Synthesis and Electrochemistry of Dialkylosmium-(IV) and -(V) Porphyrins. Crystal Structure of [Os(ttp)(CH_2SiMe_3)$_2$] [H_2ttp = 5,10,15,20-tetra(*p*-tolyl)porphyrin]‡

Wa-Hung Leung,*,[a] **Tom S. M. Hun,**[a] **Kwok-Yin Wong**[b] **and Wing-Tak Wong**†,[c]
[a] *Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong*
[b] *Applied Biology and Chemical Technology Department, Hong Kong Polytechnic, Hunghom, Kowloon, Hong Kong*
[c] *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong*

Reaction of [Os(por)O_2] [por = 5,10,15,20-tetra(*p*-tolyl)porphyrinate (ttp) or 2,3,7,8,12,13,17,18-octaethylporphyrinate (oep)] with thionyl chloride gave [Os(por)Cl_2] in good yields. The dichloride compounds are paramagnetic with μ_{eff} *ca.* 2.7 μ_B and display temperature-independent contact-shifted ^1H NMR spectra. Reaction of [Os(por)Cl_2] with an excess of LiR (R = Ph or Me_3SiCH_2) gave air-stable diamagnetic dialkyl compounds [Os(por)R_2]. The structure of [Os(ttp)(CH_2SiMe_3)$_2$] has been established by X-ray crystallography. Cyclic voltammograms of the diphenyl compounds exhibit reversible metal-centred Os^V–Os^{IV} and Os^{IV}–Os^{III} couples. Treatment of [Os(ttp)Ph_2] with Ce^{IV} or $AgBF_4$ afforded the diphenylosmium(V) compound [Os(ttp)Ph_2]BF_4, which is paramagnetic with μ_{eff} *ca.* 1.7 μ_B.

Organometallic chemistry of porphyrins[1,2] has attracted attention because of their relevance to the reactivity of vitamin B_{12} coenzymes[3] and their roles in metalloporphyrin-catalysed reactions such as the oxidation of hydrocarbons[4] and cyclopropanation of alkenes.[5] Our interest in organoosmium porphyrins was stimulated by a recent report that carbene complexes of osmium porphyrins are well defined catalysts for cyclopropanation of alkenes.[6] Although alkyl and aryl compounds of iron[1,2] and ruthenium porphyrins[1,2,7,8] are well documented, there are relatively few studies on the osmium cogeners. Carbene and alkene complexes of osmium porphyrins have been isolated from reactions of osmium(II) porphyrin dimers with the appropriate alkyl halides.[9]

Another focus of interest in the chemistry of metalloporphyrins containing σ-bonded alkyls is their redox reactivity, in particular in relation to metal-to-nitrogen migration reactions.[2] Oxidation of [Fe(por)R] (por = porphyrinate dianion) initially gives unstable alkyliron(IV) species, which subsequently undergo M-to-N migration of the alkyl group to yield iron(III) *N*-alkylporphyrins, a process relevant to the suicidal deactivation of haem enzymes.[10] Migration with loss of one alkyl/aryl group is observed upon oxidation of dialkyl and diaryl complexes of ruthenium(IV) porphyrins [Ru(por)R_2].[8] By contrast, monoalkyl ruthenium(III) porphyrins [Ru(por)R] are found to resist oxidative migration.[8] In an effort to understand the electronic factors governing alkyl migration reactions of metalloporphyrins, we herein report the synthesis and electrochemistry of diphenyl complexes of osmium-(IV) and -(V) porphyrins.

Experimental

All manipulations were carried out under nitrogen using Schlenk techniques. Solvents were dried by standard procedures and distilled prior to use. 2,3,7,8,12,13,17,18-Octaethylporphyrin (H_2oep) and [$Os_3(CO)_{12}$] were obtained from Aldrich; [Os(ttp)O_2][11] [H_2ttp = 5,10,15,20-tetra(*p*-tolyl)porphyrin] and [Os(oep)O_2][12] were prepared by the literature methods. Proton NMR spectra were obtained on a JEOL EX 400 spectrometer and chemical shifts (δ) are reported with reference to $SiMe_4$. Infrared spectra (Nujol mull) were recorded on a Nicolet MAGNA-IR 550 FTIR spectrophotometer, UV/VIS spectra on a Milton Roy Spectronic 3000 diode-array spectrophotometer. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) model 175 universal programmer and a model 173 potentiostat. Potentials were controlled with respect to a Ag^+–Ag reference electrode in acetonitrile but are reported with respect to the ferrocenium–ferrocene couple as measured in the same solution. Microanalyses were performed by Medac Ltd., Brunel University, UK.

Preparations.—[Os(ttp)Cl_2] **1**. To a solution of [Os(ttp)O_2] (100 mg) in CH_2Cl_2 (25 cm^3) at room temperature was added an excess of $SOCl_2$ (0.3 cm^3) and the reaction mixture was stirred for 2 h. The volatiles were removed *in vacuo* and the residue was redissolved in benzene and loaded onto a column of neutral alumina. The brown band eluted with benzene was collected and evaporated to dryness leaving a brown solid, which was recrystallised from CH_2Cl_2–MeCN to give violet crystals (yield 80%). ^1H NMR ($CDCl_3$): δ −4.56 (s, 8 H, pyrrolic), 3.06 (s, 12 H, *p*-Me), 8.30 (d, 8 H, H_m) and 10.68 (d, 8 H, H_o) (Found: C, 59.3; H, 3.7; N, 6.0. $C_{48}H_{36}Cl_2N_4Os\cdot 2H_2O$ requires C, 59.7; H, 4.1; N, 5.8%). μ_{eff} = 2.7 μ_B (Evans' method[13]). UV/VIS (CH_2Cl_2): λ_{max}/nm 396 (Soret), 510, 539 and 614.

