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Properties and Molecular Structures of Osmium(II) Porphyrin Carbene Complexes: (5,10,15,20-Tetra-*p*-tolylporphyrinato)osmium Di-*p*-tolylmethylidene and (5,10,15,20-Tetra-*p*-tolylporphyrinato)osmium (Trimethylsilyl)methylidene

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The first molecular structures of two (porphyrinato)osmium(II) alkylidene complexes are described. The carbene fragments of (5,10,15,20-tetra-*p*-tolylporphyrinato)osmium (trimethylsilyl)methylidene (**1**) and (5,10,15,20-tetra-*p*-tolylporphyrinato)osmium di-*p*-tolylmethylidene (**2**) adopt different conformations in the solid state. With respect to the porphyrin ring nitrogen atoms, a staggered conformation is found for the complex **1** carbene moiety (d_{Os-C} = 1.79(2) Å, torsion angle ϕ = 23(1)°). A similar conformation appears in complex **2** (d_{Os-C} = 1.865(5) Å, torsion angle ϕ = 28.4(4)°). The carbene fragments in the two molecular structures are distorted and do not possess ideal sp^2 geometries. Complex **1** displays a large distortion with an Os−C−Si angle of 142(2)°. The complex **2** carbene moiety has a C_{Ar}−C−C_{Ar} angle of 113.0(4)°. Complex **1**, $C_{52}H_{46}N_4OsSi{\cdot}OC_4H_8$, crystallizes with a *trans*-coordinated molecule of THF as **1·THF** in the monoclinic space group $P2_1/n$ with a = 13.954(2) Å, b = 9.522(2) Å, c = 17.969(2) Å, β = 101.42(1)°, V = 2340.3(6) Å^3, Z = 2, $R1$ = 0.0532, and $wR2$ = 0.1276. Complex **2**, $C_{63}H_{50}N_4Os{\cdot}OC_4H_8{\cdot}C_7H_8{\cdot}{}^1/_2OC_4H_8$, crystallizes as a *trans*-THF adduct, **2·THF**, in the monoclinic space group $C2/c$ with a = 28.003(6) Å, b = 14.385(3) Å, c = 33.748(8) Å, β = 114.51(2)°, V = 12370(5) Å^3, Z = 8, $R1$ = 0.0389, and $wR2$ = 0.1165. Other metrical parameters and spectroscopic properties of these complexes are discussed.

Introduction

We recently reported that (*meso*-tetra-*p*-tolylporphyrinato)osmium complexes such as $Os_2(TTP)_2$, $Os(TTP)(py)_2$, and Os(TTP)(CO)(py)[2] are able to catalyze C−C bond-forming reactions in the stereoselective formation of olefins by the condensation of diazoalkanes[3a] and the cyclopropanation of alkenes with diazoalkanes.[3b] Osmium−carbene species, (TTP)Os=CRR′, may be important intermediates in these reactions, and several have been isolated and characterized analytically and spectroscopically. The Os porphyrin carbene complexes are efficient catalysts for cyclopropanation. Moreover, these complexes are also active in the stoichiometric cyclopropanation of alkenes (Scheme 1).

Although a series of (porphyrinato)metal carbene complexes have been isolated[4] in past years, only two have been characterized by single-crystal X-ray diffraction analysis.[5] Molecular structures of osmium porphyrin carbene complexes are relevant to our study of catalytic reactions mediated by osmium porphyrin complexes and may provide important information with regard to both mechanistic and reactivity aspects. Previous investigations of cyclopropanation reactions[6] catalyzed by rhodium(III) metalloporphyrin complexes provided spectroscopic information on some of the reaction intermediates.[6b,c] However, none of the key rhodium porphyrin carbene species have been fully characterized structurally because of their very transient nature. We report herein the first X-ray structural characterizations of two osmium porphyrin carbene complexes, *trans*-(TTP)Os=$CHSiMe_3$·THF (**1·THF**) and *trans*-(TTP)Os=$C(p\text{-}CH_3\text{-}C_6H_4)_2$·THF (**2·THF**).

Results and Discussion

Preparation of *trans*-(TTP)Os=$CHSiMe_3$·THF (1·THF) and *trans*-(TTP)Os=$C(C_6H_4\text{-}p\text{-}CH_3)_2$·THF

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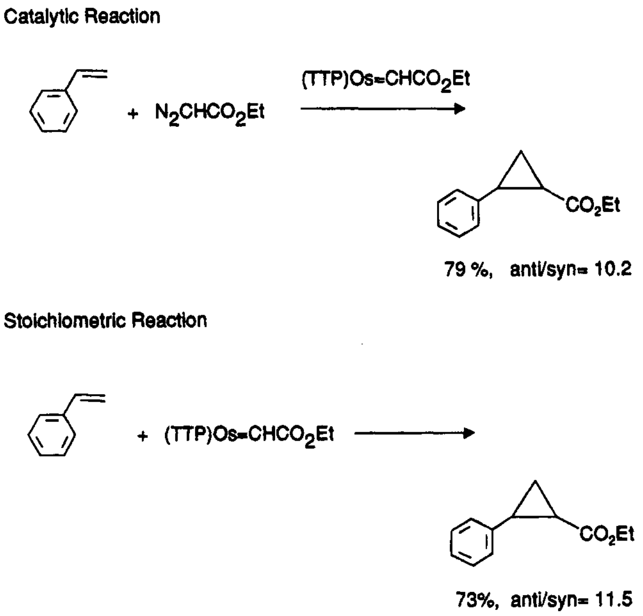
Table 1. Crystallographic Data

