1992

Osmium porphyrin silylene and carbene complexes: synthesis, characterization, and catalytic reactions

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Iowa State University, 1992

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Osmium porphyrin silylene and carbene complexes:
Synthesis, characterization, and catalytic reactions

by

Daniel Allen Smith

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1992

I dedicate this dissertation to my wife, Nancy Gaye Smith.

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Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
dcpe	bis(dicyclohexylphospino)ethane
dmpe	bis(dimethylphosphino)ethane
dppe	bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
Et	Ethyl
Fp	Cp(CO)$_2$Fe
HMPA	hexamethylphosphoramide
HMS	hexamethylsilacyclopropane
^{i}Pr	*iso*-propyl
IR	infrared
Me	methyl
Mes	mesityl
NMR	nuclear magnetic resonance
Np	neopentyl
OEP	octaethylporphyrinato
OTf	triflate anion
Ox	oxalate dianion
Ph	phenyl

Py	pyridine
^{t}Bu	*tert*-butyl
THF	tetrahydrofuran
TMP	5,10,15,20-tetramesitylporphyrin
TPP	5,10,15,20-tetraphenylporphyrin
TTP	5,10,15,20-*meso*-tetra-*p*-tolylporphyrinato
UV-Vis	ultraviolet-visible

CHAPTER 1: INTRODUCTION TO PORPHYRINS

The growing use of porphyrins in organometallic chemistry is derived in part from the ease with which steric and electronic properties of the porphyrin ligand can be varied. For example, by incorporating bulky substituents into a molecule containing a reactive species both organic[1] and inorganic[2] species have been stabilized. An illustration of a porphyrin stabilizing a reactive titanium(II) center has been recently reported.[3] The steric interactions around the metal binding site can be changed by placing organic substituents on the ortho positions of the *meso*-tetra-arylporphyrins. An example of such a porphyrin is *meso*-tetramesitylporphyrin (TMP), Figure 1.1. When a metal is bound by TMP, further ligation in the axial positions is inhibited due to steric interaction between the ortho methyls of the porphyrin and these potential ligands.

Meso-tetra-arylporphyrins have several useful features. They are easily prepared by

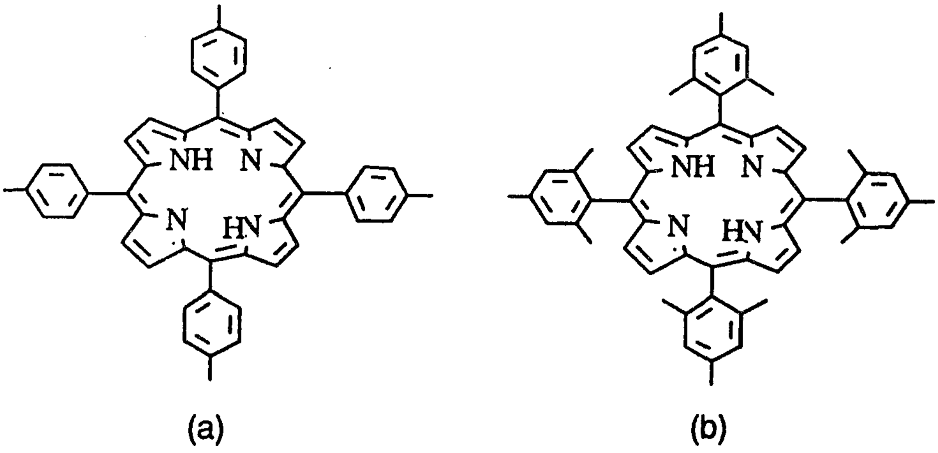


Figure 1.1. *meso*-tetra-arylporphryins; a) *meso*-tetra-*p*-tolylporphryins b) *meso*-tetra-mesitylporphryins

the procedure of Adler from pyrrole and aryl aldehydes.[4] This method is general in its utility and a variety of substituted porphyrins can be prepared. Once the macrocycle has been prepared, it is thermally stable and can be sublimed at temperatures of 350 °C. This semi-rigid, planar ligand has a chelating diameter of approximately 4 Å and can accomodate a wide range of metals and metalloids. Because of the common metal coordination geometry provided by the porphyrin ligand, comparisons of metalloporphyrin chemistry across the periodic table are more meaningful.

Porphyrins not only chelate a wide variety of metals but also stabilize a large range of oxidation states. Formal oxidation states of 0 to +6 are known for metalloporphyrins derived from the iron triad. This property has been recently utilized in multi-electron transfer studies since the ligand coordination sphere is essentially conserved for all of the oxidation states of a particular metal.

Porphyrins are excellent spectroscopic tags in both the UV/vis and ^{1}H NMR spectroscopies. The UV/vis spectrum typically exhibits an intense absorption, known as the Soret band, which appears between 350 nm and 500 nm and has a molar absorptivity as high as 10^5 $M^{-1}cm^{-1}$. Several less intense peaks called Q-bands can be observed from 450 nm to 700 nm with molar absorptivities of 10^3-10^4 $M^{-1}cm^{-1}$. Proton NMR spectroscopy for *meso*-tetra-*p*-tolylporphyrin complexes can reveal molecular symmetry. When the four-fold symmetry of the porphyrin is maintained on the NMR time scale, the ^{1}H NMR resonances for the β-pyrrole and tolyl methyl protons are singlets. When the metalloporphyrin complex has mirror symmetry in the horizontal (porphyrin) plane, such as in (TTP)Os(Py)$_2$, the *o*- and *m*-tolyl protons appear as two doublets. In complexes which lack horizontal mirror symmetry, the *o*- and *o*'-tolyl protons as well as the *m*- and *m*'-tolyl protons are magnetically inequivalent. For example, in (TTP)Os(CO)(Py) the *o*-, *o'*-, *m*- and *m'*-protons appear as four distinct resonances. However, fast rotation of the tolyl groups about the *meso*-carbon bond on the NMR time scale can result in the appearance of higher symmetry. This is the case for (TTP)Ti=O, which exhibits only two doublets for the aryl protons in the NMR spectrum.

The presence of axial ligands is often readily established by proton NMR. Substituents bound to the metal typically have an upfield shift relative to the corresponding resonances of the unbound ligand. This upfield shift is due to the ring current of the porphyrin π-system.

Porphyrin silylene and carbene complexes

The useful attributes of the porphyrin macrocycles described above appeared to be ideal for stabilizing silylene and carbene complexes. Molecules containing silicon multiple bonds commonly are unstable with respect to dimerization to form silicon single bonds. For example, $Me_2Si=CH_2$ can only be observed in the gas phase[5] and attempts to isolate this silaethene resulted in the formation of 1,3-disilacyclobutane. Generally, to avoid this problem, bulky substituents are placed on the silicon atom to kinetically stabilize the multiple bond. The use of porphyrins to sterically stabilize transition metal silylene complexes might allow the isolation of complexes with small substituents on silicon. The work presented here describes the successful use of this approach to prepare osmium porphyrin silylene complexes. Also described are osmium porphyrin carbene complexes and their ability to catalyze the formation of alkenes and cyclopropanes.

CHAPTER 2: LOW COORDINATE SILICON

Introduction

Molecules containing silicon multiple bonds have long been proposed as transient species.[6] In spite of this, their chemistry remained undeveloped until 1966 when Nametkin and Gusel'nikov observed transient 1,1-dimethylsilaethene spectroscopically.[7] This observation marks the beginning of the intensive study of double and triple bonds involving silicon. Since 1966 many species such as silabenzenes,[8] silaethenes (or silenes, Si=C),[9] silaketimines (or silaimines Si=N),[10] silaphosphines (Si=P),[4] silaketones (Si=O),[11] and disilenes (Si=Si)[12] have been observed indirectly through chemical trapping experiments and isolation in argon matrices at 10 K. Other, more exotic species, have been proposed and observed in the gas phase, including SiCH, SiC_2 and the radical cation $CHNSi^{\cdot +}$.[13]

In the last ten years the organometallic chemistry of silicon has grown tremendously. The isolation of the first disilenes in 1981 and 1982 by West and Masamune stimulated this interest.[14] Since these initial efforts, molecules have been prepared which contain silicon double bonds to a variety of elements (Si=E where E = Si, C, N, P or transition metals). Initially, many of these molecules were isolated as adducts in which a base stabilizes the low coordinate silicon. Recent synthetic advances have lead to the preparation of base-free examples. With the exception of the transition metal silylene complexes, X-ray structures have now been reported for the base-free molecules containing the Si=E fragment.

Low valent silicon species have been postulated as reactive intermediates in a variety of reactions. For example, transition metal silylene complexes have been invoked as intermediates in metal catalyzed polymerization and oligomerization reactions of silanes.

Unlike some low valent silicon species, particularly disilenes, the chemistry of silylene complexes has been relatively unexplored. The lack of understanding of the chemistry of transition metal silylene complexes is primarily due to the inability of the synthetic chemist to isolate these molecules until very recently. When our work began in 1988, only four examples of terminal transition metal silicon double bonds had been prepared and structurally characterized. All of them contained a base donor stabilizing the silicon.[15] Since that time, a number of reports have appeared which detail the synthesis and isolation of silylene complexes. Reports of other metal stabilized low valent silicon molecules, M(η^2-Si=E) (E is Si, C, or N) have also appeared. Since these are pertinent to this dissertation, they will be reviewed along with the metal silylene complexes.

Base-Stabilized Transition Metal Silylene Complexes

Theoretical Studies

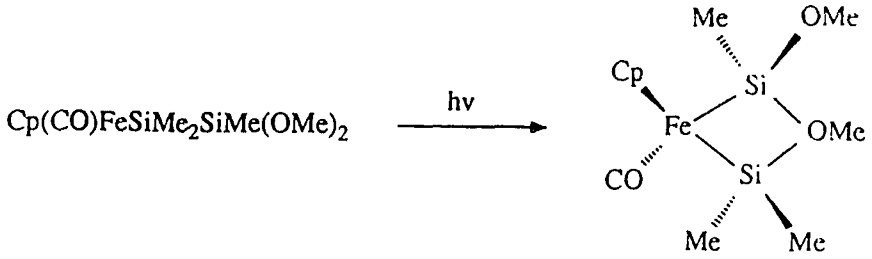
Several calculations have been done at various levels on model silylene complexes. A general obstacle in theoretical studies involves the complexity of real molecules, such as $(CO)_5Cr{=}Si(O^tBu)_2{\bullet}HMPA$, which greatly extends computation times. Consequently, models for silylene complexes have been simplified by replacing the alkyl substituents on silicon with hydrogen and/or hydroxy groups. In general, calculations indicate that metal silylene complexes are analogous to Fischer-type carbene complexes; the group 14 atom is electron deficient. An ab initio SCF calculation on $(CO)_5Cr{=}Si(OH)H$[15b] indicates that the LUMO is located primarily on silicon and is π-antibonding between chromium and silicon. Therefore, coordination of a donor molecule to silicon not only stabilizes the electron deficient silicon but simultaneously weakens the metal silicon bond. Calculations on $(CO)_5Mo{=}SiH_2$ predict that the silicon should be pyramidal.[16] This effect arises from the lowering of the Si p atomic function contribution to the SiH_2 lone pair. The calculated angles agree well with X-ray structural data on base-stabilized silylene complexes and suggest that the base-free analogs will also be pyramidalized at silicon, much like silicon in disilenes. The Mo=Si bond strength (47.22kcal/mol) is calculated to be only 2/3 that of Mo=C (76.53 kcal/mol).

Synthesis

Transition metal silylene complexes have been prepared by a) proton migration, b) photochemical activation of silyl complexes, c) oxidative addition of silanes to coordinatively unsaturated metals d) electrophilic abstraction from silyl complexes and e) salt eliminations between metal dianions and dichlorosilanes. The latter two methods are thus far the most significant with (e) providing a wide variety of silylene complexes and (d) providing the first base-free silylene complex observed by proton NMR.

The first observed base-stabilized iron silylene complex, $(Et_2NH)Me_2Si{=}Fe(CO)_4$, was prepared by a 1-3 proton shift from (diethylamino)(dimethylsilyl)tetracarbonyliron hydride.[17] This silylene complex was stable below -20 °C for long periods. A chloroaminosilylene complex, (2-chloro-1,3-diphenyl-1,3-diaza-2-silacyclopentane)$Si{=}Fe(CO)_4$ was prepared from a similar reaction.