[Os(oep)Cl_2] **2**. This complex was prepared as for **1** from [Os(oep)O_2] (50 mg) with $SOCl_2$ (0.5 cm^3). The product was purified by column chromatography (neutral alumina), eluted with benzene, and recrystallised from CH_2Cl_2–MeCN. Yield 65%. ^1H NMR ($CDCl_3$): δ 4.45 (t, 24 H, CH_3CH_2), 19.50 (q, 16 H, CH_3CH_2) and 22.54 (s, 4 H, *meso* H). UV/VIS (CH_2Cl_2): λ_{max}/nm 386 (Soret). μ_{eff} 2.6 μ_B (Evans' method).

[Os(ttp)Ph_2] **3**. To a solution of complex **1** (100 mg) in toluene (20 cm^3) at room temperature was added an excess of LiPh (0.5 cm^3 of a 1.5 mol dm^{-3} solution in diethyl ether). The reaction mixture was stirred at room temperature for 1 d and

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* To whom general correspondence should be addressed.

† To whom crystallographic correspondence should be addressed

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

water (10 cm^3) was added. The toluene layer was separated, dried over anhydrous $MgSO_4$, concentrated and purified on a column of neutral alumina. The product was eluted with benzene and recrystallised from CH_2Cl_2–MeCN. Yield 50%. ^1H NMR ($CDCl_3$): δ 1.73, 2.61 (s, 12 H, *p*-Me), 5.45 (m, 5 H, axial C_6H_5), 7.41 (d, 8 H, H_m), 7.82 (d, 8 H, H_o) and 7.89 (s, 8 H, pyrrolic) (Found: C, 67.3; H, 4.2; N, 5.1. $C_{60}H_{46}N_4Os{\cdot}2H_2O$ requires C, 68.7; H, 4.7; N, 5.3%). UV/VIS (CH_2Cl_2): λ_{max}/nm 412 (Soret) 468 and 611.

[Os(oep)Ph_2] **4**. This was prepared as for complex **3** from [Os(oep)Cl_2] with an excess of LiPh in toluene. The product was purified on a column of neutral alumina using CH_2Cl_2 as eluent and recrystallised from CH_2Cl_2–MeCN. Yield 35%. UV/VIS (CH_2Cl_2): λ_{max}/nm 370 (Soret). ^1H NMR ($CDCl_3$): 1.25 (m, 4 H, axial Ph), 2.06 (t, 24 H, CH_3CH_2), 3.80 (m, 3 H, axial Ph), 4.26 (q, 16 H, CH_3CH_2) and 10.67 (s, 4 H, *meso* H) (Found: C, 64.5; H, 6.3; N, 6.3. $C_{48}H_{54}N_4Os$ requires C, 65.8; H, 6.2; N, 6.4%).

[Os(ttp)$(CH_2SiMe_3)_2$] **5**. To complex **1** (50 mg) in toluene (10 cm^3) at 0 °C was added an excess of Li(CH_2SiMe_3) (0.5 cm^3 of a 1 mol dm^{-3} solution in hexane). The mixture was stirred at room temperature overnight and washed with water (2 × 10 cm^3). The toluene fraction was dried over anhydrous $MgSO_4$ and evaporated to dryness. The brown residue was extracted with hexane (5 cm^3) and loaded onto a column of neutral alumina. The product was eluted with light petroleum (b.p. 40–60 °C) and recrystallised from CH_2Cl_2–MeCN. Yield 45%. ^1H NMR ($CDCl_3$): δ −2.32, −2.29 (s, 18 H, Me_3Si), 0.07 (s, 2 H, Me_3SiCH_2), 2.60 (s, 12 H, *p*-Me), 7.41 (d, 8 H, H_m), 7.73 (s, 8 H, pyrrolic) and 7.84 (d, 8 H, H_o). UV/VIS (CH_2Cl_2): λ_{max}/nm 408 (Soret) (Found: C, 63.7; H, 5.5; N, 5.3. $C_{56}H_{58}N_4OsSi_2$ requires C, 65.0; H, 5.6; N, 5.4%).

[Os(ttp)Ph_2]BF_4 **6**. To a solution of complex **3** (35 mg) in CH_2Cl_2 (10 cm^3) was added 1 equivalent of $AgBF_4$ (8 mg) and the mixture was stirred for 1 h at room temperature then filtered. The filtrate was layered with hexane at room temperature overnight. The violet powder formed was collected and washed with hexane. Yield 25%. μ_{eff} = 1.7 μ_B (Evans' method). UV/VIS (CH_2Cl_2): λ_{max}/nm 391 (Soret). IR (cm^{-1}): 1100 (br, BF_4).