	1	2
empirical formula	$C_{52}H_{46}N_4OsSi{\cdot}OC_4H_8$	$C_{63}H_{50}N_4Os{\cdot}OC_4H_8{\cdot}C_7H_8{\cdot}{}^1/_2OC_4H_8$
cryst size (mm)	0.44 × 0.18 × 0.09	0.35 × 0.35 × 0.12
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$
a (Å)	13.954(2)	28.003(6)
b (Å)	9.522(2)	14.385(3)
c (Å)	17.969(2)	33.748(8)
β (deg)	101.42(1)	114.51(2)
V (Å^3)	2340.3(6)	12370(5)
Z	2	8
fw	1017.32	1253.53
density (calcd) (Mg/m^3)	1.444	1.345
μ (mm^{-1})	5.729	4.270
diffractometer	Siemens P4/RA	Siemens P4/RA
radiation	Cu Kα (λ = 1.541 78 Å)	Cu Kα (λ = 1.541 78 Å)
temp (K)	213(1)	223(1)
monochromator	graphite	graphite
2θ range (deg)	5.0−115.0	5.0−115.0
scan type	$2\theta-\theta$	$2\theta-\theta$
no. of reflns collected	6061	18 182
no. of indep rflns	3056 (R_{int} = 0.0179)	8334 (R_{int} = 0.0432)
no. of obsd rflns	3056 ($I \geq 2\sigma(I)$)	7833 ($I \geq 2\sigma(I)$)
no. of params refined	333	720
$R1^a$	0.0532	0.0389
$wR2^b$	0.1276	0.1185
goodness of fit^c	1.447	1.107
largest and mean Δ/σ	−0.011, 0.001	0.005, 0.000
largest diff peak (e/Å^3)	0.615	1.01
largest diff hole (e/Å^3)	−1.530	−1.28

[a] $R1 = \sum||F_o - |F_c||\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$; $w = 1/[\sigma^2(F_o^2) + (XP)^2 + (UP)]$ where $P = (\mathrm{MAX}(F_o^2,0) + 2F_c^2)/3$ and X and Y are adjusted for each refinement. [c] GOF = $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{0.5}$.

Scheme 1



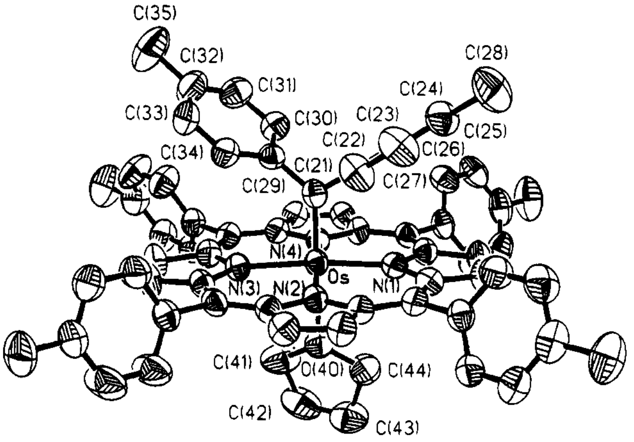


Figure 1. ORTEP drawing of *trans*-(TTP)Os=C(C_6H_4-*p*-CH_3)$_2$(THF). The thermal ellipsoids are drawn at the 50% probability level.

(2·THF). Complexes **1** and **2** were prepared by treating $Os_2(TTP)_2$ with the corresponding diazoalkanes $N_2CHSiMe_3$ and $N_2C(p\text{-}CH_3\text{-}C_6H_4)_2$ (eq 1) and purified by chromatography on Florisil.[3a] Complexes **1** and **2** were then recrystallized from a mixture of toluene, THF, and hexane to afford purple crystals of the THF adducts suitable for single-crystal X-ray structure analysis.

$$Os_2(TTP)_2 + 2\,N_2CRR' \xrightarrow{\text{Toluene}} 2(TTP)Os{=}CRR' \;+\; 2\,N_2 \qquad (1)$$

1, R= H, R'= Si(CH$_3$)$_3$, 77%
2, R= R'= *p*-CH$_3$C$_6$H$_4$, 96%

Molecular Structures of (TTP)Os=CHSiMe$_3$ and (TTP)Os=C(C$_6$H$_4$-*p*-CH$_3$)$_2$. Crystallographic data for the structure determinations of both compounds are given in Table 1. Fractional coordinates for non-hydrogen atoms are listed in Tables 2 ((TTP)Os=CHSiMe$_3$) and 3 ((TTP)Os=C(C$_6$H$_4$-*p*-CH$_3$)$_2$).

The ditolylcarbene complex **2** crystallizes in the monoclinic space group *C2/c* with eight molecules per unit cell. Figure 1 illustrates the molecular structure and atom-labeling scheme. Selected bond distances and angles are given in Table 4. As expected for a six-coordinate complex, the porphyrin ligand in this complex is nearly planar. The largest deviation occurs at N(2), which is 0.069 Å out of the mean porphyrin plane. The coordination sphere of the osmium atom approaches an ideal octahedral geometry with bond angles between *cis*-related ligands ranging from 84.2 to 94.2°. The osmium atom is slightly out of the mean porphyrin plane 0.14 Å toward the carbene ligand. The Os—O(40) distance of 2.328(3) Å in **2** is similar to the distance

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for *trans*-(TTP)Os=CH(SiMe$_3$)·THF