Photochemical generation of transient metal silylene complexes has been demonstrated by trapping reactions. Pannell[18] and Couldwell[19] have shown similarly that iron silylene complexes could be generated upon the photolysis of $Cp(CO)_2FeSiMe_2SiMe_3$. Using a similar method, Ogino has isolated base-stabilized bis-silylene complexes, $(\eta^5\text{-}C_5Me_5)(CO)Fe(SiMeOMe)(SiMe_2)(\mu\text{-}OMe)$ eq. 2.1,[20] and $(CO)_4Mn(SiMe_2)_2(\mu\text{-}OMe)$.[21] Ogino has also isolated a mixed silylene germylene species.[22]



(2.1)

Indirect evidence supports the formation of metal silylene complexes from the oxidative addition of dihydrosilanes to coordinatively unsaturated metal centers. Wilkinson's catalyst effectively catalyzes the polymerization of dihydrosilanes, H_2SiR_2. When Et_3SiH is present in dihydrosilane polymerization reactions catalyzed by Wilkinson's catalyst, the silylene insertion product Et_3SiSiR_2H is observed. Formation of this product may involve silylene complexes.[23] Silylenes were also trapped by substituted acetylenes to form 1,4-disila-2,5-cyclohexadienes and 1-silacyclopentadienes when dihydrosilanes were heated in the presence of trans-$[PtCl_2(PEt_3)_2]$ and $NiCl_2(PEt_3)_2$ respectively.[24] Other platinum reagents also polymerize dihydrosilanes, presumably via metal silylene complexes. Platinum disilenes and silylene dimers, $(PtSi)_2$, have been isolated from similar reactions.[25] Early transition metal complexes also catalyze polymerization and oligomerization of dihydrosilanes. The mechanisms for transition metal catalyzed silane polymerizations are still being debated with evidence both for[26] and against[27] silylene complex intermediates. Differences in the systems may lower the energy of one mechanism over another. It appears that late transition metals are more apt to form silylene complexes than are the early transition metals.

Only two silylene complexes have been isolated from reactions involving oxidative addition of dihydrosilanes to metal complexes. Corriu and co-workers have prepared and characterized $(CO)_4Fe{=}Si(Ph)$(1-N,N-dimethylaminonaphthyl) and $(\eta^5\text{-}C_5Me_4H)(CO)_2Mn{=}Si(Ph)$(1-N,N-dimethylaminonaphthyl).[28] The silicon NMR of the iron complex has a resonance at 101.1 ppm, while the silicon resonance for the manganese complex is at 124.0 ppm.

Electrophilic abstraction of a silicon substituent to produce transition metal silylene complexes has been reported by both Gladysz and Tilley. Gladysz treated $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SiMe_2Cl)$ with Me_3SiOTf to produce $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SiMe_2OTf)$.[29] The triflate ion can be subsequently displaced by pyridine. NMR studies of the reaction between the chlorosilyl complex and $AlCl_3$ suggest that a base-free cationic silylene may be present in solution. Tilley has also prepared several ruthenium silylenes by a similar reaction.[30] The first base-free silylene complexes, $[(\eta^5\text{-}C_5Me_5)(PMe_3)_2Ru(SiSR_2)][BPh_4]$ (R = Et, p-tolyl), observed by ^1H NMR were prepared by this method.[31]

The most general synthetic route to silylene complexes is the salt elimination reaction utilized by Zybill and Muller.[15a,b,32] Carbonylate anions, $Na_2M(CO)_n$ (M=Fe, n=4; M=Cr, Mo, or W, n=5) have been effectively used to prepare silylene complexes when treated with dichlorosilanes, Cl_2SiR_2, eq. 2.2. These reactions were conducted in a donor solvent such as THF or HMPA and resulted in donor stabilized silylene complexes. Silylene complexes containing silicon substituents such as alkyls, halides, alkoxides, and alkylsulfides have successfully been isolated from this type of reaction.

A unique reaction that deserves mention but does not fit in any of the above categories was reported by Jutzi.[33] In benzene, decamethylsilicocene, $(\eta^5\text{-}C_5Me_5)_2Si$, was treated with carbonylgold(I) chloride, (CO)AuCl, to produce

Table 2.1. Known transition metal silylene complexes

Silylene Complex	^{29}Si δppm	$d_{(M=Si)}$ Å	$d_{(Do\text{-}Si)}$ Å	Ref.
$(CO)_4FeSi(HMPA)(^tBuO)_2$	7.1	2.289(2)	1.730(3)	32c
$(CO)_4FeSi(HMPA)(^tBuS)_2$	74.7	2.278(1)	1.734(2)	32c
$(CO)_4FeSi(HMPA)(Me)_2$	92.3	2.280(1) 2.294(1)	1.735(3) 1.731(3)	32c
$(CO)_4FeSi(HMPA)Cl_2$	59.7	2.214(1) 2.221(1)	1.683(3) 1.676(3)	32c
$(CO)_5CrSi(HMPA)(^tBuO)_2$	12.7	2.432(1)	1.736(3)	32c
$(CO)_5CrSi(HMPA)(^tBuS)_2$	83.2			32c
$(CO)_5CrSi(HMPA)(Me)_2$	101.4	2.410(1)	1.743(2)	32c
$(CO)_5CrSi(HMPA)Cl_2$	55.0	2.342(1)	1.690(2)	32c
$(CO)_5CrSi(HMPA)(1\text{-}AdaO)_2$	11.9			32c
$(CO)_5CrSi(HMPA)(2\text{-}AdaO)_2$	11.7			32c
$(CO)_5CrSi(HMPA)(NpO)_2$	12.5			32c
$(CO)_5CrSi(HMPA)(tritylO)_2$	10.9			32c
$(\eta^5\text{-}C_5Me_5)(PMe_3)(NO)Re(SiMe_2F)$				29
$(\eta^5\text{-}C_5Me_5)(PMe_3)(NO)Re(SiMe_2Cl)$	48.09			29
$(\eta^5\text{-}C_5Me_5)(PMe_3)(NO)Re(SiMe_2Br)$				29
$(\eta^5\text{-}C_5Me_5)(PMe_3)(NO)Re(SiMe_2I)$				29
$(\eta^5\text{-}C_5Me_5)(PMe_3)(NO)Re(SiMe_2OTf)$				29
$[(\eta^5\text{-}C_5Me_5)(PMe_3)(NO)Re\{SiMe_2(Py)\}][OTf]$				29
$(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuSiPh_2Cl$	74.07			30a
$(\eta^5\text{-}C_5Me_5)(PMe_3)Ru(SiPh_2Cl)_2H$	57.81			30a
$(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuSiPh_2OTf$	112.39	2.349(2)	1.853(5)	30a
$[(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuSiPh_2NCMe][BPh_4]$	95.75	2.328(2)	1.932(8)	30a,b
$(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuSi(SEt)_2OTf$	86.05			31
$(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuSi(S\text{-}p\text{-}tolyl)_2OTf$	77.14			31
$(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuSi(S\text{-}p\text{-}tolyl)(OTf)_2$	37.10			31
$[(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuSi(S\text{-}p\text{-}tolyl_2)NCMe][BPh_4]$	58.30			31
$[(\sigma\text{-}C_5Me_5)(\pi\text{-}C_5Me_5)Si]AuCl$	82.8			33
$(CO)_4FeSi(HNEt_2)(Me)_2$				17
$(CO)_4FeSi(Cl)(NPhCH_2CH_2NPhH)$				17
$(\eta^5\text{-}C_5Me_5)(CO)Fe(SiMeOMe)(SiMe_2)(\mu\text{-}OMe)$ cis/trans isomers	127.4 121.1 101.9 93.9	2.222(3) 2.207(3)	1.793(9) 1.799(8)	20
$Cp^*COFe(GeMe_2)(SiMe_2)\mu\text{-}OMe$				22
$Cp^*COFe(GeMe_2)(SiMe_2)\mu\text{-}O^tBu$				22

Table 2.1 cont.

Silylene Complex	^{29}Si δppm	$d_{(M=Si)}$ Å	$d_{(Do\text{-}Si)}$ Å	Ref.
$(CO)_4Mn(SiMe_2)_2(\mu\text{-}OMe)$	115.4	2.336(2) 2.344(2)	1.784(5) 1.795(4)	21
$(CO)_4FeSi(Ph)$(aminonaphthyl)	101.1			28
$(\eta^5\text{-}C_5MeH_4)(CO)_2MnSi(Ph)$(aminonaphthyl)	124.0			28
$(CO)_5CrSi$(dimethylaminomethylphenyl)$_2$	124.9	2.408(1)	2.046(2)	32a
$[(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuSiPh_2][OTf]$				30a
$[(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuSi(S\text{-}p\text{-}tolyl_2)][BPh_4]$	259.4			31
$[(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuSi(SEt_2)][BPh_4]$	264.4			31
$(\eta^5\text{-}C_5Me_5)(CO)_2ReSi(^tBu)_2$				32c
$(CO)_4FeSi(^tBuS)_2$	83.2			32b

$$Na_2M(CO)_n + Cl_2SiR_2 \rightarrow (CO)_nM{=}SiR_2\cdot B \qquad (2.2)$$

$$M{=}Fe,\ n{=}4;\ M{=}Cr,\ Mo,\ or\ W,\ n{=}5$$

$$B = THF\ or\ HMPA$$

[bis-(pentamethylcyclopentadienyl)silanediyl] gold chloride. ^1H NMR indicates that the two cyclopentadienyl rings are inequivalent and supports the formula $[(\sigma\text{-}C_5Me_5)(\pi\text{-}C_5Me_5)Si]AuCl$. The ^{29}Si NMR at 82.8 ppm suggests that this complex contains a low valent silicon atom. However, the unusual π-coordinated Si does not clearly represent a base-free silylene complex.

Characterization Methods

Metal silylene complexes have been characterized by NMR, IR, Mossbauer, and single crystal X-ray diffraction studies. The most important techniques are ^{29}Si NMR and X-ray diffraction. ^{29}Si chemical shifts are diagnostic for unsaturated silicon. Typical resonances for four-coordinate silicon occur between +20 and -200 ppm as referenced against tetramethylsilane, while resonances of low valent silicon have a diagnostic downfield shift ($Mes_2Si=SiMes_2$, 63.6 ppm; $(Mes^tBuSi)_2$, 90.3 ppm; $HSiMe_3$, -16.34 ppm; $SiCl_4$, -18.5 ppm; SiH_4, -91.9 ppm; Ph_2SiMe_2, -8.19 ppm; Me_3SiOEt, 15.1 ppm; see also Table 2.1). The presence of halogens or metal coordination widens the range in both directions ($FSiMe_3$, +33 ppm; I_4Si, -346 ppm; $Me_3SiCo(CO)_4$, 44.42 ppm). Therefore when metal coordination is involved, a comparison of ^{29}Si signals between metal silylene complexes and the corresponding metal silyl complexes gives a better indication of low valency, $[(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuSi(SEt_2)][BPh_4]$, 264.4 ppm and $(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuSi(SEt)_2OTf$, 86.05 ppm.[31]

X-ray diffraction studies are invaluable in determining low coordination and multiple bonding of silicon. A short metal silicon bond is expected in true silylene complexes. The base-stabilized silylene complexes that have been isolated exhibit M=Si distances that are 0.01 - 0.2 Å shorter than their respective M-Si single bonds. Further evidence for partial multiple bond character is indicated by long silicon to donor base oxygen or nitrogen distances, Table 2.1. Typical four coordinate Si-O and Si-N distances are 1.63-1.66 Å[34] and 1.7-1.8 Å,[30] respectively. Diffraction studies of carbonyl silylene complexes $[(CO)_5Cr=SiR_2{\bullet}HMPA]$ show an umbrella effect, in which the equatorial carbonyls are bent towards the silylene group rather than away from it as expected on steric grounds.[32c] This umbrella distortion was reproduced by an *ab initio* calculation and is explained by an electronic interaction between the electrophilic silicon and the carbonyls.[16]

IR data indicate that the silylene ligand is comparable to the carbene ligand in electron donating ability to metal centers[35,36,37] (Table 2.2). Zybill[32c] notes a slightly stronger donor influence of the silylene ligand in iron complexes [$(CO)_4Fe{=}Si(O^tBu)_2{\bullet}HMPA$: 2005, 1920, 1883 cm^{-1}] versus chromium complexes [$(CO)_5Cr{=}Si(O^tBu)_2{\bullet}HMPA$: 2015, 1991, 1930 cm^{-1}]. Mossbauer data[32c,38] also indicate a significant donor ability of the silylene ligand. For example, isomeric shifts for two silylene complexes, $(CO)_4Fe{=}Si{=}Fe(CO)_4{\cdot}(HMPA)_2$ (IS= -0.488 mm/s) and $(CO)_4Fe{=}Si(O^tBu)_2{\bullet}HMPA$ (IS= -0.477 mm/s) indicate that higher electron density is located at the metal center as compared to $Fe(CO)_5$,[39] Table 2.3.