Reaction of [Os(ttp)Cl_2] *with* LiMe.—To complex **1** (50 mg) in toluene (20 cm^3) at 0 °C was added an excess of LiMe (0.5 cm^3 of a 1 mol dm^{-3} solution in Et_2O). After stirring overnight, the reaction mixture was washed with water (10 cm^3), dried over anhydrous $MgSO_4$ and evaporated to dryness, redissolved in benzene and purified by column chromatography (neutral alumina). The product was eluted with benzene and recrystallised from CH_2Cl_2–MeCN. ^1H NMR ($CDCl_3$): δ −2.60 (s, *p*-Me), 2.70 (s, *p*-Me′), 7.42 (d, H_m), 7.85 (d, H_o) and 7.90 (s, pyrrolic). UV/VIS (CH_2Cl_2): λ_{max}/nm 336, 410 (Soret), 446 and 520.

X-Ray Crystallography.—Crystals of complex **5** suitable for a diffraction study were obtained by recrystallisation from CH_2Cl_2–MeCN at 0 °C. Intensity data were collected on an Enraf–Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å). Three check reflections were monitored periodically throughout data collection and showed no significant variations. All intensity data were corrected for Lorentz polarisation effects and an absorption correction by the ψ-scan method was also applied. Crystal data and a summary of data collection and structure parameters are given in Table 1. Calculations were carried out on a MicroVax II computer using the SDP package.[14] The structure was solved by the Patterson method and refined by full-matrix least-squares analysis. The Os, Si and N atoms were refined anisotropically. Positional disorder of one $SiMe_3$ group was encountered. A partially occupied model with an occupancy factor of 0.5 for both sites was used in the final stage of the refinement to give more reasonable bond and thermal parameters. The hydrogen atoms were generated in their ideal positions (C–H 0.95 Å) except those associated with the disordered carbon atoms which were not included in the structure. Selected bond lengths and angles are listed in Table 2, final atomic coordinates in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Syntheses.—Collman *et al.*[9] first reported that reactions of osmium porphyrinate with alkyl halides gave osmium(II) carbene and alkene complexes, which were characterised by NMR spectroscopy. The crystal structure of a silylene complex of osmium porphyrin has been described recently.[15] In this work, dichloroosmium(IV) porphyrins were used as the starting

Table 1 Crystal and X-ray structural analysis data for [Os(ttp)$(CH_2SiMe_3)_2$]

Empirical formula	$C_{56}H_{58}N_4OsSi_2$
M	1033.47
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
a/Å	14.214(4)
b/Å	17.125(5)
c/Å	21.678(5)
β/°	103.55(2)
U/Å^3	5129.8
μ(Mo-Kα)/cm^{-1}	25.78
F(000)	2104
Crystal size/mm	0.21 × 0.24 × 0.40
D_c/g cm^{-3}	1.338
T/K	293
2θ range/°	2–45
Scan speed/° min^{-1}	1.08–8.24
Scan range ω/°	0.80 + 0.34 tanθ
Reflections measured	7289
Unique reflections	6959 (R_{int} = 0.029)
Observed reflections [$I > 3\sigma(I)$]	3422
Weighting scheme, *w*	$4F_o^2/[\sigma^2(F_o^2) + 0.06F_o^2]^2$
*R**	0.062
R′	0.080
Residual extrema in the final difference map/e Å^{-3}	0.865 to −0.626 close to Os

* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{\frac{1}{2}}$.

Table 2 Selected bond lengths (Å) and angles (°) for [Os(ttp)$(CH_2SiMe_3)_2$]

Os–N(1)	2.09(2)	Os–N(2)	2.03(1)
Os–N(3)	1.98(2)	Os–N(4)	2.00(1)
Os–C(21)	2.07(3)	Os–C(25)	2.17(3)
Si(1)–C(21)	1.83(3)	Si(1)–C(22)	1.92(3)
Si(1)–C(23)	1.83(3)	Si(1)–C(24)	2.06(4)
Si(2)–C(25)	1.83(3)	Si(2)–C(26)	1.90(7)
Si(2)–C(27)	1.93(7)	Si(2)–C(28)	1.88(4)
N(1)–Os–N(2)	89.0(7)	N(1)–Os–N(3)	178.3(6)
N(1)–Os–N(4)	90.8(6)	N(2)–Os–N(3)	89.6(7)
N(2)–Os–N(4)	178.5(6)	N(3)–Os–N(4)	90.7(6)
N(1)–Os–C(21)	71.1(9)	N(1)–Os–C(25)	69.2(9)
N(2)–Os–C(21)	86.4(9)	N(2)–Os–C(25)	90.4(9)
N(3)–Os–C(21)	108.0(9)	N(3)–Os–C(25)	111.6(9)
N(4)–Os–C(21)	92.2(9)	N(4)–Os–C(25)	90.0(9)
C(21)–Os–C(25)	140(1)	C(21)–Si(1)–C(22)	116(1)
C(21)–Si(1)–C(23)	110(1)	C(21)–Si(1)–C(24)	109(1)
C(22)–Si(1)–C(23)	112(1)	C(22)–Si(1)–C(24)	109(1)
C(23)–Si(1)–C(24)	101(1)	C(25)–Si(2)–C(26)	100(2)
C(25)–Si(2)–C(27)	123(2)	C(25)–Si(2)–C(28)	111(2)
C(26)–Si(2)–C(27)	109(3)	C(26)–Si(2)–C(28)	103(2)
C(27)–Si(2)–C(28)	109(2)		