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
Os	103(2)	239(2)	43(1)	24(1)	C(52)	−3181(8)	2996(12)	977(8)	75(4)
Si	1684(5)	986(8)	1730(4)	45(1)	C(53)	−4088(9)	3521(13)	1046(9)	88(4)
C(21)	826(16)	1219(28)	805(14)	38(7)	C(54)	−4921(8)	3096(13)	607(8)	69(4)
C(22)	2780(14)	130(25)	1567(13)	69(7)	C(55)	−4858(8)	2045(16)	107(8)	84(4)
C(23)	2051(18)	2694(24)	2198(15)	68(7)	C(56)	−3957(7)	1513(15)	23(7)	74(4)
C(24)	1055(16)	7(26)	2363(12)	67(6)	C(57)	−5908(9)	3716(16)	664(10)	113(6)
O	−868(11)	−1044(17)	−1009(9)	38(5)	C(6)	−1674(6)	2142(9)	−138(5)	37(2)
C(31)	−1184(25)	−281(27)	−1711(11)	80(9)	C(7)	−2002(6)	3439(9)	−528(5)	43(2)
C(32)	−1921(30)	−1313(32)	−2140(22)	131(19)	C(8)	−1346(6)	3841(9)	−937(5)	41(2)
C(33)	−2079(31)	−2336(48)	−1647(19)	153(20)	C(9)	−575(6)	2795(9)	−821(5)	37(2)
C(34)	−1507(17)	−2106(21)	−919(12)	61(6)	C(10)	230(6)	2816(10)	−1171(5)	40(2)
N(1)	−964(5)	−560(7)	669(4)	36(2)	C(101)	341(6)	4055(8)	−1648(5)	33(2)
N(2)	−788(5)	1738(8)	−346(4)	40(2)	C(102)	508(7)	5369(9)	−1325(5)	45(2)
C(1)	−940(6)	−1756(9)	1097(5)	39(2)	C(103)	604(7)	6547(11)	−1771(6)	53(3)
C(2)	−1787(7)	−1794(10)	1448(6)	51(3)	C(104)	563(7)	6433(10)	−2534(6)	48(2)
C(3)	−2299(7)	−586(10)	1223(6)	51(3)	C(105)	398(7)	5120(11)	−2861(5)	51(2)
C(4)	−1817(6)	174(10)	722(5)	41(2)	C(106)	279(7)	3957(10)	−2432(5)	46(2)
C(5)	−2136(6)	1406(9)	348(5)	41(2)	C(107)	684(9)	7686(13)	−3010(7)	77(4)
C(51)	−3112(6)	1980(9)	459(5)	41(2)					

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for *trans*-(TTP)Os=C(*p*-CH$_3$-C$_6$H$_4$)$_2$·THF