Table 2.2. IR data

Compound	$\nu_{(CO)}$ cm^{-1}	Reference
$[Cl_2SiFe(CO)_4]_2$	2094, 2053, 2048, 2038	35
$(Cl_3Si)_2Fe(CO)_4$	2125, 2078, 2071, 2061	35
$Fe(CO)_4CHNMe_2$	2049, 1977, 1949, 1937	36
$Cr(CO)_5CHNMe_2$	2057, 1970, 1941, 1933	36
$Cr(CO)_5CHN(C_5H_{10})$	2055, 1969, 1935, 1931	36
$Fe(CO)_4[CN(Me)CH_2CH_2N(Me)]$	2040, 1959, 1938	37
$Fe(CO)_3[CN(Me)CH_2CH_2N(Me)]_2$	1959, 1841	37
$[(CO)_4Fe{=}Si(O^tBu)_2{\bullet}HMPA$	2005, 1920, 1883	32c
$[(CO)_5Cr{=}Si(O^tBu)_2{\bullet}HMPA$	2015, 1991, 1930	32c

Table 2.3. ^{57}Fe Mossbauer data

Compound	Isomeric Shift (mm/s)	Quadrople Splitting (mm/s)	Reference
cis-$Fe(CO)_4Cl_2$	0.29	0.24	39
cis-$Fe(CO)_4Br_2$	0.31	0.30	39
cis-$Fe(CO)_4I_2$	0.31	0.30	39
$[(CO)_4Fe{=}SiHMPA_2$ $Fe(CO)_4$	-0.49	1.62	32c,38
$[(CO)_4Fe{=}Si(O^tBu)_2{\bullet}$ HMPA	-0.48	1.46	32c,38
$Na_2Fe(CO)_4$	-0.33		38
$Fe(CO)_5$	-0.18		38

Reactivity

Preparation of Base-Free Silylene Complexes.

Several workers have examined the possibility of preparing base-free transition metal silylene complexes from base-stabilized silylene complexes. Zybill has observed the loss of THF from base-stabilized complexes, $(CO)_nM{=}SiR_2{\bullet}THF$ (M=Fe, n=4; M=Cr, n=5), to produce silylene dimers at -40 °C even in THF solvent.[38] In the presence of reagents such as dimethylcarbonate, the base-free silylene complexes react via a formal [2+2] cycloaddition and subsequent cycloreversion to produce (dimethoxycarbene)chromium carbonyl and cyclic trisiloxanes. Tilley has also observed base-free silylene complexes by NMR techniques.[30] Dissociation of silicon-bound acetonitrile from $[(\eta^5\text{-}C_5Me_5)(PMe_3)_2Ru{=}SiPh_2{\bullet}\ NCMe][BPh_4]$ produces the transient species $[(\eta^5\text{-}C_5Me_5)(PMe_3)_2Ru{=}SiPh_2][BPh_4]$ in dichloromethane. Treating $(\eta^5\text{-}C_5Me_5)(PMe_3)(NO)Re(SiMe_2Cl)$ with $AlCl_3$ results in the formation of the adduct $(\eta^5\text{-}C_5Me_5)(PMe_3)(NO)Re({=}SiMe_2\text{-}AlCl_4)$ and the base-free cationic silylene complex $[(\eta^5\text{-}C_5Me_5)(PMe_3)(NO)Re({=}SiMe_2)]^+$.[29]

Trapping Reactions.

Transition metal silylene complexes have been shown to thermally and photolytically transfer silylene groups.[32b,d] Photolysis of $(CO)_4Fe{=}Si(R)_2{\cdot}HMPA$, where R is ^{t}BuO, ^{t}BuS, or Me, in the presence of 2,3-dimethylbutadiene produces the silacyclopentenes and (2,3-dimethylbutadiene)iron tricarbonyl. Interestingly, photolysis of $(CO)_4Fe{=}Si(R)_2{\cdot}HMPA$ in the presence of triphenylphosphine first generates the isolable trans-phosphinesilyleneiron tricarbonyl complexes. Further photolysis produces the *trans*-bisphosphine complexes. In the absence of a trapping reagent thermolysis or photolysis produces low molecular weight silicon polymers and iron carbonyl clusters. Mildly heating the dimethyl derivative for a short period results in the dissociation of HMPA and the formation of a dimer with two bridging silylene units.

The reactivity of $[(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuSiPh_2NCMe][BPh_4]$ with a variety of nucleophiles has been reported by Tilley.[30a,40] $[(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuSiPh_2NCMe][BPh_4]$ reacts with $LiAlH_4$ to produce the silyl complex $[(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuSiPh_2H$. In acetonitrile solutions, alcohols (ROH; R= Me, Et, ^{t}Bu) and water cleave the base-stabilized silylene ligand to produce the acetonitrile complex $(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuNCMe$ and $HSiPh_2OR$ or $Ph_2Si(H)\text{-}O\text{-}(H)SiPh_2$, respectively. Enolizable ketones also undergo a similar cleavage reaction to produce $H_2C{=}C(R)\text{-}O\text{-}Si(H)Ph_2$. When $[(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuSiPh_2NCMe][BPh_4]$ is treated with acetic acid, the silicon containing product is $HSiPh_2(O_2CMe)$.

η^2-Si=E Metal Complexes

Only a few species with η^2-coordinated silaethenes, silaketimines, and disilenes are known. There are two general synthetic approaches for preparing these complexes. These involve intramolecular oxidative addition of a silicon-hydrogen bond to a metal center or reductive coupling of a metal chloride and a chlorosilane.

η^2-Silaketimines

The only reported η^2-$R_2Si{=}NR'$ metal complex was prepared by Berry using the reactions outlined in Scheme 2.1.[41] The key step is the elimination of tetramethylsilane to produce the silicon-zirconium bonded complex, $Cp_2Zr(PMe_3)(\eta^2\text{-}N^tBuSiMe_2)$. The zirconium silicon bond distance, 2.645(1) Å, is 0.1 Å shorter than a zirconium silicon single bond, while the silicon nitrogen distance, 1.687(3) Å, is comparable to a silicon nitrogen single bond ($d_{Si\text{-}N}$ = 1.64-1.80 Å,[42] $d_{Si=N}$= 1.568(3) Å[43]). Berry also described the reactivity of $Cp_2Zr(PMe_3)(\eta^2\text{-}N^tBuSiMe_2)$. H_2 adds across the Zr-Si bond to give $Cp_2Zr(H)(PMe_3)(N^tBuSiMe_2H)$. Ethylene inserts into the Zr-Si bond to produce an azasilametallocyclopentane. Similarly, reaction with formaldehyde produces the insertion product, $Cp_2\overline{Zr(N^tBuSiMe_2CH_2O})$. Surprisingly, for a d^0 metal center, carbon monoxide displaces the phosphine in $Cp_2Zr(PMe_3)(\eta^2\text{-}N^tBuSiMe_2)$.

Scheme 2.1

$$Cp_2Zr(I)(N^tBuSiMe_2H) + LiCH_2SiMe_3 \rightarrow Cp_2Zr(CH_2SiMe_3)(N^tBuSiMe_2H)$$

$$Cp_2Zr(CH_2SiMe_3)(N^tBuSiMe_2H) \rightarrow Cp_2Zr(\eta^2\text{-}N^tBuSiMe_2) + Me_4Si$$

$$Cp_2Zr(\eta^2\text{-}N^tBuSiMe_2) + PMe_3 \rightarrow Cp_2Zr(PMe_3)(\eta^2\text{-}N^tBuSiMe_2)$$

η^2-Silaethenes

Although metal stabilized silaethenes were postulated as reactive intermediates for several years, a tungsten complex was the first to be observed spectroscopically.[44] This was accomplished in 1983 and required low temperature. Photoejection of CO from $CpW(CO)_3(CH_2SiMe_2H)$ followed by intramolecular oxidative addition of Si-H to the tungsten center generated the silaethene complex $CpW(H)(CO)_2(\eta^2\text{-}CH_2SiMe_2)$. In 1987, a similar reaction involving $CpFe(CO)_2(\eta^2\text{-}CH_2SiMe_2H)$ to produce $CpFe(H)(CO)(\eta^2\text{-}CH_2SiMe_2)$ was reported.[45] Neither of these complexes could be isolated. The following year Tilley expanded the procedure to ruthenium. Addition of the Grignard reagent $ClMgCH_2SiR'_2H$ to the 16-electron complex $Cp^*(R_3P)RuCl$ (R = cyclohexyl, i-Pr; R' = Me, Ph) at -78 °C produced $Cp^*(R_3P)Ru(H)(\eta^2\text{-}CH_2SiR'_2)$.[46] When R= i-Pr and R'= Ph, the complex was sufficiently stable to obtain a crystal structure which contained two independent molecules in the assymmetric unit. The Si-C bond lengths, 1.78(2) and 1.79(2) Å, fall between a single bond (1.87-1.91 Å)[47] and a double bond (1.702(5) Å[48]-1.764 Å[49]). The ^{13}C (-29.04 ppm) and ^{29}Si (6.14 ppm) NMR resonances are at lower field than expected for a free silaethene but are in the range typical for metal coordinated silaethenes (Table 2.4). Similarly, an iridium silaethene complex, $Cp^*PMe_3Ir(\eta^2\text{-}CH_2SiPh_2)$, was prepared by treating $Cp^*PMe_3Ir(Me)(Cl)$ with $ClMgCH_2SiPh_2H$. This reaction involves the elimination of methane.[50] A high field ^{13}C signal at -33.37 is assigned to the CH_2 fragment of $Cp^*PMe_3Ir(\eta^2\text{-}CH_2SiPh_2)$. A single crystal X-ray diffraction study on $Cp^*PMe_3Ir(\eta^2\text{-}CH_2SiPh_2)$ indicates that the C=Si distance is 1.810(6) Å. Reactivity studies indicate that the iridium complex is remarkably stable. For example, no reaction occurs with excess phosphine at 140 °C after several days. Similarly, neither photolysis nor the addition of hydrogen gas produces any reaction. Methyliodide adds across the metal silicon bond as does methanol resulting in $Cp^*PMe_3Ir(I)(CH_2SiPh_2Me)$ and $Cp^*PMe_3Ir(H)(CH_2SiPh_2OMe)$, respectively.

Berry and coworkers have prepared a tungsten silaethene complex via an intramolecular reductive coupling reaction.[51] Treating $Cp_2W(Cl)(CH_2SiMe_2Cl)$ with magnesium results in the formation of $MgCl_2$ and $Cp_2W(\eta^2\text{-}CH_2SiMe_2)$. As is typical of this type of complex, the ^{13}C and ^{29}Si resonances occur at high field (^{13}C, -41.09 ppm; ^{29}Si, -15.7 ppm). An X-ray diffraction study indicates that the Si=C bond length is 1.800(8) Å. Addition of ligands (L) such as phosphine or ethylene results in migration of the silicon to a Cp ring to generate $Cp(\eta^4{:}\eta^1\text{-}C_5H_5SiMe_2CH_2)W(L)$. The migration is reversible; on the removal of the coordinating ligand (L) the η^2 structure is reformed. Methanol adds across the W-Si bond to produce $Cp_2W(H)(CH_2SiMe_2OMe)$ while hydrogen or trimethylsilane add across the W-C bond to produce $Cp_2W(H)(SiMe_3)$ or $Cp_2W(SiMe_3)_2$, respectively.

η^2-Disilenes

Mononuclear and dinuclear disilene complexes have been prepared. In the dinuclear complexes the disilene ligand bridges the two metal centers in an η^2,η^2 fashion. The first observed mononuclear coordinated disilene complex was $Hg(OCOCF_3)_2(\eta^2\text{-}Mes_2Si{=}SiMes_2)$. This compound was generated at low temperature from $Hg(OCOCF_3)_2$ and SiR_2SiR_2. Upon warming, $CF_3OCOSiR_2SiR_2OCOCF_3$ is formed.[52] Molybdenum and tungsten disilenes have been prepared by intramolecular reductive coupling of $Cp_2M(Cl)(\eta^2\text{-}SiMe_2SiMe_2Cl)$ with magnesium to produce $Cp_2M(\eta^2\text{-}SiMe_2SiMe_2)$.[53] In these complexes, the ^{29}Si NMR resonances are at high field (-20.3 ppm, M = Mo; -48.1 ppm, M = W, $^1J_{W\text{-}Si}$= 50.7 Hz). The Si-Si distance in the tungsten compound is 2.260(3) Å as indicated from an X-ray crystal structure. This is between Si-Si single (2.35 Å) and double (2.14 Å) bonds. Platinum disilene complexes have been prepared by the lithium reduction of platinum bisphosphinedichlorides in the presence of tetra-substituted disilanes. The disilene is presumably formed by an oxidative addition-reductive elimination process, Figure 2.1.[54] Alternatively the disilene platinum complexes may be prepared by displacement of ethylene