Table 3 Positional parameters and their estimated standard deviations

Atom	x	y	z
Os	0.016 53(5)	0.136 09(5)	0.242 80(4)
Si(1)	−0.163 5(5)	0.219 9(5)	0.133 8(4)
Si(2)	0.141 7(6)	0.052 3(5)	0.378 5(4)
N(1)	0.093 2(9)	0.089(1)	0.180 6(6)
N(2)	0.106(1)	0.230 1(9)	0.254 4(7)
N(3)	−0.055(1)	0.184 4(8)	0.301 0(7)
N(4)	−0.073 6(9)	0.044 8(8)	0.229 2(6)
C(1)	0.075(1)	0.017(1)	0.150 2(8)
C(2)	0.148(1)	0.001(1)	0.115 2(9)
C(3)	0.210(1)	0.065(1)	0.122(1)
C(4)	0.171(1)	0.118(1)	0.163 2(8)
C(5)	0.213(1)	0.190(1)	0.186 1(9)
C(6)	0.183(1)	0.242(1)	0.224 3(9)
C(7)	0.224(1)	0.319(1)	0.243(1)
C(8)	0.177(1)	0.353(1)	0.283(1)
C(9)	0.104(1)	0.295(1)	0.291 8(9)
C(10)	0.038(1)	0.304(1)	0.328 9(9)
C(11)	−0.033(1)	0.255(1)	0.334 9(9)
C(12)	−0.100(1)	0.265(1)	0.372(1)
C(13)	−0.164(1)	0.206(1)	0.364(1)
C(14)	−0.139(1)	0.153(1)	0.318(1)
C(15)	−0.181(1)	0.081(1)	0.296 7(9)
C(16)	−0.151(1)	0.034(1)	0.255 0(9)
C(17)	−0.198(1)	−0.040(1)	0.234 4(9)
C(18)	−0.148(1)	−0.070(1)	0.194 9(9)
C(19)	−0.067(1)	−0.022(1)	0.190 7(9)
C(20)	0.003(1)	−0.033(1)	0.156 7(8)
C(5A)	0.302(1)	0.217(1)	0.161(1)
C(5B)	0.389(2)	0.211(1)	0.199(1)
C(5C)	0.469(2)	0.244(2)	0.174(1)
C(5D)	0.440(2)	0.272(1)	0.107(1)
C(5E)	0.361(2)	0.275(1)	0.070(1)
C(5F)	0.279(2)	0.249(1)	0.096(1)
C(5G)	0.534(2)	0.306(2)	0.082(2)
C(10A)	0.051(1)	0.376(1)	0.372 3(9)
C(10B)	−0.003(2)	0.440(1)	0.353(1)
C(10C)	0.018(2)	0.514(2)	0.393(1)
C(10D)	0.085(2)	0.508(1)	0.446(1)
C(10E)	0.148(2)	0.445(2)	0.471(1)
C(10F)	0.131(2)	0.371(1)	0.429(1)
C(10G)	0.111(2)	0.584(2)	0.494(1)
C(15A)	−0.271(1)	0.058(1)	0.319 4(9)
C(15B)	−0.256(2)	0.022(1)	0.380(1)
C(15C)	−0.345(2)	−0.002(2)	0.399(1)
C(15D)	−0.431(2)	0.008(1)	0.356(1)
C(15E)	−0.445(2)	0.047(1)	0.300(1)
C(15F)	−0.359(1)	0.070(1)	0.282(1)
C(15G)	−0.531(2)	−0.023(2)	0.377(1)
C(20A)	−0.010(1)	−0.108(1)	0.118 2(9)
C(20B)	−0.043(2)	−0.106(1)	0.051(1)
C(20C)	−0.052(2)	−0.179(1)	0.016(1)
C(20D)	−0.026(2)	−0.247(1)	0.049(1)
C(20E)	0.008(2)	−0.249(2)	0.114(1)
C(20F)	0.016(2)	−0.179(1)	0.150(1)
C(20G)	−0.037(2)	−0.326(1)	0.010(1)
C(21)	−0.041(2)	0.179(2)	0.152(1)
C(22)	−0.266(2)	0.149(2)	0.137(1)
C(23)	−0.185(2)	0.270(1)	0.057(1)
C(24)	−0.169(2)	0.312(2)	0.194(2)
C(25)	0.134(2)	0.063(2)	0.293(1)
C(26)	0.190(5)	0.152(4)	0.408(3)
C(27)	0.031(4)	0.029(3)	0.412(3)
C(28)	0.243(3)	−0.015(3)	0.416(2)
C(29)	0.160(5)	−0.046(4)	0.409(3)
C(30)	0.258(5)	0.106(5)	0.403(4)
C(31)	0.049(5)	0.100(4)	0.408(3)