atom	*x*	*y*	*z*	*U*(eq)[a]	atom	*x*	*y*	*z*	*U*(eq)[a]
Os	3157(1)	3627(1)	1423(1)	40(1)	C(17)	1942(2)	1571(4)	1066(2)	51(1)
N(1)	3734(2)	2846(3)	1379(1)	44(1)	C(18)	2323(2)	1050(4)	1026(2)	51(1)
N(2)	3683(2)	4689(3)	1685(1)	43(1)	C(19)	2776(2)	1631(3)	1141(2)	43(1)
N(3)	2604(2)	4366(3)	1533(1)	44(1)	C(20)	3252(2)	1353(3)	1131(2)	47(1)
N(4)	2669(2)	2500(3)	1256(1)	46(1)	C(201)	3283(2)	371(3)	1008(2)	52(1)
C(1)	3695(2)	1922(3)	1246(2)	48(1)	C(202)	2948(2)	44(4)	600(2)	63(2)
C(2)	4190(2)	1630(4)	1243(2)	56(1)	C(203)	2955(3)	−896(4)	497(2)	71(2)
C(3)	4519(2)	2363(4)	1378(2)	55(1)	C(204)	3288(3)	−1515(4)	794(3)	75(2)
C(4)	4244(2)	3123(4)	1465(2)	48(1)	C(205)	3619(3)	−1183(4)	1192(3)	75(2)
C(5)	4454(2)	4002(4)	1615(2)	47(1)	C(206)	3614(2)	−258(4)	1303(2)	63(2)
C(51)	5002(2)	4207(3)	1663(2)	49(1)	C(207)	3283(3)	−2532(5)	687(3)	102(3)
C(52)	5401(2)	4418(4)	2058(2)	56(1)	C(21)	2923(2)	4061(3)	852(2)	44(1)
C(55)	5607(2)	4421(5)	1337(2)	72(2)	C(22)	3276(2)	4165(3)	616(2)	45(1)
C(54)	6009(2)	4634(4)	1736(2)	66(2)	C(23)	3325(2)	3466(4)	359(2)	60(2)
C(53)	5897(2)	4630(4)	2096(2)	62(2)	C(24)	3649(3)	3570(4)	140(2)	66(2)
C(56)	5111(2)	4215(4)	1299(2)	64(2)	C(25)	3923(2)	4384(5)	171(2)	67(2)
C(57)	6563(2)	4840(5)	1782(3)	87(2)	C(26)	3872(3)	5076(5)	429(2)	76(2)
C(6)	4191(2)	4726(3)	1716(2)	47(1)	C(27)	3562(2)	4974(4)	655(2)	69(2)
C(7)	4390(2)	5641(3)	1845(2)	53(1)	C(28)	4276(3)	4481(6)	−68(3)	101(2)
C(8)	4015(2)	6150(4)	1892(2)	55(1)	C(29)	2376(2)	4348(3)	586(2)	47(1)
C(9)	3568(2)	5560(3)	1789(2)	46(1)	C(30)	2008(2)	3721(4)	319(2)	56(1)
C(10)	3091(2)	5835(3)	1792(2)	46(1)	C(31)	1498(2)	4005(5)	66(2)	70(2)
C(101)	3044(2)	6830(4)	1904(2)	51(1)	C(32)	1342(2)	4899(5)	74(2)	80(2)
C(102)	3298(3)	7166(4)	2315(2)	88(2)	C(33)	1706(3)	5513(5)	349(2)	75(2)
C(103)	3268(3)	8099(4)	2407(2)	92(2)	C(34)	2214(2)	5258(4)	598(2)	59(1)
C(104)	3000(3)	8731(4)	2090(2)	60(2)	C(35)	784(3)	5189(7)	−213(3)	127(3)
C(105)	2748(3)	8393(4)	1683(2)	71(2)	O(40)	3432(1)	3051(2)	2128(1)	54(1)
C(106)	2768(2)	7450(4)	1586(2)	66(2)	C(41)	3059(3)	2912(7)	2319(2)	88(2)
C(107)	3004(3)	9747(4)	2192(2)	79(2)	C(42)	3331(3)	2285(5)	2708(2)	92(2)
C(11)	2652(2)	5272(3)	1681(2)	48(1)	C(43)	3884(3)	2177(5)	2754(2)	89(2)
C(12)	2165(2)	5543(4)	1705(2)	61(1)	C(44)	3853(3)	2398(5)	2308(2)	77(2)
C(13)	1837(2)	4814(4)	1573(2)	61(2)	C(71)	1114(4)	7808(6)	617(3)	271(4)
C(14)	2104(2)	4073(4)	1460(2)	51(1)	C(70)	1539(5)	8369(10)	555(6)	271(4)
C(15)	1888(2)	3195(4)	1304(2)	48(1)	C(72)	596(4)	7865(8)	309(3)	271(4)
C(151)	1334(2)	3026(4)	1230(2)	53(1)	C(73)	206(4)	7351(9)	365(4)	271(4)
C(152)	1212(2)	2382(4)	1482(2)	62(1)	C(74)	335(5)	6780(8)	730(5)	271(4)
C(153)	701(2)	2196(5)	1403(2)	71(2)	C(75)	855(6)	6724(8)	1038(4)	271(4)
C(154)	294(2)	2631(5)	1077(2)	78(2)	C(76)	1244(4)	7238(8)	981(3)	271(4)
C(155)	412(2)	3263(5)	828(2)	87(2)	O(80)	0	5102(15)	2500	403(9)
C(156)	920(2)	3456(5)	893(2)	75(2)	C(81)	199(11)	4619(13)	2220(7)	403(9)
C(157)	−268(3)	2409(6)	995(3)	115(3)	C(82)	137(13)	3637(13)	2349(10)	403(9)
C(16)	2153(2)	2478(3)	1217(2)	47(1)					

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

reported in the literature for a diethylsilylene complex, *trans*-(TTP)Os=SiEt$_2$THF·THF (Os—O$_{THF}$, d = 2.40(2) Å).[7] The carbene fragment is slightly distorted since the angle formed by C(22)—C(21)—C(29) is 113.0(4)°, a value which is significantly smaller than the 120° angle for ideal sp^2 hybridization.[8] The distortion of this carbene fragment can be reasonably explained by the

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Table 4. Selected Bond Distances (Å) and Angles (deg) for *trans*-(TTP)Os=C(*p*-CH_3-C_6H_4)$_2$·THF

Os—N(1)	2.024(4)	Os—C(21)	1.865(5)
Os—N(2)	2.050(4)	Os—O(40)	2.328(3)
Os—N(3)	2.036(4)	C(21)—C(22)	1.512(7)
Os—N(4)	2.042(4)	C(21)—C(29)	1.478(7)
N(1)—Os—N(2)	89.6(2)	N(4)—Os—C(21)	94.2(2)
N(1)—Os—N(3)	174.0(2)	N(1)—Os—O(40)	86.7(1)
N(2)—Os—N(3)	89.8(2)	N(2)—Os—O(40)	87.1(1)
N(1)—Os—N(4)	90.2(2)	N(3)—Os—O(40)	87.3(1)
N(2)—Os—N(4)	171.3(2)	N(4)—Os—O(40)	84.2(1)
N(3)—Os—N(4)	89.5(2)	C(21)—Os—O(40)	178.4(2)
N(1)—Os—C(21)	93.4(2)	Os—C(21)—C(22)	123.5(3)
N(2)—Os—C(21)	94.5(2)	Os—C(21)—C(29)	123.6(3)
N(3)—Os—C(21)	92.6(2)	C(22)—C(21)—C(29)	113.0(4)

steric interactions between the two substituents of the carbene moiety and the tolyl groups of the porphyrin ligand. In addition, the two *p*-tolyl groups of the carbene ligand have their mean planes perpendicular to the plane formed by Os—C(27)—C(21)—C(29). This presumably decreases the intramolecular strain. From the projection of the carbene fragment on the mean plane of the porphyrin, it is clear that the conformation of the carbene is staggered with respect to the Os—N bonds of the (TTP)Os·THF fragment (Figure 2). In solution, such a conformation is likely to be disfavored by steric interactions with the tolyl groups at the four *meso* porphyrin positions. In the case of the unique structure known for a rhodium(II) porphyrin carbene, (TPP)Rh(=C(NHCH$_2$Ph)$_2$)·CNCH$_2$Ph,[5] the bulky carbene fragment adopts a nearly staggered conformation with respect to the rhodium–nitrogen bonds. In addition, the Rh carbene ligand has an ideal trigonal geometry. The same staggered conformation is adopted in the (porphyrinato)iron carbene complex (TPP)-Fe=CCl$_2$, first isolated and structurally characterized by Mansuy and co-workers.[4a,5a]