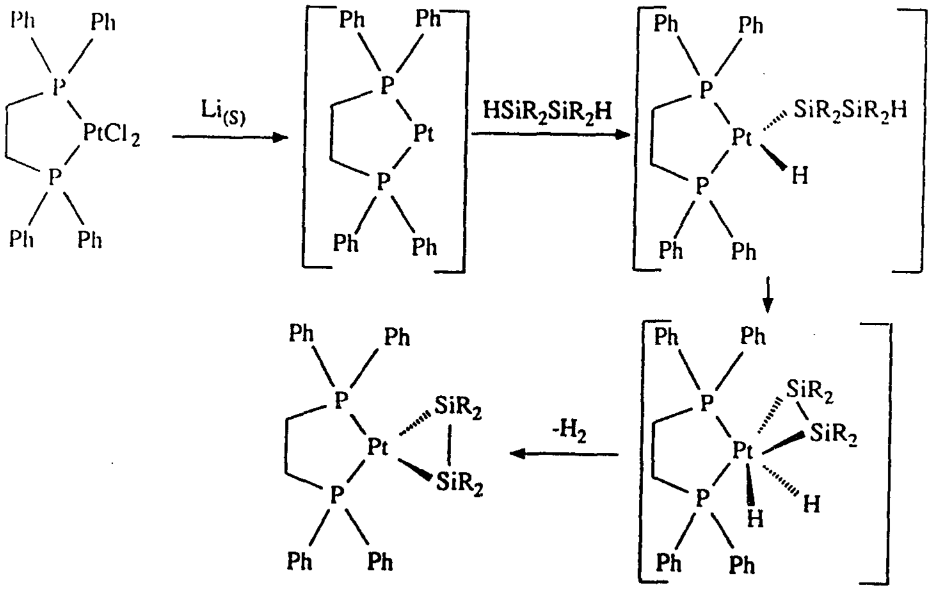


Figure 2.1. Proposed mechanism for the formation of platinum disilenes

from a platinum bisphosphine ethylene complex or by photolytic ejection of oxalate from $(Et_3P)_2Pt(Ox)$ in the presence of $Mes_2Si{=}SiMes_2$.[55]

Bimetallic bridging disilenes are prepared by the addition of primary (H_3SiR) silanes to platinum(0) bisphosphine complexes.[56] Frequently the Pt(0) complex is generated in situ from bisphosphineplatinumdichlorides and an alkali metal.[57] Tessier-Youngs and Youngs have also prepared a bridging disilene by the addition of lithiumdiphenylsilane to bis(triethylphosphine)platinumdichloride.[57b] Tilley has reported the synthesis of a novel μ-η^1,η^1-disilene diplatinum species which also contains two bridging silylene fragments,[56] Figure 2.2.

Table 2.4. η^2-Si=E metal complexes

Compound	^{29}Si δ	E (^{29}Si, ^{13}C) δ	$d_{(Si=E)}$ Å	$d_{(M-Si)}$ Å	$d_{(M-E)}$ Å	Ref.
$\mathrm{Cp_2Zr(PMe_3)(\eta^2\text{-}N^tBuSiMe_2)}$			1.687(3)	2.654(1)	2.167(3)	41
$\mathrm{Cp_2Zr(CO)(\eta^2\text{-}N^tBuSiMe_2)}$	-69.9					41
$\mathrm{CpFe(CO)_2(CH_2SiMe_2H)}$						45
$\mathrm{Cp^*(Cy)_3PRu(H)(\eta^2\text{-}CH_2SiMe_2)}$						46
$\mathrm{Cp^*(Cy)_3PRu(H)(\eta^2\text{-}CH_2SiPh_2)}$		-29.68				46
$\mathrm{Cp^*(i\text{-}Pr)_3PRu(H)(\eta^2\text{-}CH_2SiPh_2)}$	6.14	-29.04	1.78(2) 1.79(2)	2.382(4) 2.365(5)	2.25(2) 2.26(1)	46
$\mathrm{Cp^*PMe_3Ir(\eta^2\text{-}CH^2SiPh^2)}$		-33.37	1.810(6)	2.317(2)	2.189(8)	50
$\mathrm{Cp^*PMe_3Ir(\eta^2\text{-}CH^2SiMe^2)}$						50
$\mathrm{Cp^*PMe_3Rh(\eta^2\text{-}CH^2SiPh^2)}$						50
$\mathrm{Cp_2W(\eta^2\text{-}CH_2SiMe_2)}$	-15.7	-41.09	1.800(8)	2.534(2)	2.329(7)	51
$\mathrm{Cp(CO)_2W(\eta^2\text{-}CH_2SiMe_2)}$		*				44
$\mathrm{Hg(OCOCF_3)_2(\eta^2\text{-}SiR_2SiR_2)}$						52
$\mathrm{Cp_2W(\eta^2\text{-}SiMe_2SiMe_2)}$	-48.1	-48.1	2.260(3)	2.606(2)	2.606(2)	53
$\mathrm{Cp_2Mo(\eta^2\text{-}SiMe_2SiMe_2)}$	-20.3	-20.3				53
$\mathrm{(dppe)_2Pt(Sii\text{-}Pr_2Sii\text{-}Pr_2)}$	19.60	19.60				54
$\mathrm{(dcpe)_2Pt(Ph_2SiSiPh_2)}$	-7.84	-7.84				54
$\mathrm{(\mu\text{-}\eta^2,\eta^2\text{-}PhXSiSiXPh)Pt(Et_3P)_2}$ X = H, Cl			2.575(15)- 2.602(4)	2.355(7)- 2.383(8)		57b
trans- $\mathrm{(\mu\text{-}\eta^1,\eta^1\text{-}CyXSiSiXCy)Pt(Et_3P)_2}$ X = H, Cl			2.554(8)	2.384(4)	2.402(4)	57a
cis- $\mathrm{(\mu\text{-}\eta^1,\eta^1\text{-}CyXSiSiXCy)Pt(Et_3P)_2}$ X = H, Cl			2.648(11)	2.395(5)	2.405(6)	57a

* -1.1, -8.0, -27.6 ppm for the three carbons of the silene ligand, no assignments have been made.

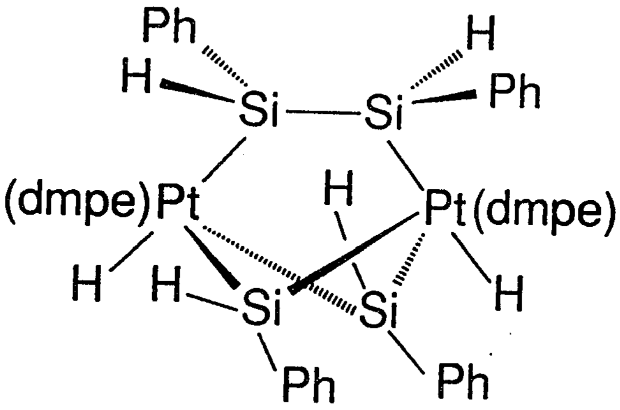


Figure 2.2. (dmpe)(H)Pt(μ-SiHPh)$_2$[μ-η^1,η^1-PhHSiSiHPh]Pt(H)(dmpe)

CHAPTER 3: LOW VALENT SILICON STABILIZED BY AN OSMIUM PORPHYRIN

Introduction

To date, no coordination complex, consisting primarily of classical ligands (e.g. amines, cyanides, etc.) is known to stabilize silylene ligands. This is not surprising since classical coordination compounds have not shown any propensity to form stable carbene complexes, despite recent studies which demonstrate that strong π-bonds with η^2-arenes and alkynes are possible.[58] Thus, it is clear that distinct boundaries still divide organometallic and classical coordination chemistry. However, metalloporphyrin compounds serve an important role in unifying these two traditional areas of chemistry.[59] Although metalloporphyrins have been of long-standing interest in classical coordination chemistry, they have recently been found to bind organic π-acid ligands.[60-61]

As an extension of the utility of metalloporphyrins, we describe here the synthesis and characterization of donor-stabilized metalloporphyrin silylene complexes. Previous attempts at preparing terminal silylene complexes have utilized bulky substituents on silicon to increase kinetic stability. Our approach was to employ large, planar porphyrin ligands as a means of providing steric bulk at the metal for similar reasoning. In addition, an electron rich, late-transition metal was chosen in hopes that further stabilization of the adjacent electron deficient three-coordinate silicon atom would be realized. Furthermore, hexamethylsilacyclopropane serves as a useful reagent for producing transient dimethylsilylene under mild conditions.[62] Using this rationale, we report a new method for the preparation of silylene complexes which involves silylene transfer as well as a method which uses dichlorosilanes as the silylene source.

Experimental Section

General

All manipulations of reagents and products were carried out under a nitrogen atmosphere using a VACUUM/ATMOSPHERES glove box equipped with a model MO40H Dri-Train gas purification system or on a vacuum line using standard Schlenk techniques. All solvents were dried and distilled from purple solutions of sodium/benzophenone. ^1H NMR spectra were recorded on Nicolet 300 MHz or Varian VXR 300 MHz spectrometers. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN or Oneida Research Services, Whitesboro, NY. Dichlorodialkylsilanes were purchased from commercial sources, distilled from K_2CO_3 or CaH_2, and degassed by three freeze-pump-thaw cycles prior to use. $[Os(TTP)]_2$ was prepared by the literature procedure.[63]

Hexamethylsilacyclopropane, HMS, was prepared from $(CH_3)_2Si(CH(CH_3)_2)_2$,[64] and obtained free of THF by trap to trap distillation.[65]

Synthesis

$(CH_3)_2Si(CH(CH_3)_2)_2$.

A 1.5 M solution of LiMe in Et_2O (72.0 mL, 108 mmol) was added dropwise over 1.75 h to $Cl_2Si(^iPr)_2$ (9.962 g, 53.85 mmol) while cooling at -78 °C under N_2. The reaction mixture was allowed to warm slowly to ambient temperature and subsequently heated at reflux for 18 h. The solution was cooled to ambient temperature and hydrolyzed with 1 M HCl (~100 mL) until evolution of methane stopped. After the aqueous layer was washed with Et_2O (3 x 50 mL), the combined organic fractions were concentrated to 100 mL under reduced pressure, and dried over $MgSO_4$. Distillation and collection of the 137-140 °C-fraction produced 3.651 g (47%) of product. ^1H NMR ($CDCl_3$): 0.92 (br m, 14H, ^{i}pr), 0.14 (s, 6H, Si-C*H*$_3$) ppm.

(TTP)Os=Si(CH$_3$)$_2$·OC$_4$H$_8$ (1·THF).

Method A. $[Os(TTP)]_2$ (15.0 mg, 8.72 μmol) was stirred in 3 mL of THF with potassium (approximately 20 mg) until the brown solution became emerald green. After filtering the solution through a glass wool plug to remove the potassium, 2.2 μL (18 μmol) of Cl_2SiMe_2 dissolved in 3 mL of THF were added dropwise to the stirred solution of $K_2[Os(TTP)]$ at ambient temperature to form an orange-brown solution. After stirring for 1 h, THF and excess silane were removed under reduced pressure. The residues were redissolved in C_6H_6 and filtered on a medium glass frit to remove all salts. Removal of the solvent from the filtrate under reduced pressure afforded 17.0 mg of brown solid (98.5% yield). ^1H NMR (C_6D_6): 8.25 (s, 8H, β-H), 8.07 (d, 4H, aryl), 7.95 (d, 4H, aryl), 7.36 (d, 4H, aryl), 7.30 (d, 4H, aryl), 2.39 (s, 12H, tolyl-CH_3), -2.10 (s, 6H, $SiCH_3$), 1.36 (m, 4H, α-THF), 0.55 (m, 4H, β-THF) ppm. UV/Vis (C_6H_6): 408 (Soret), 504 nm. Anal. calcd. for $C_{54}H_{50}N_4OOsSi$: C, 65.56; H, 5.09; N, 5.66. Found: C, 66.29; H, 4.79; N, 5.45.

Method B. Approximately 3 mL of benzene containing 10.4 μL (73.2 μmol) of HMS and 7.0 μL (86 μmol) of THF were added to $[Os(TTP)]_2$ (12.2 mg, 7.09 μmol) dissolved in 2 mL of dry benzene. The solution was stirred at 24 °C for 1 h before the solvent was removed under reduced pressure. The resulting orange-brown solid was dispersed in hexane (2 mL), cooled to -20 °C for 20 min., and filtered on a medium porosity glass frit. The solid was washed from the frit with 5 mL of benzene containing 5 drops of THF. Removal of the solvent under reduced pressure produced 7.3 mg of **1·THF** (52% yield). MS (M^+-THF) found: 918.2802, calc: 918.2793.

(TTP)Os=$SiMe_2·NC_5H_5$ (1·py).

To 3.8 mg (3.8 μmol) of (TTP)Os=$SiMe_2$·THF in 0.5 mL C_6D_6 was added 0.6 μL (7.4 μmol) of pyridine (py) to produce **1·py** quantitatively by ^1H NMR. Removal of the solvent under reduced pressure produces 3.8 mg of brown solid which is found by ^1H NMR to consist of a 65:35 ratio of **1·py**:Os(TTP)$(py)_2$. ^1H NMR (C_6D_6): 8.16 (s, 8H, β-H), 7.97 (d, 8H, aryl), 7.36 (d, 4H, aryl), 7.23 (d, 4H, aryl), 2.39 (s, 12H, tolyl-CH_3), -1.84 (s, 6H, $SiCH_3$), 6.50 (t, 1H, py-H_p), 6.00 (t, 2H, py-H_m), 5.70 (d, 2H, py-H_o) ppm. UV-vis (C_6D_6): 414 (Soret), 498 nm.