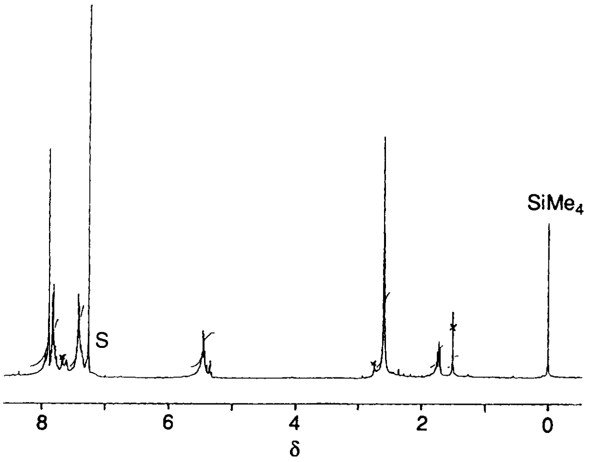


Fig. 1 Proton NMR spectrum (CDCl$_3$) of [Os(ttp)Ph$_2$]; S = solvent

materials for organoosmium(IV) porphyrins. Previously, Che *et al.*[16] showed that treatment of [Os(oep)O$_2$] with bromine yields [Os(oep)Br$_2$] in *ca.* 50% yield. We found that [Os(por)Cl$_2$] (por = ttp **1** or oep **2**) can be conveniently prepared from [Os(por)O$_2$] and SOCl$_2$ in *ca.* 80% yield. Chlorination of [Os(por)O$_2$] can also be achieved by other reagents such as Si$_2$Cl$_6$ and oxalyl chloride albeit in lower yields ($<$ 50%).

The dichloride compounds **1** and **2** are paramagnetic with measured magnetic moments of *ca.* 2.7 μ_B, suggesting a $S = 1$ ground-state electronic configuration. Similar magnetic moments have been found for related dialkoxoosmium(IV) porphyrins.[16] Like other paramagnetic osmium(IV) porphyrins, **1** and **2** show well resolved contact-shifted ^{1}H NMR spectra. The contact shifts presumably arise from temperature-independent paramagnetism and are temperature invariant. The pyrrolic resonance for **1** is shifted considerably more upfield than that for [Os(ttp)(OR)$_2$][16–18] (at δ *ca.* 4.7) but less than that for [Ru(tpp)Cl$_2$].[7b]

Interactions of complexes **1** and **2** with an excess of LiPh in toluene give diphenylosmium(IV) compounds **3** and **4**, respectively, in good yields. Alkyllithium is the preferred alkylating agent for dialkylosmium porphyrins [equation (1)]

$$[\mathrm{Os(por)Cl_2}] + (\text{excess})\ \mathrm{LiPh} \longrightarrow [\mathrm{Os(por)Ph_2}] + 2\mathrm{LiCl} \quad (1)$$

(por = ttp **3** or oep **4**)

as reactions with Grignard reagents usually led to a mixture of products. The ^{1}H NMR spectrum of **3** in CDCl$_3$ (Fig. 1) shows the pyrrolic resonance at the position expected for diamagnetic porphyrins. The signals for axial phenyl protons are shifted upfield due to the ring current of the porphyrin.

Treatment of complex **1** with an excess of LiMe in toluene gave the dimethyl compound methyl resonance at δ −1 together with an unidentified species as evidenced by ^{1}H NMR spectroscopy (two *p*-methyl signals). We have not yet been able to separate these two species by chromatography or recrystallisation.

Reaction of complex **1** with an excess of Li(CH$_2$SiMe$_3$) afforded hexane-soluble [Os(ttp)(CH$_2$SiMe$_3$)$_2$] **5**. Its structure has been confirmed by X-ray crystallography. A perspective view of the molecule is shown in Fig. 2. The complex has a distorted-octahedral geometry. The Os–N(pyrrole) bond distances are normal by comparison with those for [Os(tpp)(OPr^i)$_2$][17] and [Os(tpp)(SC$_6$F$_4$H)$_2$].[19] The Os–C bond distances are 2.07 and 2.17 Å. Of particular note, the C–Os–C′ bond is bent with an angle of *ca.* 140°. This can be explained in terms of the steric repulsion between the SiMe$_3$ group of the axial alkyl with the *meso* phenyl protons, as illustrated by the space-filling model in Fig. 3.