In complex **2**, the Os—C(21) distance of 1.865(5) Å is slightly shorter than typical osmium–carbon double bonds reported for other molecular structures of osmium carbene complexes. For example, the Os=C distances in $Cl_2(CO)(PPh_3)_2Os(=CHPh)_2$ and $Cl(NO)(PPh_3)_2Os(=CH_2)_3$ are 1.94(1)[9a] and 1.92(1) Å,[9b] respectively.

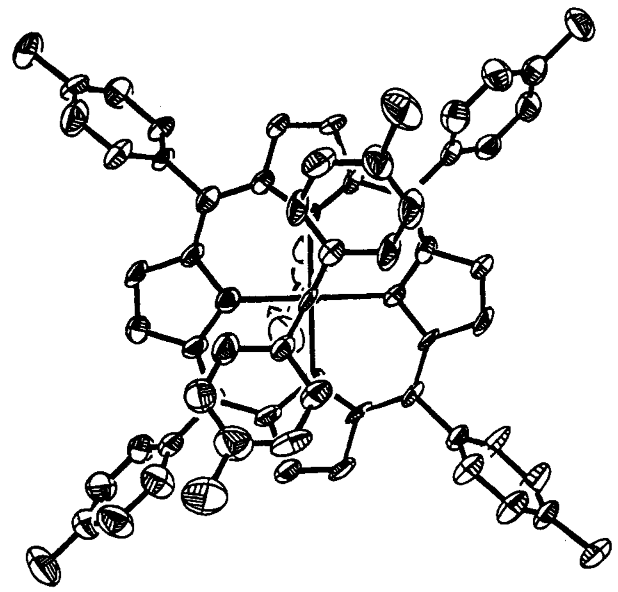

Figure 2. ORTEP drawing of *trans*-(TTP)Os=C(C_6H_4-*p*-CH_3)$_2$(THF): axial view showing the relationship between the di-*p*-tolylmethylidene fragment and the porphyrin ring.

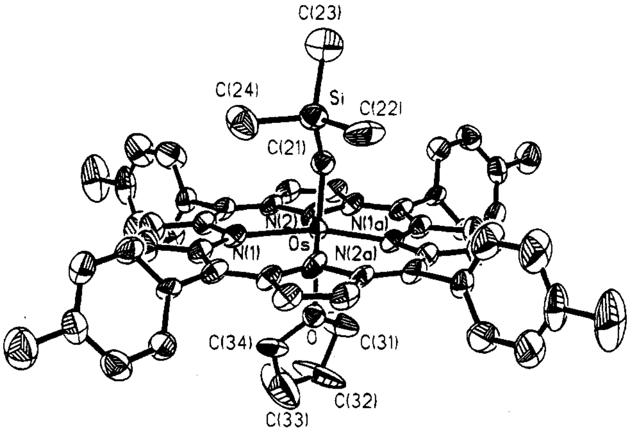

Figure 3. ORTEP drawing of *trans*-(TTP)Os=CHSiMe$_3$-(THF). The structural solution indicates that the (trimethylsilyl)methylidene fragment and the tetrahydrofuran group are 50:50 disordered about the origin. Only one orientation is shown. The thermal ellipsoids are drawn at the 50% probability level.

Table 5. Selected Bond Distances (Å) and Angles (deg) for *trans*-(TTP)Os=CHSiMe$_3$·THF

Os—C(21)	1.79(2)	Si—C(22)	1.81(2)
Os—N(2)	1.930(7)	Si—C(24)	1.82(2)
Os—N(1)	2.174(7)	Si—C(23)	1.86(3)
Os—O	2.43(2)	Si—C(21)	1.86(3)
C(21)—Os—N(2)	96.7(9)	C(22)—Si—C(23)	107.6(11)
C(21)—Os—N(1)	97.3(8)	C(24)—Si—C(23)	106.8(12)
N(2)—Os—N(1)	89.3(3)	C(22)—Si—C(21)	108.9(11)
N(2)—Os—O	82.5(4)	C(24)—Si—C(21)	108.3(11)
N(1)—Os—O	83.9(4)	C(23)—Si—C(21)	111.8(12)
C(22)—Si—C(24)	113.4(12)	Os—C(21)—Si	142(2)

The (trimethylsilyl)methylidene complex **1** crystallizes in the monoclinic space group $P2_1/n$ with two molecules per unit cell. The molecular structure and atom-labeling scheme are shown in Figure 3. Table 5 lists selected bond distances and angles. In this hexacoordinate complex, the porphyrin ring remains planar. The major deviation is observed for N(1), displaced 0.0488 Å toward the carbene ligand. The osmium atom is slightly displaced from the center of the porphyrin 0.22 Å toward the carbene ligand. The Os—C(21) double-bond distance of 1.79(2) Å is similar to that of complex **2**. A value of 23(1)° for the torsional angle formed by Si—C(21)—Os—N(2) indicates clearly that the SiMe$_3$ group is staggered with respect to the Os—N(2) bond of the (TTP)Os·THF fragment (Figure 4). Two methyl groups of the trimethylsilyl moiety point toward the porphyrin ring. The Os—C(21)—Si angle of 142(2)° may represent a distortion of the carbene fragment geometry that is induced by electronic effects[8a] and by steric strain (Figure 5). Similar distortions have been observed in many electron-deficient transition-metal alkylidene complexes having a monosubstituted carbene fragment, L$_n$M=CHR.[10] In some cases neutron diffraction analysis[10a,e] indicates that the M—C—R range ranges between 150 and 160°, resulting in a displacement of the α-hydrogen atom