(TTP)Os=$SiEt_2·OC_4H_8$ (2·THF).

Using method A, **2·THF** was prepared in 95% yield from Cl_2SiEt_2 (3.0 μl, 20 μmol) and K_2Os(TTP) prepared in situ using 17.4 mg (10.1 μmol) of $[Os(TTP)]_2$. ^1H NMR (C_6D_6): 8.24 (s, 8H, β-H), 8.03 (dd, 8H, aryl), 7.37 (d, 4H, aryl), 7.30 (d, 4H, aryl), 2.39 (s, 12H, tolyl-CH_3), -0.48 (t, 6H, $SiCH_2C\mathit{H}_3$), -1.50 (m, 4H, $SiC\mathit{H}_2CH_3$), 1.60 (m, 4H, α-THF), 0.65 (m, 4H, β-THF) ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6) 24.53 (s) ppm. UV-vis (C_6H_6): 408 (Soret), 502 nm. Anal. calcd. for $C_{56}H_{54}N_4OOsSi$: C, 66.11; H, 5.35, N, 5.51. Found: C, 67.01; H, 5.53; N, 4.56.

(TTP)Os=SiEt$_2$·NC$_5$H$_5$ (2·py).

(TTP)Os=SiEt$_2$·THF (6.0 mg, 6.0 μmol) was dissolved in C$_6$D$_6$ and treated with 1.6 μL (20 μmol) of pyridine. The ^{1}H NMR spectrum of this sample showed quantitative formation of **2·py**. Removal of the solvent under reduced pressure yielded 4.4 mg of brown solid consisting of a 7:3 mixture as determined by ^{1}H NMR of **2·py**:Os(TTP)(py)$_2$. NMR (C$_6$D$_6$): 8.15 (s, 8H, β-H), 8.02 (d, 4H, aryl), 7.96 (d, 4H, aryl), 7.37 (d, 4H, aryl), 7.23 (d, 4H, aryl), 2.37 (s, 12H, tolyl-CH$_3$), -0.36 (t, 6H, SiCH$_2$C*H*$_3$), -1.25 (m, 4H, SiC*H*$_2$CH$_3$), 6.56 (t, 1H, py-H$_p$), 6.05 (t, 2H, py-H$_m$), 5.86 (d, 2H, py-H$_o$) ppm. UV-vis (C$_6$H$_6$): 390 (sh), 410 (Soret), 498 nm.

(TTP)Os=Si(i-Pr)$_2$·THF (3·THF).

Using method A, **3·THF** was prepared from [Os(TTP)]$_2$ (3.9 mg, 2.3 μmol) and Cl$_2$Si^{i}Pr (0.8 μl, 4.4 μmol) in 63% yield. ^{1}H NMR (C$_6$D$_6$) 8.25 (s, 8H, β-H), 8.08 (d, 4H, aryl), 8.01 (d, 4H, aryl), 7.36 (d, 4H, aryl), 7.28 (d, 4H, aryl), 2.38 (s, 12H, tolyl-CH$_3$), -0.43 (d, 12H, SiCH(C*H*$_3$)$_2$), -0.94 (m, 2H, SiC*H*(CH$_3$)$_2$), 1.38 (m, 4H, α-THF), 0.53 (m, 4H, β-THF) ppm. UV-vis (C$_6$H$_6$): 408 (Soret), 502 nm.

(TTP)Os(η^2-Me$_2$SiSiMe$_2$) (4).

Approximately 0.75 mL of d$_6$-benzene containing 1.4 μL (9.9 μmol) of HMS were added to [Os(TTP)]$_2$ (2.0 mg, 1.16 μmol) while stirring at ambient temperature. After an hour the sample was concentrated to approximately 0.5 mL under reduced pressure, to remove tetramethylethene. ^{1}H NMR (C$_6$D$_6$) 8.42 (s, 8H, β-H), 8.24 (d, 4H, aryl), 7.81 (d, 4H, aryl), 7.30 (d, 4H, aryl), 7.21 (d, 4H, aryl), 2.35 (s, 12H, tolyl-CH$_3$), -1.58 (s, 12H,

$Si(CH_3)_2)$ ppm.

Using method A $K_2[(TTP)Os]$ was produced from $[Os(TTP)]_2$ (4.0 mg, µmol). $ClMe_2SiSiMe_2Cl$ (0.8 µL, µmol) was added and the mixture was stirred at ambient temperature for 1.5 h. Removal of the solvent under reduced pressure produced a 1:5 mixture of **4** and **1**·**THF** as established by ^1H NMR.

X-ray Structure Determination of 2·2THF

A single crystal of $(TTP)Os{=}SiEt_2(THF)_2{\cdot}2THF$ suitable for X-ray structure analysis was grown from a THF solution layered with octane. A brown crystal having approximate dimensions of 0.32 x 0.15 x 0.25 mm was attached to a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo K_α radiation (λ = 0.71073 Å) for data collection at -62 ± 1 °C. The cell constants for data collection were determined from a list of reflections found by an automated search routine. Pertinent data collection and reduction information is given in Table 3.1. Lorentz and polarization corrections were applied. A correction based on a decay in the standard reflections of 1.4% was applied to the data. An absorption correction based on a series of ψ-scans was applied. The agreement factor for the averaging of observed reflections was 3.5% (based on F).

The space group $P2_1/c$ was unambiguously determined by systematic absences prior to the solution. The positions of the osmium and silicon atoms were determined by direct methods.[66] The remaining non-hydrogen atom positions were determined by successive difference Fourier maps. Two solvent molecules of tetrahydrofuran were located in the asymmetric unit. Only four atoms of one THF could be found by difference Fourier maps. The THF molecules appear to be caged by the porphyrin substituent groups. The closest non-bonded contact distance is 3.67 Å for a carbon of the THF group bound to the silicon

Table 3.1. Crystal data for $(TTP)Os{=}SiEt_2(THF)_2{\cdot}2THF$

Formula	$OsSiO_2N_4C_{60}H_{62}{\cdot}2(OC_4H_8)$
Formula weight	1227.67
Space Group	$P2_1/c$
a, Å	21.649(5)
b, Å	13.829(3)
c, Å	19.526(3)
α, deg	90.0
β, deg	98.08(2)
γ, deg	90.0
V, Å	5788(4)
Z	4
d_{calc}, g/cm^3	1.416
Crystal size, mm	0.32 x 0.15 x 0.25
$\mu(MoK_\alpha)$, cm^{-1}	22.6
Data collection instrument	Enraf-Nonius CAD4
Radiation (monochromated in incident beam)	MoK_α ($\lambda = 0.71073$ Å)
Orientation reflections, number, range (2θ)	25, $10.0 < \theta < 22.0$
Temperature, °C	-62(1)
Scan method	θ - 2θ
Data col. range, 2θ, deg	4.0-45.0
No. data collected	13644
No. unique data, total (with $F_o^2 > 3\sigma(F_o^2)$)	5134 (2406)
Number of parameters refined	283
Trans. factors, max., min. (ψ-scans)	0.999, 0.972
R^a	0.050
$R_\omega{}^b$	0.057
Quality-of-fit indicator^c	1.13
Largest shift/esd, final cycle	0.01
Largest peak, e/Å^3	1.3(1)

$^aR = \Sigma||F_o| - |F_c|/\Sigma|F_o|$ $^bR_\omega = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{½}$; $\omega = 1/\sigma^2|F_o|)$

^{c}Quality-of-fit = $[\Sigma\omega(|F_o| - |F_c|)^2/N_{obs} - N_{parameters}]^{½}$

and a THF of solvation.

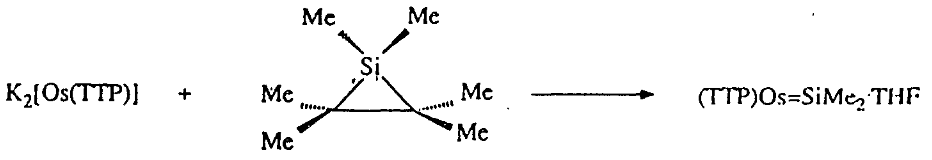
Only the osmium and silicon atoms were refined anisotropically[67] because of a lack of 3σ data. As is common in structure determinations involving THF,[68] the THF molecules of solvation of **2·2THF** exhibit a high degree of thermal motion. Consequently, these solvate molecules were not refined positionally or isotropically in the final cycle of least-squares. All hydrogens were placed in the porphyrin group at distances of 0.95 Å with isotropic temperature factors 1.3 times the respective carbon atoms.

X-ray data collection and structure solution were carried out at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Corp. MicroVAX II computer using the CAD4-SDP programs.[69]

Results

Synthesis

When a dark brown solution of the paramagnetic dimer $[Os(TTP)]_2$ is treated with a ten-fold excess of hexamethylsilacyclopropane (HMS) containing THF, a rapid color change to orange is observed at ambient temperature. The ^1H NMR spectrum for the material isolated from this reaction is consistent with a new diamagnetic metalloporphyrin complex which can be formulated as the dimethylsilylene complex $(TTP)Os{=}SiMe_2{\cdot}THF$, **1·THF**, eq. 3.1. In C_6D_6, the dimethylsilylene complex **1·THF** maintains a time-averaged four-fold porphyrin symmetry as indicated by the single β-pyrrole signal at 8.25 ppm and the single *p*-tolyl methyl peak at 2.39 ppm. The appearance of distinct resonances for the *o*-, *o'*-, *m*-, and *m'*-tolyl protons at 8.07, 7.95, 7.36 and 7.30 ppm indicate that mirror symmetry in the porphyrin plane is absent. The coordinated dimethyl silylene ligand gives rise to a new six-proton singlet at -2.10 ppm. The far-upfield position of this signal is characteristic of protons held above a porphyrin ring current. Resonances for a single THF molecule are also observed at 1.36 (m, 4H) and 0.55 (m, 4H) ppm. The upfield shift of these signals also indicate that THF is bound above the porphyrin. Coordination of the THF molecule directly to silicon and not to osmium was established by 2D-NOESY NMR. A cross peak between the THF resonance at 1.36 ppm and the $SiMe_2$ resonance at -2.10 ppm indicates that the THF and silylene methyl groups are indeed proximal to each other. Further support for the composition of the silylene complex was provided by mass spectral analysis. Electron impact ionization of a sample of **1·THF** allowed observation of an ion fragment having an exact mass of 918.2802 amu. This corresponds to a daughter ion formed by loss of THF (calcd. mass: 918.2793 amu).



(3.1)

A more versatile method for preparing silylene complexes involves a simple metathetical reaction between the dianionic complex $[Os(TTP)]^{2-}$ and dichlorosilanes. Venburg and Collman have independently reported a similar procedure.[70] Thus, when a dark green THF solution of $K_2[Os(TTP)]$[71] is treated with one equivalent of dichlorodimethylsilane, formation of **1·THF** occurs within minutes, eq. 3.2. The ^1H NMR

$$K_2[Os(TTP)] + Cl_2SiR_2 \rightarrow (TTP)Os{=}SiMe_2{\cdot}THF + 2\,KCl \qquad (3.2)$$

and 2D-NOESY spectra of **1·THF** prepared from $[Os(TTP)]^{2-}$ are identical to those of material prepared from the HMS method.

As indicated by eq. 3.2, the diethyl- and di(isopropyl)silylene complexes can also be prepared. However the more sterically hindered silanes, $Cl_2Si^tBu_2$ and Cl_2SiPh_2, undergo no reaction with $[Os(TTP)]^{2-}$ at 22 °C. At higher temperatures, destruction of both $[Os(TTP)]^{2-}$ and the dichlorosilanes occurs. In both **2·THF** and **3·THF**, a single coordinated THF molecule is present, as indicated by significant upfield shifts for the α- and β-protons in the ^1H NMR spectrum. Particularly noteworthy in the NMR spectrum of **2·THF** are the ethyl CH_2 resonances. These appear as a diastereotopic multiplet at -1.50 ppm, indicating that the silicon must be pyramidalized. Irradiation of the ethyl triplet at -0.48 ppm collapses the methylene signal into an AB quartet. The 2D-NOESY spectrum for **3·THF** demonstrates that THF is coordinated to silicon in this case also. The proton-decoupled silicon NMR spectrum of **2·THF** has a single resonance at 24.53 ppm.