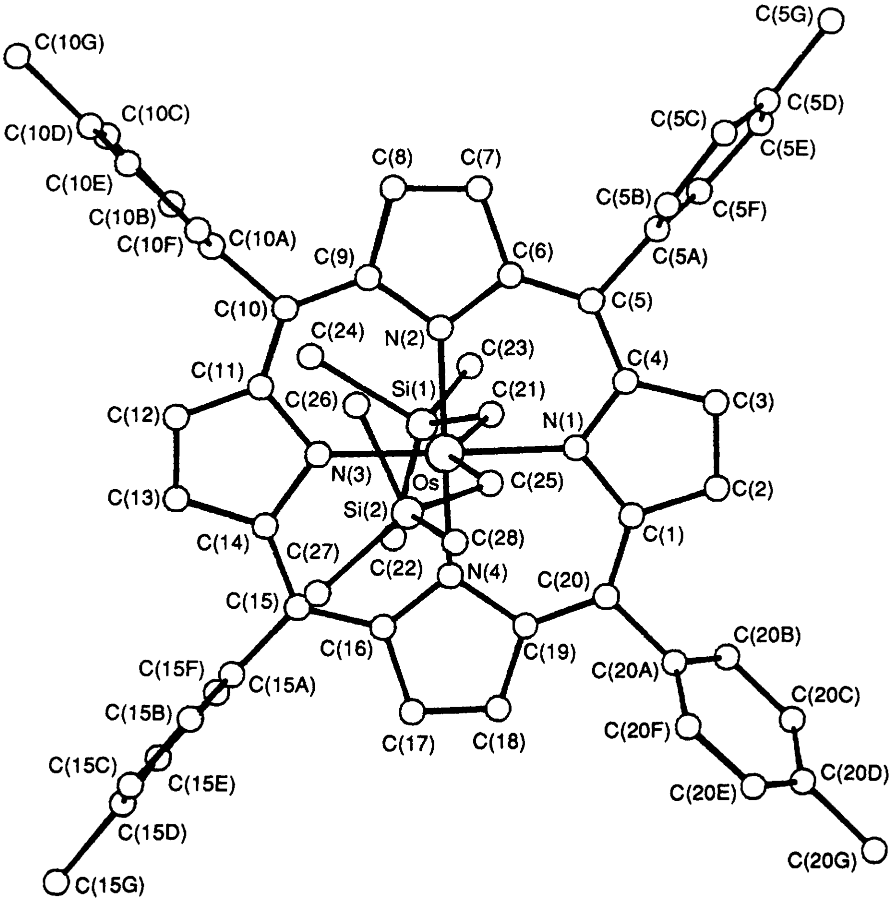


Fig. 2 A perspective view of $[Os(ttp)(CH_2SiMe_3)_2]$

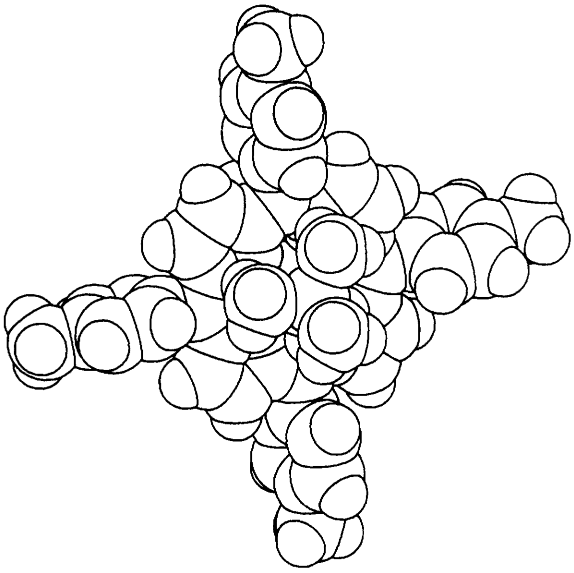
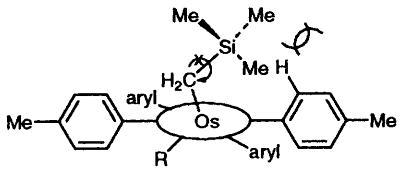


Fig. 3 Space-filling model for $[Os(ttp)(CH_2SiMe_3)_2]$

The room-temperature ^1H NMR spectrum of complex **5** shows one pyrrolic signal at δ 7.73 and two doublets at δ 7.41 and 7.84, assignable to the *ortho* and *meta meso*-phenyl protons, respectively, indicating that the solution structure of the molecule has D_{4h} symmetry. However, two methyl signals for the $SiMe_3$ group at δ −2.29 and −2.32 and with relative intensity 1:2 were observed. These two resonances do not coalesce at higher temperature, thus ruling out the possibility of rotamers. It seems likely that non-bonding repulsion between the $SiMe_3$ group and phenyl *o*-protons prevents free rotation around the Si–C bond. As a result, two methyls of $SiMe_3$ point away from and one toward the *meso*-phenyl ring.

The dialkylosmium(IV) compounds are stable in solution and do not show any reactivity toward small molecules such as CO. In contrast to $[Ru(por)R_2]$, which undergoes thermolysis to give alkyl and alkylidene ruthenium(III) species, dialkylosmium(IV) compounds are thermally stable.



Electrochemistry of Osmium(IV) *Porphyrins*.—The reduction potentials of the osmium(IV) porphyrins were determined by cyclic voltammetry and are listed in Table 4. The cyclic voltammogram of complex **3** in CH_2Cl_2 shown in Fig. 4 consists of one reversible oxidation couple and two reversible reduction couples. The oxidation couple at 0.32 V is assigned to the metal-centred Os^V–Os^{IV} couple [equation (2)] because oxidation

$$[Os(ttp)Ph_2]^+ + e \longrightarrow [Os(ttp)Ph_2] \qquad (2)$$

of the porphyrin ring is known to occur at higher potentials.[2,20] The Os^V–Os^{IV} potential for **3** is comparable to that found for $[Os(ttp)(OEt)_2]$[16] at 0.29 V but is less anodic than that for the dichloride **1** (0.77 V) and $[Os(tpp)(SPh)_2]$[16] (0.56 V, tpp = 5,10,15,20-tetraphenylporphyrinate). This demonstrates that the ability to stabilise Os^V decreases in the order OR ≈ Ph > RS > Cl. The first reduction for **3** is tentatively assigned as the

Table 4 Reduction potentials ($E°$)[a] for osmium(IV) porphyrins

Compound	$E°$/V *vs.* ferrocene–ferrocenium Oxidation	Reduction
$[Os(ttp)Cl_2]$	0.77	−0.33, −1.42
$[Os(ttp)Ph_2]$	0.32	−1.01, −1.58
$[Os(ttp)(OEt)_2]$[b]	0.29	−1.15
$[Os(tpp)(SPh)_2]$[b]	0.56[c]	−1.00
$[Os(oep)Cl_2]$	0.7	−0.54, −1.69
$[Os(oep)Ph_2]$	1.04[c], 0.04	−1.24, −1.62,[c] −1.96
$[Os(oep)(SPh)_2]$[b]	0.31[c]	−1.05
$[Ru(oep)Ph_2]$[d]	0.71	−1.00, −1.48

[a] Measured in CH_2Cl_2 with 0.1 mol dm^{-3} $[NBu^n_4][BF_4]$ as supporting electrolyte; scan rate = 100 mV s^{-1}. [b] Ref. 16. [c] Irreversible. [d] Ref. 8(*d*); potential *vs.* Ag–AgCl.