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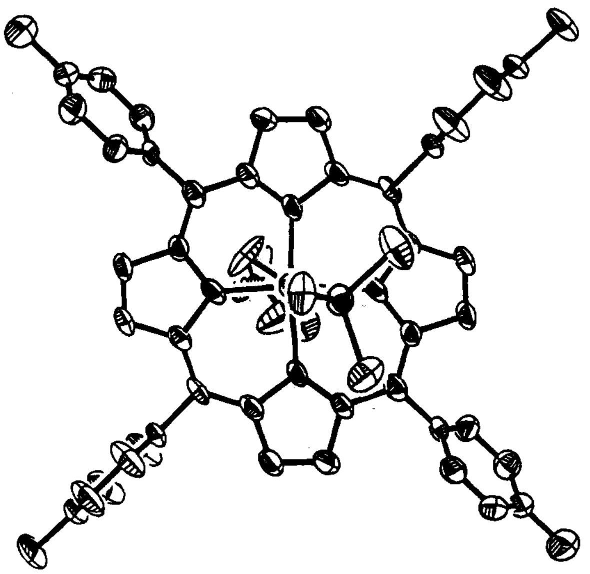

Figure 4. ORTEP drawing of *trans*-(TTP)Os=CH-SiMe$_3$(THF): axial view showing the relationship between the (trimethylsilyl)methylidene fragment and the porphyrin ring.

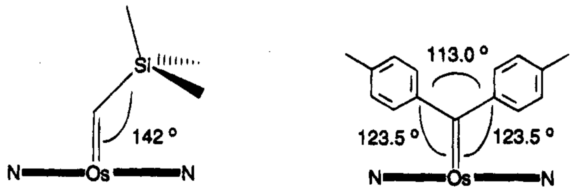

Figure 5. Representation of the carbene fragment geometries in *trans*-(TTP)Os=CHSiMe$_3$·THF and *trans*-(TTP)-Os=C(*p*-CH$_3$-C$_6$H$_4$)$_2$·THF.

toward the metal. Moreover, the large M—C—R angles observed in several Ta and W complexes correlate with short M=C bonds, as in the case for **1**.

Spectroscopic Properties of (TTP)Os=CHSiMe$_3$ and (TTP)Os=C(C$_6$H$_4$-*p*-CH$_3$)$_2$. In general, osmium porphyrin carbene complexes exhibit α-proton resonances between 9.59 and 20.38 ppm.[11] With the exception of the Fisher type carbene complexes, the osmium α-proton resonances are approximately 7 ppm further downfield than those of their ruthenium analogs. For example, the ruthenium complexe (TTP)Ru=CHSiMe$_3$[4f] displays an α-proton resonance at 19.44 ppm in d_8-THF and (TTP)Os=CHSiMe$_3$[3a] exhibits an α-proton resonance at 28.95 ppm in C$_6$D$_6$. The methyl groups of the trimethylsilyl moiety in the ruthenium and osmium complexes resonate at a higher field, −2.05 and −1.41 ppm, respectively. These two upfield shifts are consistent with reported data for other (porphyrinato)metal–carbene complexes having alkyl, aryl, and alkoxy groups bound to the carbene atom.[4] Even though it would be reasonable to explain the upfield resonances of the SiMe$_3$ methyl groups by involving an effect of the porphyrin ring current, the reason for the dramatic deshielding of the carbene ligand α-proton remains unclear. However, similar deshieldings have been described in non-porphyrinic complexes such as [(PPh$_3$)$_2$-(CO)$_2$ClOs=CHSMe]CF$_3$SO$_3$ (δ_{H_α} 14.70 ppm) and Cl$_2$-(CO)(PPh$_3$)$_2$Os=CH(*p*-tolyl) (δ_{H_α} 18.05 ppm),[12] suggesting that this upfield shift is more likely to be induced by the nature of the interactions between the metal and the carbene fragment.[8] As we noticed previously, the Os—C(21)—Si angle of 142(2)° in **1** suggests a strong distortion of the carbene fragment which could place the α-proton close to the osmium atom. Several authors have reported relatively low $^1J_{C-H_\alpha}$ coupling constants, low C—H$_\alpha$ stretching frequencies, and long C—H$_\alpha$ distances in the case of a series of tantalum alkylidene complexes that possess a distorted carbene fragment.[8,10] Similar spectroscopic and metrical properties have been observed more recently for Mo and Re alkylidene complexes.[13] Theoretical studies[8a] have also pointed out that the extensive reorientation of the carbene ligand weakens the C—H$_\alpha$ bond as a result of an interaction of the H$_\alpha$—C bond σ orbital with the d orbitals of the metal. As a matter of fact, the ^{13}C-coupled NMR spectrum of **1** displays a $^1J_{C-H_\alpha}$ coupling constant of 124.4 Hz that is significantly lower than that of (TTP)Os=CHCO$_2$Et ($^1J_{C-H_\alpha}$ = 132.8 Hz).[3a]

The ^{1}H NMR spectrum[3a] of complex **2** displays three resonances for the carbene fragment at 6.03 (H$_{2,6}$), 4.26 (H$_{3,5}$), and 1.69 (CH$_3$) ppm. These may be readily assigned as the two resonances of the arene group and the resonance of the *p*-methyl group, respectively. As expected, these resonances exhibit a relative shielding due to the porphyrin ring current effect.[14] The signal at 4.26 ppm is assigned to the ortho protons as a consequence of their proximity to the porphyrin ring.

