ($CDCl_3$, 99.4 MHz) δ −116.81; UV–vis (CH_2Cl_2), λ_{max}, nm (log ε) 408 (4.64), 514 (3.61); FAB MS 844 (M^+). Anal. Calc. for $C_{51}H_{45}N_4RhSi$: C, 72.50; H, 5.37; N, 6.33. Found: C, 72.50; H, 5.37, N, 6.63.

*3.4. 5,10,15,20-Tetraphenylporphyrinato trimethylsilyl rhodium(III) Me_3SiRh(tpp) (**5**)*

The preparation of Me_3SiRh(tpp) **5** followed a procedure similar to that of **6** described above. A degassed solution of Rh(tpp)Cl **3** (0.10 g, 0.13 mmol) and Na/Hg (4%, 3 g) in freshly distilled toluene (50 ml) was degassed and stirred for 2 days under N_2 and was added to a solution of Me_3SiCl (0.84 g, 7.8 mmol) to give orange crystals (0.030 g, 29%). $R_f = 0.53$ (CH_2Cl_2:hexane = 1:3); ^{1}H-NMR ($CDCl_3$, 250 MHz) δ −3.82 (s, 9H), 7.69 (m, 12H), 8.08 (d, 4H, $J = 7.7$ Hz), 8.18 (d, 4H, $J = 7.7$ Hz), 8.63 (s, 8H); ^{13}C-NMR ($CDCl_3$, 62.9 MHz) δ −1.72, 122.79, 126.62, 126.72, 127.60, 131.28, 133.64, 133.95, 142.20, 143.41; ^{29}Si-NMR ($CDCl_3$, 99.4 MHz) δ −116.81; UV–vis (CH_2Cl_2), λ_{max}, nm (log ε) 406 (4.66), 513 (3.61); FAB MS 788 (M^+). Anal. Calc. for $C_{47}H_{37}N_4RhSi$: C, 71.56; H, 4.73; N, 7.10. Found: C, 71.24; H, 5.52; N, 6.34.

4. Supplementary material

X-ray diffraction data of complex **5** has been deposited in the Cambridege Crystallographic Data Centre as supplementary material.

Acknowledgements

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