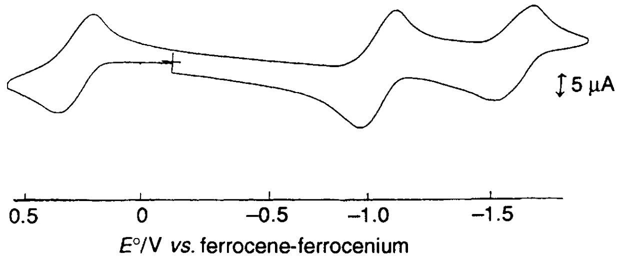


Fig. 4 Cyclic voltammogram of $[Os(ttp)Ph_2]$ in CH_2Cl_2 (0.1 mol dm^{-3} $[NBu_4][BF_4]$) at a glassy carbon electrode. Scan rate 100 mV s^{-1}

metal-centred couple Os^{IV}–Os^{III} [equation (3)], by comparison

$$[Os^{IV}(ttp)Ph_2] + e \longrightarrow [Os^{III}(ttp)Ph_2]^- \qquad (3)$$

with the related $[Os(ttp)(OEt)_2]$.[16] The second is tentatively assigned as the ligand-centred reduction of the porphyrin ring [equation (4)].

$$[Os(ttp)Ph_2]^- + e \longrightarrow [Os(ttp)Ph_2]^{2-} \qquad (4)$$

The cyclic voltammogram for complex **4** shows two oxidation and three reduction couples. The first reversible oxidation at 0.04 V is assigned to the metal-centred Os^V–Os^{IV} couple and the second irreversible oxidation at 1.04 V is tentatively assigned as the ligand-centred oxidation. The Os^V–Os^{IV} reduction potential for **4** is less anodic than that for **3**, consistent with the higher basicity of oep relative to ttp. It is also noteworthy that $E°(Os^V–Os^{IV})$ is considerably less positive than $E°(Ru^V–Ru^{IV})$ for the diphenyl oep complexes (see Table 4), demonstrating the greater stability of Os^V compared to Ru^V. The first reversible reduction for **4** at −1.24 V is assigned as the Os^{IV}–Os^{III} couple. The irreversible reduction wave and the reversible reduction couple at −1.62 and −1.96 V are tentatively assigned to ligand-centred reduction leading to the formation of porphyrin anion and dianion radical, respectively.

Osmium(V) *Porphyrins*.—The easily accessible Os^V–Os^{IV} formal potential for complex **3** suggests that diphenylosmium(V) porphyrin can be generated by chemical oxidation and is stable enough for isolation. Fig. 5 shows the optical spectral changes upon titration of **3** with $[NH_4]_2[Ce(NO_3)_6]$ in CH_2Cl_2–MeCN. On addition of Ce^{IV} to **3** the Soret band for **3** at 412 nm decreases in intensity and a new species **6** with a Soret band at 391 nm is formed gradually. The reaction was complete when an approximately equimolar amount of Ce^{IV} had been added. The lack of absorption in the 600–700 nm region argues against the formation of a porphyrin cation radical. A similar result has been reported for the oxidation of $[Os(por)(OEt)_2]$.[16] Addition of $N_2H_4{\cdot}H_2O$ to **6** immediately regenerates the starting $[Os(ttp)Ph_2]$ almost quantitatively. Apparently, Os^{IV} is oxidised by Ce^{IV} to Os^V, which can be reduced reversibly back to Os^{IV} (Scheme 1).

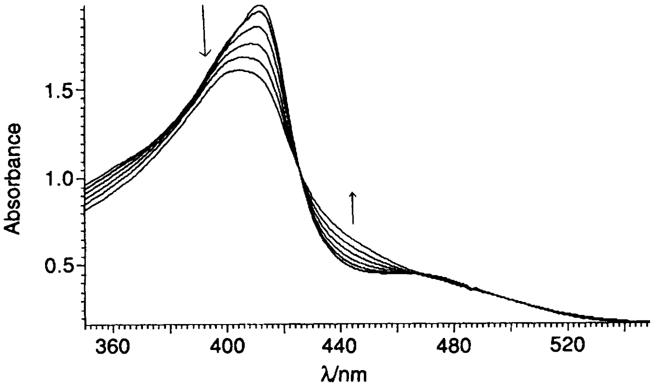


Fig. 5 Optical spectra changes upon titration of $[Os(ttp)Ph_2]$ with $[NH_4]_2[Ce(NO_3)_6]$ in CH_2Cl_2–MeCN (2:1)