Behavior of (TTP)Os=CHSiMe$_3$ and (TTP)Os=C-(C$_6$H$_4$-*p*-CH$_3$)$_2$ toward σ-Donor Ligands. As indicated by the molecular structures described above, the carbene complexes **1** and **2** exist as 6-coordinate, 18-electron species in the solid state. However, the axial ether ligand in **1·THF** and **2·THF** is weakly bound and can be quantitatively removed by exposing the solids to reduced pressure. This presumably reflects the *trans* influence of the carbene ligand. Complete removal of the axial THF was confirmed by the lack of THF proton resonances in the ^{1}H NMR spectra of (TTP)Os=CHSiMe$_3$ and (TTP)Os=C(C$_6$H$_4$-*p*-CH$_3$)$_2$. The ^{1}H NMR spectra for the 5-coordinate complexes are described above.

In solution, (TTP)Os=CHSiMe$_3$ and (TTP)Os=C-(C$_6$H$_4$-*p*-CH$_3$)$_2$ appear to adopt pseudooctahedral geometries in the presence of donor ligands, such as THF. NMR studies also indicate that the ligated THF is weakly bound and is in rapid exchange with free THF. For example, addition of 1.5 equiv of THF to (TTP)-Os=C(C$_6$H$_4$-*p*-CH$_3$)$_2$ in C$_6$D$_6$ produces insignificant shifts (±0.04 ppm) in the existing proton resonances. However, new broad signals for THF appear at 2.91 and 1.07 ppm. The positions of these signals are strongly shifted upfield relative to those of free THF (3.55 and 1.41 ppm)

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and reflect the influence of the porphyrin ring current on the bound ligand. The addition of several equivalents of THF only results in shifting the THF resonances to lower field (3.12 and 1.21 ppm) due to the increased mole fraction of free THF. Again, no significant changes in the porphyrin or carbene resonances are observed. Similar ^{1}H NMR features are observed when (TTP)-Os=CHSiMe$_3$ is treated with THF in C_6D_6.

We also examined use of triphenylphosphine in place of THF as an axial ligand for these carbene complexes. Despite the stronger σ-donor ability of triphenylphosphine, the added exogenous ligand is still in rapid exchange with bound phosphine on the NMR time scale. However, of particular importance is the fact that solutions of both (TTP)Os=CHSiMe$_3$ and (TTP)Os=C-(C_6H_4-*p*-CH_3)$_2$ are stable at ambient temperature in the presence of PPh$_3$ for more than 4 days. In neither case is decomposition to (TTP)Os(PPh$_3$)$_2$ and the olefin Me$_3$SiCH=CHSiMe$_3$ or (*p*-CH_3-C_6H_4)$_2$C=C(C_6H_4-*p*-CH_3)$_2$ observed. This indicates that σ-type ligands are not capable of effectively activating the carbene ligand toward transfer.

Concluding Remarks

The molecular structures of *trans*-(TTP)Os=CHSiMe$_3$·THF and *trans*-(TTP)Os=C(C_6H_4-*p*-CH_3)$_2$·THF indicate that a sterically demanding group, such as a trimethylsilyl moiety, can influence the conformation of the carbene fragment in the solid state. In the trimethylsilyl-substituted carbene complex as well as in the di-*p*-tolyl-substituted analog, the carbene fragment adopts a staggered conformation relative to the porphyrin nitrogen atoms. Furthermore, in both cases the geometry of the carbene α-carbon is altered. The alkylidene geometry of (TTP)Os=CHSiMe$_3$ is distorted and displays geometric and spectroscopic characteristics similar to those described for several nucleophilic group 5−7 alkylidene complexes. These properties may reflect a higher electron density at the carbene carbon of (TTP)-Os=CHSiMe$_3$ and may account for its relative chemical inertness as compared to the more electrophilic (TTP)-Os=CHCO$_2$Et.

The molecular structures presented here provide new insights about the steric interactions between carbene substituents and the porphyrin ligand. In addition, the distortion observed in the carbene ligand of (TTP)-Os=CHSiMe$_3$ affords some understanding of the chemical and spectroscopic properties of these new complexes. This information will be useful in our continued studies on the mechanisms of cyclopropanation and olefin formation catalyzed by osmium porphyrin complexes.