Simple displacement reactions at the silylene silicon are possible. When one equivalent of pyridine is added to $(TTP)Os{=}SiMe_2{\cdot}THF$, **1·THF**, in C_6D_6, a new complex $(TTP)Os{=}SiMe_2{\cdot}py$, **1·py**, is produced, quantitatively as determined by ^1H NMR. One equivalent of free THF is observed in the proton NMR spectrum at 3.57 and 1.40 ppm and new resonances for bound pyridine appear at 6.50 (t, 1H), 6.00 (t, 2H) and 5.70 (d, 2H) ppm. Coordination of the pyridine to silicon was also established by a 2D-NOESY experiment. The new silylene methyl resonance appears at -1.84 ppm, and the corresponding porphyrin signals are observed at 8.16 (s, 8H, β-H), 7.97 (d, 8H, aryl), 7.36 (d, 4H, aryl), 7.23 (d, 4H, aryl), and 2.39 (s, 12H, CH_3) ppm. Removal of the solvent under reduced pressure results in partial decomposition of the pyridine adduct, **1·py**, to $Os(TTP)py_2$. The resulting solid contains a 7:3 mixture of **1·py** and Os(TTP)py$_2$. Similarly, addition of pyridine to (TTP)Os=SiEt$_2$·THF produces (TTP)Os=SiEt$_2$·py, **2·py**. The methylene protons in this complex are also diastereotopic, indicating that pyridine is coordinated to silicon.

When a C_6D_6 solution of [Os(TTP)]$_2$ is treated with a five-fold excess of HMS at ambient temperature in the absence of THF a rapid color change from dark brown to orange is observed. The ^{1}H NMR spectrum of the new material is consistent with a diamagnetic osmium porphyrin coordinated by tetramethyldisilene, (TTP)Os(η^2-Me$_2$Si=SiMe$_2$). On the NMR time scale the four fold of the porphyrin is maintained as indicated by a single resonance at 8.42 ppm for the β-pyrrole protons and a single p-tolyl methyl resonance at 2.35 ppm. The observance of four distinct doublets for the o-, o'-, m-, and m'-tolyl protons at 8.24, 7.81, 7.30, and 7.21 ppm indicate the mirror plane of the porphyrin is absent. The coordinated tetramethyldisilene ligand produces a twelve-proton singlet at -1.58 ppm.

Complex **4** may also be prepared by treating K$_2$[Os(TTP)] in THF with ClMe$_2$SiSiMe$_2$Cl. The η^2-disilene complex produced in this manner is always contaminated with the silylene complex **1·THF**. Over a period of several days a benzene solution of complex **4** containing THF completely decomposes to **1·THF**.

X-ray Structure of 2·2THF

The molecular structure of the diethylsilylene complex, **2·2THF**, was determined by single crystal X-ray diffraction. Because of the small size and weak diffraction of the crystal, only a relatively small number of observed reflections could be collected. Consequently, in order to preserve a reasonable data-to-parameter ratio, the majority of atoms were refined with isotropic temperature factors. As a result of these limitations, small differences between bond lengths are probably not experimentally significant. Nonetheless, the structure of **2·2THF** was clearly established as a base-stabilized silylene complex as shown in Figure 3.1. Crystallographic data for the structure determination and fractional coordinates for non-hydrogen atoms are listed in Tables 3.1 and 3.2. Table 3.3 gives selected bond distances and angles.

The diethylsilylene complex **2·2THF** crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. As expected for a six-coordinate complex, the porphyrin ligand in this molecule is nearly planar. The largest deviation from planarity occurs at N1, which is 0.085(15) 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 85.4° to 95.1°. The osmium atom is slightly drawn out of the mean porphyrin plane 0.116(2) Å towards the silylene ligand. The Os-O2 distance of 2.40(2) Å[72] suggests that the silylene ligand has a strong *trans*-effect. This is supported by reactivity studies (*vide infra*).

The Os-Si bond length in **2·2THF** (2.325(8) Å) is the shortest Os-Si distance reported to date.[73] This bond distance is comparable to the shortest known Ru-Si distance, 2.328(2) Å, in the base-stabilized silylene complex reported by Tilley, $[Cp^*(PMe_3)_2Ru{=}SiPh_2{\cdot}N{\equiv}CCH_3]BPh_4$.[31a,b] The Si-O1 distance (1.82(2) Å) is longer than typical Si-O bond distances (1.63-1.66 Å) in four-coordinate silicon compounds.[34] Of the nine previously reported silylene complexes containing a coordinated oxygen donor, $Cp^*(PMe_3)_2Ru{=}SiPh_2(OTf)$ has the longest Si-O distance (1.853(5) Å).[31] Other metal-silylene complexes stabilized by neutral oxygen-bases have Si-O distances of 1.73-1.74 Å, Table 2.1. The coordination geometry about silicon in **2·2THF** is similar to that for previously reported base-stabilized silylene complexes. The Os-Si-C bond angles of 121(1) and 117(1)° are near

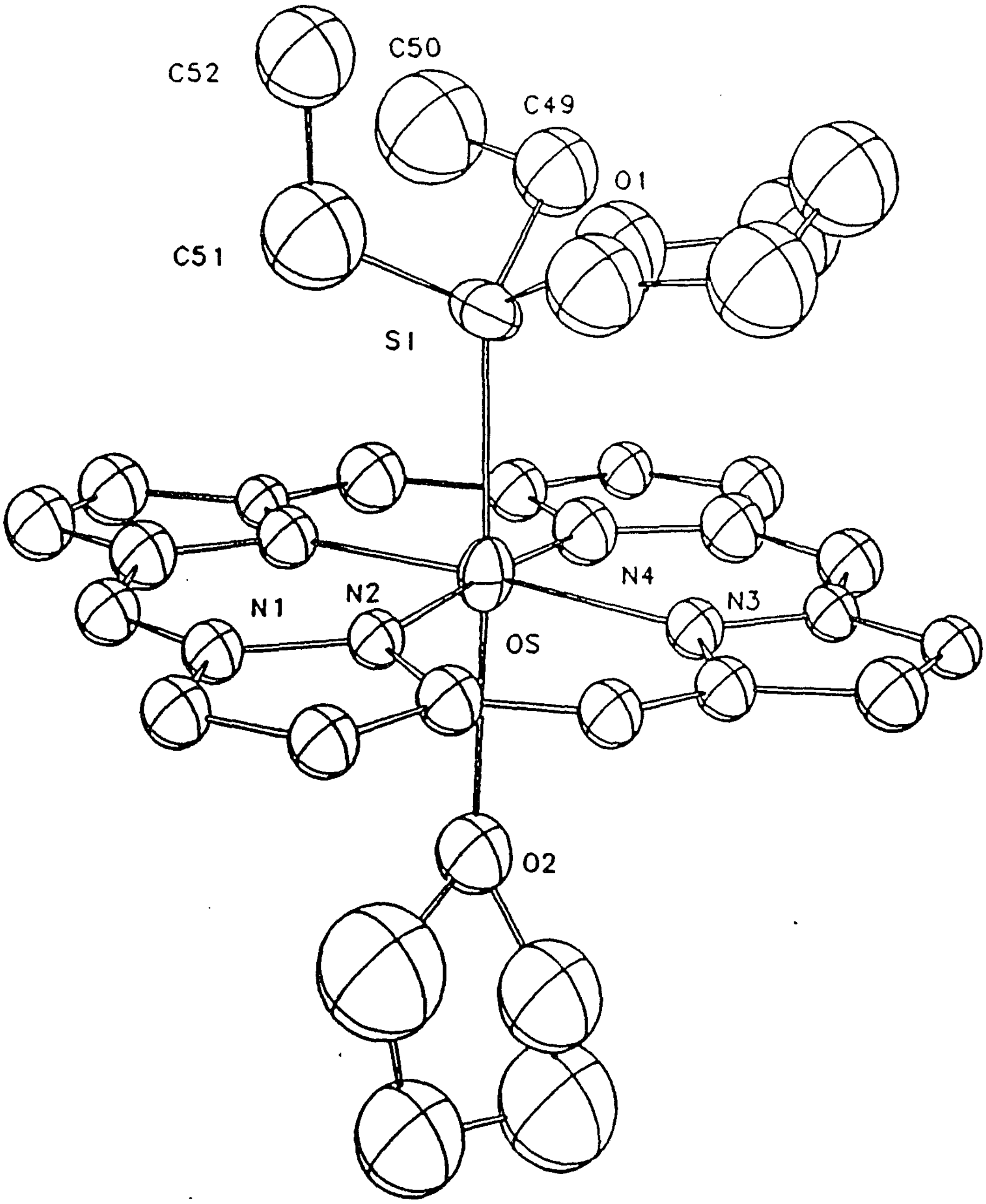


Figure 3.1. Molecular structure for (TTP)Os=SiEt$_2$·2THF with 50% probability thermal elipsoids and partial atom numbering scheme. The tolyl groups have been omitted.

Table 3.2. Positional parameters and their estimated standard deviations

Atom	x	y	z	B(Å^2)
Os	0.75180(8)	0.21829(7)	0.49835(9)	2.52(1)
N1	0.6846(7)	0.265(1)	0.5534(7)	2.2(3)*
N2	0.7566(7)	0.349(1)	0.4553(7)	1.9(3)*
N3	0.8241(7)	0.169(1)	0.4496(7)	2.1(3)*
N4	0.7508(8)	0.090(1)	0.5486(8)	2.9(4)*
C1	0.6557(7)	0.218(2)	0.6031(8)	1.7(3)*
C2	0.6126(9)	0.280(2)	0.628(1)	3.6(4)*
C3	0.615(1)	0.365(2)	0.598(1)	3.6(5)*
C4	0.6600(9)	0.360(2)	0.550(1)	2.8(5)*
C5	0.6797(9)	0.437(2)	0.513(1)	2.6(4)*
C6	0.7240(9)	0.435(1)	0.467(1)	2.2(4)*
C7	0.7430(9)	0.513(1)	0.429(1)	2.6(5)*
C8	0.789(1)	0.478(2)	0.392(1)	3.0(5)*
C9	0.7989(9)	0.377(1)	0.411(1)	2.6(4)*
C10	0.8410(9)	0.319(1)	0.385(1)	2.6(5)*
C11	0.8556(9)	0.222(2)	0.407(1)	2.7(4)*
C12	0.8969(9)	0.160(2)	0.378(1)	2.5(4)*
C13	0.8926(8)	0.072(1)	0.408(1)	2.0(4)*
C14	0.8495(8)	0.077(1)	0.4535(9)	1.9(4)*
C15	0.8324(9)	-0.001(1)	0.494(1)	2.7(5)*
C16	0.786(1)	0.007(2)	0.539(1)	3.0(5)*
C17	0.771(1)	-0.070(2)	0.582(1)	3.1(5)*

Starred atoms were refined isotropically.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos \gamma)*B(1,2) + ac(\cos \beta)*B(1,3) + bc(\cos \alpha)*B(2,3)]$.

Table 3.2. cont.

Atom	x	y	z	B(Å^2)
C18	0.7271(9)	-0.034(1)	0.618(1)	2.4(4)*
C19	0.7118(9)	0.062(1)	0.599(1)	2.5(4)*
C20	0.669(1)	0.124(2)	0.621(1)	3.1(5)*
C21	0.6513(8)	0.535(1)	0.5215(9)	1.8(4)*
C22	0.589(1)	0.551(2)	0.497(1)	4.4(6)*
C23	0.561(1)	0.637(2)	0.507(1)	5.1(6)*
C24	0.598(1)	0.712(2)	0.540(1)	6.0(6)*
C25	0.658(1)	0.704(2)	0.558(1)	4.4(5)*
C26	0.687(1)	0.611(2)	0.555(1)	5.0(6)*
C27	0.567(2)	0.811(2)	0.551(2)	8.7(9)*
C28	0.878(1)	0.366(2)	0.333(1)	3.5(5)*
C29	0.850(1)	0.396(2)	0.270(1)	3.9(5)*
C30	0.883(1)	0.440(2)	0.223(1)	4.1(6)*
C31	0.946(1)	0.454(2)	0.241(1)	4.2(6)*
C32	0.976(1)	0.423(2)	0.299(1)	3.9(5)*
C33	0.941(1)	0.379(2)	0.348(1)	3.8(5)*
C34	0.983(1)	0.498(2)	0.187(1)	6.4(7)*
C35	0.8641(9)	-0.095(1)	0.488(1)	2.3(4)*
C36	0.9240(9)	-0.110(1)	0.506(1)	2.0(4)*
C37	0.9494(9)	-0.200(2)	0.499(1)	3.3(5)*
C38	0.9157(9)	-0.279(2)	0.476(1)	3.1(4)*
C39	0.856(1)	-0.265(2)	0.457(1)	7.0(8)*
C40	0.826(1)	-0.172(2)	0.461(1)	3.3(5)*
C41	0.943(1)	-0.373(2)	0.466(1)	7.0(8)*
C42	0.6260(9)	0.082(1)	0.671(1)	2.1(4)*
C43	0.650(1)	0.056(2)	0.735(1)	3.2(5)*
C44	0.614(1)	0.025(2)	0.786(1)	5.2(7)*

Table 3.2. cont.