$$[Os(ttp)Ph_2] + Ce^{IV} \longrightarrow [Os(ttp)Ph_2]^+ + Ce^{III}$$

$$[Os(ttp)Ph_2]^+ + e \longrightarrow [Os(ttp)Ph_2]$$

Scheme 1

To isolate the diphenylosmium(V) compound we attempted the stoichiometric reaction between $[Os(ttp)Ph_2]$ and $AgBF_4$ in CH_2Cl_2. This gave an identical osmium(V) species to that obtained in the cerium(IV) oxidation. Recrystallisation from CH_2Cl_2–hexane afforded air-stable solid $[Os(ttp)Ph_2]BF_4$. The IR spectrum does not show any absorption around 850 cm^{-1} thus ruling out the possibility of formation of oxoosmium species. The measured μ_{eff} for **6** of *ca.* 1.7 μ_B is consistent with a low-spin d^3 ground electronic configuration for Os^V. It should be noted that oxidation of the analogous $[Os(por)(OR)_2]$ by Ce^{IV}, though reversible on the cyclic voltammetric time-scale, led to isolation of $[Os(por)O_2]$ presumably *via* C–O bond cleavage in the alkoxide ligands.[16] Apparently the high affinity of Os^V for the strongly π-donating oxo group provides the driving force for the C–O bond scission. Osmium(V) organometallic compounds are very rare. The only example in the literature is the homoleptic aryl $[Os(2\text{-}MeC_6H_4)_4]BF_4$, which is synthesised by reaction of $Os(2\text{-}MeC_6H_4)_4$ with $AgBF_4$.[21]

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References

1 P. J. Brothers and J. P. Collman, *Acc. Chem. Res.*, 1986, **19**, 209.
2 R. Guilard and K. M. Kadish, *Chem. Rev.*, 1988, **88**, 1121; R. Guilard, C. Lecomte and K. M. Kadish, *Struct. Bonding* (*Berlin*), 1987, **64**, 205.
3 J. Halpern, *Science*, 1985, **227**, 869; L. G. Marzilli, in *Bioinorganic Catalysis*, ed. J. Reedijk, Marcel Dekker, New York, 1993, p. 227 and refs. therein.
4 D. Mansuy and P. Battioni, in *Activation and Functionalization of Saturated Alkanes*, ed. C. L. Hill, Wiley, New York, 1989, p. 195 and refs. therein.
5 H. J. Callot, F. Metz and C. Piechoki, *Tetrahedron*, 1982, 2365.
6 D. N. Reynolds and L. K. Woo, *J. Am. Chem. Soc.*, 1993, **115**, 2511.
7 (*a*) C. Sishta, M. Ke, B. R. James and D. Dolphin, *J. Chem. Soc., Chem. Commun.*, 1986, 787; (*b*) M. Ke, C. Sishta, B. R. James, D. Dolphin, J. W. Sparapany and J. A. Ibers, *Inorg. Chem.*, 1991, **30**, 4766.
8 J. W. Seyler and C. R. Leidner, *J. Chem. Soc., Chem. Commun.*, 1989,

1794; (*b*) J. W. Seyler and C. R. Leidner, *Inorg. Chem.*, 1990, **29**, 3636; (*c*) J. W. Seyler, L. K. Safford, P. E. Fanwick and C. R. Leidner, *Inorg. Chem.*, 1992, **31**, 1545; (*d*) J. W. Seyler, L. K. Safford and C. R. Leidner, *Inorg. Chem.*, 1992, **31**, 4300.

9 J. P. Collman, P. J. Brothers, L. McElwee-White, E. Rose and L. J. Wright, *J. Am. Chem. Soc.*, 1985, **107**, 4570; J. P. Collman, L. McElwee-White, P. J. Brothers and E. Rose, *J. Am. Chem. Soc.*, 1986, **108**, 1332.

10 K. L. Kunze and P. R. Oritz de Motellano, *J. Am. Chem. Soc.*, 1983, **105**, 1380; P. R. Oritz de Motellano, *Acc. Chem. Res.*, 1987, **20**, 289 and refs. therein.

11 C. M. Che, C. K. Poon, W. C. Chung and H. B. Gray, *Inorg. Chem.*, 1985, **24**, 1277.

12 J. W. Buchler and P. D. Smith, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 341.

13 D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

14 SDP Structure Determination Package, Enraf–Nonius, Delft, 1985.

15 (*a*) L. K. Woo and D. A. Smith, *Organometallics*, 1992, **11**, 2344; (*b*) L. K. Woo, D. A. Smith and V. G. Young, *Organometallics*, 1991, **10**, 3977.

16 C. M. Che, W. H. Leung and W. C. Chung, *Inorg. Chem.*, 1990, **29**, 1841.

17 C. M. Che, J. S. Huang, Z. Y. Li, C. K. Poon, W. F. Tong, T. F. Lai, M. C. Cheng, C. C. Wang and Y. Wang, *Inorg. Chem.*, 1992, **31**, 5220.

18 J. W. Buchler and P. D. Smith, *Chem. Ber.*, 1976, **109**, 1465.

19 J. P. Collman, D. S. Bohle and A. K. Powell, *Inorg. Chem.*, 1993, **32**, 4004.

20 K. M. Kadish, *Prog. Inorg. Chem.*, 1986, **34**, 435.

21 J. Arnold, G. Wilkinson, B. Hussain and M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.*, 1988, 1349; *J. Chem. Soc., Dalton Trans.*, 1989, 2149.

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