Experimental Section

All manipulations of reagents and products were carried out under a dry nitrogen atmosphere using a Vacuum/Atmospheres glovebox equipped with a Model MO40DH DriTrain gas purification system or on a vacuum line using Schlenk techniques. All solvents were dried and distilled from purple solutions of sodium benzophenone ketyl anion. ^{1}H NMR and ^{13}C NMR spectra (reported in parts per million downfield of SiMe$_4$) were recorded on Nicolet NT300 and Varian VXR300 instruments. ^{1}H NMR spectra were referenced against the residual proton resonance of the deuterated solvent (δ (ppm) C_6D_6) 7.15). ^{13}C NMR spectra were referenced against the resonance of the deuterated solvent (δ (ppm; C_6D_6): 128.00). Di-*p*-tolyldiazomethane was prepared by oxidation of hydrazones by yellow mercury(II) oxide in hexane. (Trimethylsilyl)-diazomethane was purchased from Aldrich Chemical Co. as a 2 M solution in hexane. Bis[(5,10,15,20-tetra-*p*-tolylporphyrinato)osmium(II)], Os$_2$(TTP)$_2$, was prepared from (TTP)Os-(CO)(py) and (TTP)Os(py)$_2$ according to a published procedure.[2] X-ray data collection and structure resolution were carried out at the Iowa State University Molecular Structure Laboratory. Refinement calculations were performed on Digital Equipment VAX Station 3100 and DecStation 5000 computers using the SHELXTL-Plus programs and SHELX-93, respectively.[15]

Structure Determination by Single-Crystal X-ray Diffraction. General Procedures. Crystals of both complexes suitable for X-ray structure analysis were grown from toluene/THF/hexane solutions. **1·THF** and **2·THF** were mounted on glass fibers on a Siemens P4/RA diffractometer with Cu K_α radiation (λ = 1.541 78 Å). Both were collected at subambient temperatures as indicated in Table 1 by means of a cryostatic stream of nitrogen gas. High-angle cell constants were determined from a subset of intense reflections in the range of 35.0–50.0° for **1·THF** only. Lorentz and polarization corrections were applied to the data for both specimens. A nonlinear correction based on the decay in three standard reflections was applied to both data sets: **1·THF** decayed 1.8%, and **2·THF** decayed 3.4%. **1·THF** was corrected for absorption effects by applying a face-indexed analytical absorption correction. **2·THF** was corrected for absorption effects by the application of a semiempirical absorption correction determined from six azimuthal scans.

***trans*-(TTP)Os=CHSiMe$_3$·THF.** The space group $P2_1/n$ was chosen on the basis of the systematic absences and intensity statistics. There were several violations of the screw-axis reflection condition, $0k0$ ($k = 2n$), but these were relatively weak. This assumption proved to be correct, as found by a successful direct-methods solution and subsequent refinement. All porphyrin non-hydrogen atoms were placed directly from the *E*-map. The osmium, the (trimethylsilyl)carbene ligand, and the tetrahydrofuran group are required by this setting to be 50:50 disordered about the origin. The solution/refinement cycles proceeded by placing the metal at the origin and locating the atoms in both the (trimethylsilyl)carbene and the tetrahydrofuran group. These remaining atoms were included at 50% occupancy. Once all atoms were located, reasonable distance restraints were used to keep the bond distances and angles of the (trimethylsilyl)carbene ligand and tetrahydrofuran groups realistic. All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were refined as riding atoms with isotropic displacement parameters linked to 1.1 times the isotropic equivalent of the host carbon. Refinement proceeded with difficulty by forcing the osmium atom to remain at the origin. However, allowing it to move from the origin improved the agreement significantly. Remaining difficulties were high correlations in the Os, C(21), and O positional and thermal parameters. C(21) and O are nearly related by the inversion operation. The anisotropic thermal parameters for these atoms were exaggerated by the correlation. These were converted to isotropic atoms as a last resort. Osmium was left as an anisotropic atom, but it does exhibit some effects of self-correlation, because it is still very close to the center of inversion.

In the space group $P2_1/n$ Os, the (trimethylsilyl)carbene, and the THF must be disordered about the crystallographic origin, while the porphyrin group behaves well. The THF group lies completely within the envelope of the trimethylsilyl group. As long as there are no intermolecular contacts between the THF, the trimethylsilyl group, and the tetratolylporphyrin less than van der Waals, then solution as presented above is physically plausible. The packing diagram reveals no intermolecular contacts less than van der Waals interactions.

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[15] (a) SHELXTL-PLUS, Siemens Analytical X-ray, Inc., Madison, WI. (b) Scheldrick, G. M. *J. Appl. Crystallogr.*, in press.

Another equally possible solution for this structure is in space group *Pn*, which is noncentrosymmetric. In an attempt to refine the structure in *Pn*, a racemic twin model was assumed. The Os atom, the carbene, and the THF were refined well; however, all atoms in the porphyrin correlated extremely highly with their pseudocentrosymmetrically related atoms. Also, the ratio of twin scale factor was within 1.0 esd of 50:50. This solution can be dismissed on the basis of these factors.

***trans*-(TTP)Os=C(C_6H_4-*p*-CH_3)$_2$·THF.** The centric space group *C*2/*c* was initially indicated by systematic absences and intensity statistics. The positions of most of the porphyrin complex atoms were determined by direct methods. The remaining non-hydrogen atom positions were determined by successive difference Fourier maps. All non-hydrogen atoms of the porphyrin complex were refined with anisotropic displacement parameters. After the least squares converged, all hydrogen atoms were placed as riding atoms with refined isotropic displacement factors. A solvent molecule of toluene was found and constrained to refine as an idealized rigid group. Three atoms near a crystallographic 2-fold operation center, O(80), C(81), and C(82), were found and appear to belong to a THF molecule of solvation. This THF was constrained to have reasonable bond distances. Both molecules of solvation have greater thermal motion than the porphyrin complex but appear to be fully occupied. No unusually short intermolecular nonbonded contacts were observed.

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Supplementary Material Available: Tables of structure determination details, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen coordinates and isotropic thermal parameters for **1** and **2** and a table of least-squares planes for **2** (33 pages). Ordering information is given on any current masthead page.

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