Atom	x	y	z	B(Å^2)
C45	0.552(1)	0.013(2)	0.762(1)	3.2(5)*
C46	0.527(1)	0.034(2)	0.696(1)	3.3(5)*
C47	0.5641(9)	0.067(2)	0.648(1)	3.0(5)*
C48	0.507(1)	-0.019(2)	0.817(2)	6.7(8)*
Si	0.6734(3)	0.1653(5)	0.4129(3)	3.4(2)
C49	0.637(1)	0.045(2)	0.418(1)	5.3(6)*
C50	0.581(1)	0.049(2)	0.464(2)	8.0(9)*
C51	0.615(1)	0.251(2)	0.380(2)	6.9(8)*
C52	0.564(1)	0.228(2)	0.323(1)	6.5(7)*
O1	0.6982(8)	0.140(1)	0.3295(8)	5.6(4)*
C53	0.732(1)	0.046(2)	0.314(2)	7.4(8)*
C54	0.740(1)	0.068(2)	0.240(2)	7.3(8)*
C55	0.758(1)	0.171(2)	0.236(2)	7.6(9)*
C56	0.714(1)	0.219(2)	0.284(1)	5.9(6)*
O2	0.8296(6)	0.279(1)	0.5879(6)	3.3(3)*
C57	0.891(1)	0.239(2)	0.596(1)	5.7(7)*
C58	0.926(2)	0.292(3)	0.653(2)	10.(1)*
C59	0.899(1)	0.391(2)	0.650(2)	7.3(8)*
C60	0.846(1)	0.375(2)	0.596(2)	8.5(9)*
O3	0.149	0.376	0.285	13.5*
C61	0.146	0.313	0.344	9.2*
C62	0.098	0.235	0.315	10.0*
C63	0.115	0.223	0.234	13.2*
C64	0.135	0.324	0.223	10.7*
C65	0.610	0.798	0.279	10.0*
C66	0.638	0.776	0.360	10.0*

Table 3.2. cont.

Atom	x	y	z	B(Å^2)
C67	0.690	0.758	0.323	10.0*
C68	0.659	0.779	0.246	10.0*

Table 3.3. Selected intramolecular bond distances and angles

Bond distances in angstroms			**Bond angles in degrees**			
Atom 1	Atom 2	Distance	Atom 1	Atom 2	Atom 3	Angle
Os	N1	2.03(2)	N1	Os	Si	88.7(5)
Os	N2	2.01(2)	N1	Os	02	89.1(6)
Os	N3	2.06(2)	N2	Os	Si	93.5(6)
Os	N4	2.03(2)	N2	Os	02	85.3(7)
Os	Si	2.324(8)	N3	Os	Si	95.2(4)
Os	02	2.40(2)	N3	Os	02	87.1(5)
Si	C49	1.85(3)	N4	Os	Si	90.9(5)
Si	C51	1.79(4)	N4	Os	02	90.3(7)
Si	01	1.82(2)	Si	Os	02	177.4(5)
			Os	Si	C49	121.(1)
			Os	Si	C51	117.(1)
			Os	Si	01	115.2(6)
			C49	Si	C51	110.(1)
			C49	Si	01	93.(1)
			C51	Si	01	95.(1)
			Si	C49	C50	111.(2)
			Si	C51	C52	122.(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

the values expected for an sp^2 hybridized silicon. Consistent with the partial double bondcharacter in the Os-Si interaction is the C-Si-C bond angle of 111.0(2)°. This is more typical of the C-Si-C bond angles of 115-118° in disilenes, $R_2Si=SiR_2$, and may reflect some sp^2 character.[12] Note that in other base-stabilized transition metal silylene complexes, the R-Si-R angles range from 102° to 104°.

Discussion

The reaction of $[Os(TTP)]_2$ with HMS represents a new method for the preparation of base-stabilized silylene complexes. The formation of **1·THF** from this reaction occurs rapidly at 22 °C. Since the generation of the free silylene (Me_2Si:) from HMS has a half-life of greater than nine days at ambient temperature, formation of **1·THF** is unlikely to arise from thermal extrusion of Me_2Si: from HMS. The formation of the dimethyl silylene complex **1·THF** may involve a prior electron-transfer step between $[Os(TTP)]_2$ and HMS leading to a chain radical process.[74]

Unoptimized yields of **1·THF** from the HMS method are typically on the order of 50%. For a significant reaction to take place, an excess of HMS (HMS:Os > 3) is required. As a result, major by-products (presumably oligomeric and polymeric dimethylsilanes) arises from the decomposition of HMS. The majority of these silicon contaminants can be removed by washing with hexanes, but traces of impurities still remain. However, we have found that **1·THF** can be prepared independently from $K_2[Os(TTP)]$ and Cl_2SiMe_2 using a method similar to that reported by Zybill and Müller.[15,32] This reaction proceeds rapidly at 22 °C and produces high yields of much cleaner **1·THF**. In an analogous manner, the diethyl, **2·THF**, and di(isopropyl), **3·THF**, derivatives can be prepared. These compounds are all thermally and air-sensitive materials and slowly decompose to uncharacterized materials over a few days at 23 °C. Qualitatively, the stability towards decomposition appears to decrease with the size of the alkyl substituent on Si. For example, we have found that **3·THF** completely decomposes in less than 48 h.

In all three complexes, one molecule of coordinated THF is present as demonstrated by ^{1}H NMR integrations. All isolated silylene complexes have a donor molecule coordinated to the silylene ligand, with one exception, $[Cp^*(PMe_3)_2Ru{=}Si(SR)_2]BPh_4$ where R is *p*-tolyl or ethyl.[31] This latter example can be considered to be base-stabilized by an internal donation of a lone pair from sulfur to silicon. In any event, all of these examples involve 18-electron metal complexes. The base-free complex (TTP)Os=SiR$_2$ is formally a 16-electron complex. Thus, THF could coordinate to either the osmium or silicon. In fact, both sites can bind THF, as indicated by the X-ray crystal structure of **2·THF**. However, it is apparent that under normal work-up conditions, one of the THF molecules is easily removed. The question of which site binds the donor molecule when only one THF is present was answered by 2D-NOESY. The appearance of a cross peak between the THF signal at 1.34 ppm and the SiMe$_2$ signal in **1·THF** indicates that THF is coordinated to silicon. This is further supported by the diastereotopic nature of the CH$_2$-ethyl signals of the mono-THF adduct **2·THF**. Pyramidalization of the silicon of the diethylsilylene group is likely to be due to coordination of THF to Si.

Further evidence for the coordination of a donor molecule to the silylene ligand in **2·THF** is provided by ^{29}Si NMR. The ^{29}Si chemical shift for **2·THF** appears at 24.53 ppm in C_6D_6. Other base-stabilized silylene complexes exhibit ^{29}Si resonances in the range -9 to +127 ppm, Table 2.1. In contrast the base-free silylene complexes, $[Cp^*(PMe_3)_2Ru{=}Si(SR)_2]$ $[BPh_4]$, have characteristic ^{29}Si signals that appear at very low field (250-264 ppm).[31]

The 16-electron valence configuration for the five-coordinate (TTP)Os=SiR_2·THF complexes suggested that a sixth ligand could bind to osmium to produce 18-electron complexes. Surprisingly, when one equivalent of pyridine was added to the dimethyl silylene complex **1·THF**, loss of THF from the complex was observed by ^{1}H NMR and a new species, **1·py**, appeared. The fact that free THF was observed indicates that simple substitution at silicon had occurred. Verification that pyridine was bound to silicon and not to osmium in **1·py** was established by 2D-NOESY ^{1}H NMR. In a similar manner, when the diethyl analog, **2·THF**, was treated with one equiv. of pyridine, formation of the new base-stabilized complex, **2·py**, was observed. The diastereotopic methylene protons of the SiEt_2 ligand indicate that pyridine is bound to silicon. It is remarkable that the osmium center prefers to remain five-coordinate in the base-stabilized silylene complexes, (TTP)Os=SiR_2·L. This suggests that the silylene ligand has a stronger *trans*-effect than carbon monoxide in osmium porphyrin complexes.[72] Despite the presence of a neutral, electron rich, d^6, third row transition metal π-donor fragment, the silylene complexes prepared here still have a strong tendency to form base-stabilized, four-coordinate silicon. In an attempt to prevent coordination of donor molecules to Si, use of bulky alkyl substituents to hinder four-coordination at Si was examined. Unfortunately, ^{t}Bu$_2$SiCl$_2$ and Ph$_2$SiCl$_2$ do not react with K$_2$[Os(TTP)] in THF at 22 °C. No appearance of the desired silylene complex is observed, and destruction of the dianion and the dichlorosilane occurs after several hours at higher temperatures.

The reaction between [Os(TTP)]$_2$ and HMS in the absence of THF rapidly produces (TTP)Os(η^2-Me$_2$Si=SiMe$_2$) and represents a new method for producing η^2-disilene metal complexes. A possible mechanism for the formation of the η^2-disilene ligand involves formation of a base-free dimethyl silylene complex which is trapped by a second dimethylsilyl fragment.

As in the formation of **1·THF**, a large excess of HMS is required for the formation of the disilene complex. Consequently major by-products (oligomeric and polymeric silanes) are present from the decomposition of HMS. Although **4** could not be obtained pure, hexane removed most of these by-products. Preparation of **4** by the salt elimination reaction between $K_2[Os(TTP)]$ and $ClMe_2SiSiMe_2Cl$ in THF does produce $(TTP)Os(\eta^2\text{-}Me_2Si{=}SiMe_2)$. However, a significant amount of $(TTP)Os{=}SiMe_2{\cdot}THF$ is also formed in the reaction. The silylene complex apparently results from subsequent attack of THF on the η^2-disilene complex. The use of less nucleophilic solvents such as 2,5-dimethyl-THF and 2,2,5,5-tetramethyl-THF, were not possible since they were unable to support the in situ formation of $K_2Os(TTP)$.

Concluding Remarks

The preparation and structural characterization of the first base-stabilized osmium silylene complexes have been accomplished. Despite the use of an electron-rich metal system, the strong π-donor ability of osmium in these systems is still insufficient to allow isolation of a true base-free silylene complex. The fact that these complexes are also the first 16-electron species known to contain the silylene ligand may account for this observation. These novel complexes also show little tendency to achieve an 18-electron valence configuration at osmium. Substitution of the neutral base bonded to silicon is the preferred reaction on treatment with additional ligands. This illustrates a strong *trans*-effect of the silylene ligand.

The preparation and characterization of the first osmium η^2-disilene complex was also discussed. Although the η^2-disilene osmium complex could be observed by NMR it was not able to be isolated as a pure material. The coordinated disilene ligand appears to be susceptible to nucleophilic clevage of the silicon-silicon bond to form the base-stabilized osmium silylene complex.

CHAPTER 4: METAL CARBENE COMPLEXES

Introduction

Several general reviews[75] have appeared covering metal carbene chemistry, including synthesis and characterization. More specific topics such as bonding models,[76] carbenes on metal clusters,[77] and halocarbenes[78] are covered in separate review articles. A review by Gallop and Roper on osmium carbene complexes is particular relevant to this work.[79] Only literature specifically related to metalloporphyrin carbene complexes will be reviewed here. A brief discussion of metal centers containing multiple carbene ligands will also be present since they are particularly germane to the work described in chapter 5.

Metalloporphyrin Carbene Complexes

Synthesis

In spite of the large number of metals chelated by porphyrins and the variety of axial ligands involved, metalloporphyrin carbene chemistry has remained largely undeveloped. Carbene complexes of metalloporphyrins have only been prepared with iron, ruthenium, osmium and rhodium. Portions of the iron and ruthenium work are covered in a review by Guilard and Kadish[80] and by Mansuy.[81]

Mansuy reported the preparation of the first metalloporphyrin complex, (TPP)Fe=CCl_2 by the reaction of (TPP)Fe(II) and CCl_4 in the presence of iron powder.[82] A single crystal X-ray diffraction study of the aqua complex, (TPP)$FeCCl_2(H_2O)$•2DMF, confirmed the carbene structural assignment.[83] The Fe=C bond distance, 1.83(3) Å, is significantly shorter than a typical Fe-C single bond, 1.997 - 2.168 Å.[84] Under similar reducing conditions (in the presence of iron powder or sodium dithionite) iron(II) porphyrins react with a variety of halogenated reagents to produce substituted carbene complexes, (Por)Fe=CXR (CXR can be CCl_2, CF_2, CFCl, CFBr, CBr_2, CCl(CN),[85] $CCl(CO_2Et)$,[86] $CCl(CF_3))$,[87] $CCl(SCH_2Ph)$,[88] CCl(SPh), $CCl(SeCH_2Ph)$,[89] CH(SPh), CClMe, CClCH(OH)(Me), and derivatives of 1,3-benzodioxole, Table 4.1. Attempts to prepare $(TPP)FeCl_2$ under the same conditions led to the μ-carbido porphyrin dimer, $[(TPP)Fe]_2C$.[90] $[(TPP)Fe]_2C$ is also generated when (TPP)Fe(II) is treated with $Cl_3C(TMS)$ in the presence of iron powder.[91] An X-ray crystal structure of the μ-carbido complex indicates a linear Fe=C=Fe arrangement with an Fe=C bond distance of 1.675 Å.[92] The reaction of $Cl_3CCH(p\text{-}Cl\text{-}C_6H_4)_2$ with (TPP)Fe(II) produces the intermediate carbene complex $(TPP)Fe{=}C(Cl)C(H)(p\text{-}Cl\text{-}C_6H_4)_2$. Upon the elimination of HCl the vinylidene complex $(TPP)Fe{=}C{=}C(p\text{-}Cl\text{-}C_6H_4)_2$ is produced.[93] This complex has been independently prepared by Balch by treating the N,N'-dialkylated porphyrin, $TPPC{=}C(p\text{-}Cl\text{-}C_6H_4)_2$ (Figure 4.1), with $Fe_3(CO)_{12}$.[94]

Formation of carbene complexes have been proposed when cytochrome P450 reductively metabolizes derivatives of 1,3-benzodioxole, which are insecticide synergists. A model complex, (TPP)Fe(1,3-benzodioxol-2-ylidene) (Figure 4.2), has been prepared by

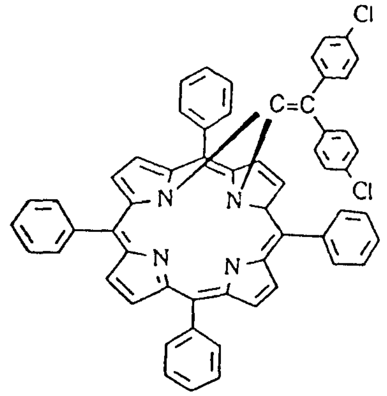


Figure 4.1. $TPPC{=}C(p\text{-}Cl\text{-}C_6H_4)_2$

Table 4.1. Known metalloporphyrin carbene complexes

Complex	$D_{M=C}$ Å	UV-Vis (nm)	^{13}C δ ppm	^{1}H δ αH ppm	Ref.
$[(TPP)Fe]_2C$	1.675	400, 530			91, 90, 92
$(TPP)FeCCl(CF_3)$		410, 528			87
$(TPP)FeCBr_2$		409, 525			97, 81
$(TPP)FeCCl_2$	1.83(3)	409, 525, 550	224.7		97, 83, 82, 85
$(TMP)FeCCl_2$		409, 525			97
$(TPP)FeCF_2$					81
$(TPP)FeCFCl$					81
$(TPP)FeCFBr$					81
$(TPP)FeCCl(CN)$			210.0		86, 85
$(TPP)FeCCl(CO_2Et)$			234.0		86, 85
$(TPP)FeCCl(SCH_2C_6H_4)$			266.4		88
$(TPP)FeCCl(SeCH_2C_6H_4)$		411, 521, 548	265.4		85, 89
$(TPP)FeCCl(CH_3)$		411, 522, 543			85
$(TPP)FeCCl(CH_3)$		411, 521, 545			85
$(TPP)FeCClC(H)(OH)(CH_3)$			312		85
$(TPP)FeC{=}C(p\text{-}Cl\text{-}C_6H_4)_2$		417, 521, 543			93, 94

Table 4.1 cont.

Complex	$D_{M=C}$ Å	UV-Vis (nm)	^{13}C δ ppm	^{1}H δ αH ppm	Ref.
(TPP)FeC(1,3-benzodioxol-2-ylidene)		412, 516, 540			95
[(TPP)FeC(1,3-benzodioxol-2-ylidene)(S^nBu)]-					95
(TPP)FeCCl(SC_6H_5)		411, 520, 548	288.5		88
(TPP)FeCCl(SR^1)^a		408, 520, 544	264.3		88
(TPP)FeCCl(SR^2)^b		411, 521, 544			88
(TPP)FeCH(SC_6H_5)		413, 521, 545		13.83	88
(TPP)FeC(OCH_3)(CH_3)		412, 515, 541	332		85
(TPP)FeC(OEt)(CH_3)		413, 515, 541	330.7		85
(TPP)FeC($SCH_2C_6H_4$)(CH_3)		413, 516, 543	303.7		85
(TPP)FeC(OCH_3)($CH(CH_3)_2$)		414, 515, 543	337.7		85
(TTP)FeC(OCH_3)(CH_3)		411, 513, 541	324		85
(TTP)FeC(OEt)(CH_3)		411, 514, 541			85
(TTP)FeC($SCH_2C_6H_4$)(CH_3)		413, 517, 544			85
(TPP)FeC(Cl)($CH(CH_3)_2$)		412, 520, 547			85
(TPP)FeC(Cl)(CH_2OH)			302.7		85
(TPP)FeC(Cl)($CHOHC_6H_5$)			303.6		85

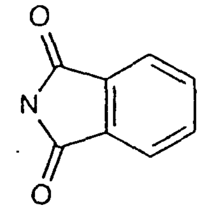
Table 4.1 cont.

Complex	$D_{M=C}$ Å	UV-Vis (nm)	^{13}C δ ppm	^{1}H δ αH ppm	Ref.
$[(TPP)RhC(NHCH_2C_6H_5)_2]^+$					101
$[(TPP)RhC(NH\text{-}p\text{-}Cl\text{-}C_6H_5)_2]^+$					101
$[(OEP)RhC(NHCH_2C_6H_5)_2]^+$					101
$[(OEP)RhC(NH\text{-}p\text{-}Cl\text{-}C_6H_5)_2]^+$					101
$[(TPP)RhC(NHCH_2C_6H_5)_2(P(OMe)_3)]^+$					101
$[(TPP)RhC(NHCH_2C_6H_5)_2(P(Me)_3)]^+$					101
$[(TPP)RhC(NHCH_2C_6H_5)_2(CNCH_2C_6H_5)]^+$	2.030(11)				101
$[(OEP)RhC(NHCH_2C_6H_5)_2(P(OMe)_3)]^+$					101
$(TTP)RuCHCO_2Et$		408, 529		13.44	98, 70
$(TTP)RuCHCH_3$		395, 421, 527		13.03	98, 70
$(TTP)RuCHSi(CH_3)_3$		408, 527		19.54	100, 70
$(TTP)RuC{=}C(p\text{-}Cl\text{-}C_6H_4)_2$					100
$(TPP)RuC{=}C(p\text{-}Cl\text{-}C_6H_4)_2$		416, 522, 542			94
$(TTP)RuCH(OCH_3)$				7.50	70
$(TTP)OsCH(OCH_3)$				9.80	70
$(TMP)RuCHCO_2Et$		404, 525		13.79	70
$(OEP)RuCHCH_3$				12.48	70
$(OEP)RuC(CH_3)_2$					70

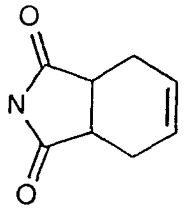
Table 4.1 cont.

Complex	$D_{M=C}$ Å	UV-Vis (nm)	^{13}C δ ppm	^{1}H δ αH ppm	Ref.
(OEP)RuCHC$_6$H$_5$				13.06	70
(OEP)RuC(C$_6$H$_5$)$_2$					70
(OEP)RuCHCO$_2$Et		335, 381, 396 420, 559		12.91	70
(OEP)RuCH(OCH$_3$)				7.07	70
(OEP)RuCHSi(CH$_3$)$_3$		342, 383 428, 555		18.85	70
(OEP)OsC(CH$_3$)$_2$					70
(OEP)OsCHC$_6$H$_5$				20.10	70
(OEP)OsCHCO$_2$Et		375, 427, 550		21.38	70
(OEP)OsCH(OCH$_3$)				9.59	70

[a] R^1 =



[b] R^2 =



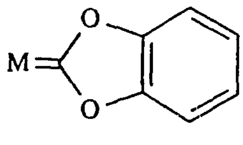


Figure 4.2. 1,3-benzodioxol-2-ylidene

Mansuy's method.[95] Upon treating this complex with an excess of n-butylthiolate, the six coordinate anion, [(TPP)Fe(1,3-benzodioxol-2-ylidene)(S^{n}Bu)]$^-$, was prepared.

Treating (TPP)Fe=CClR with alcohols or thiols leads to the formation of new carbene complexes, (TPP)Fe=CRR' where CRR' is C(OCH$_3$)(CH$_3$), C(OEt)(CH$_3$), C(OCH$_3$)(CH(CH$_3$)$_2$), or C(SCH$_2$Ph)(CH$_3$). The reaction of primary amines with (TPP)Fe=CCl$_2$ generates isonitrile complexes rather than new carbene complexes.[96]

Resonance Raman and infrared spectra of (TPP)Fe=CCl$_2$ and (TPP)Fe=CBr$_2$ have been measured by Nakamoto and coworkers.[97] The spin state marker, ν_2, at 1569 cm^{-1} and the oxidation sensitive band at 1370 cm^{-1} suggest that the iron(IV) centers are low spin in these complexes.

Collman and co-workers reported the preparation of ruthenium porphyrin carbene complexes. Treating the ruthenium dimer complex [(TTP)Ru]$_2$ with ethyl diazoacetate produces (TTP)Ru=CHCO$_2$Et.[98] Similarly (TTP)Ru=CHCH$_3$ can be prepared from [(TTP)Ru]$_2$ and N$_2$CHCH$_3$. (TTP)Ru=CHCH$_3$ is also a prepared by the decomposition of (TTP)Ru(Et)$_2$. In solution the ethylidene complex rearranges to the η^2-ethylene complex over the course of weeks. The decomposition of the diethyl ruthenium porphyrin to the carbene complex is believed to take place via a radical process.[99] A third method for preparing carbene complexes is the reaction of 1,1-dichloro reagents with the ruthenium porphyrin dianion K$_2$[Ru(TTP)]. Several carbene complexes, (TTP)RuCRR' where CRR' is CHCH$_3$, CHTMS, or C=C(p-Cl-C$_6$H$_4$)$_2$, have been prepared in this manner.[100] The TPP analog of the vinylidene complex was previously prepared by Balch et al.[94]

Venburg expanded the work in ruthenium porphyrin carbene complexes and prepared the first osmium porphyrin carbenes.[70] Starting from either [(Por)Ru]$_2$ or K$_2$[Ru(Por)] a variety of new porphyrin carbene complexes, (Por)RuCRR' were prepared (Por = TTP, CRR' = $CHOCH_3$; Por = TMP CRR' = $CHCO_2Et$; Por = OEP, CRR' = CHTMS, $CHOCH_3$, $C(C_6H_5)_2$, $CH(C_6H_5)$, or $C(CH_3)_2$). The osmium analogs were also prepared from $[(Por)Os]_2$ or $K_2[Os(Por)]$ resulting in (Por)OsCRR' (Por = TTP, CRR' = $CHOCH_3$; and Por = OEP, CRR' = $CHOCH_3$, $CH(C_6H_5)$, $C(CH_3)$, or $CHCO_2Et$).

Although a number of reports implicate rhodium porphyrin carbene complexes as catalytic intermediates (see Chapter 7) only one report of isolated rhodium carbene complexes exists in the literature. Boschi et al. have prepared $[(Por)Rh{=}C(NHR)_2]PF_6$, with OEP or TPP and R = p-Cl-C_6H_4, or CH_2Ph by refluxing $(RNC)_2Rh(Por)$ in methanol.[101] When excess phosphine or isocyanide is present, the alkyl complexes $[(Por)RhC(NHCH_2Ph)_2(L)]PF_6$ (Por = TPP, L = $P(Ph)_3$, $P(OMe)_3$, and $PhCH_2NC$; Por = OEP, L = $P(OMe)_3$) are isolated. A crystal structure has been obtain for $(PhCH_2NC)(TPP)Rh[{=}C(NHCH_2Ph)_2]PF_6$ which indicates that the Rh bond is 2.030(11) Å. Typical Rh=C distances are in the range 1.930 - 1.968 Å.[102] The long Rh=C bond in the porphyrin complex presumably results from a trans-effect of the isocyanide ligand.

Characterization

Proton NMR is the most common technique for characterizing metalloporphyrin carbene complexes. α-Proton chemical shifts of the ruthenium porphyrin carbene complexes typically fall in the range 12.9 to 13.8 ppm, Table 4.1. Electron donating groups cause resonances to be further upfield (=C*H*OCH_3, 7.07 ppm) and electron withdrawing groups cause downfield shifts (=C*H*TMS, 19.44 ppm).[70] Osmium carbene complexes exhibit α-proton resonances between 9.59 and 20.38 ppm.[70] With the exception of the Fischer type carbene complexes (M=CHOR) the osmium α-proton resonances are approximately 7 ppm further down field than their ruthenium analogs. For example the α-H shift in (OEP)Os=CHOMe is 9.59 ppm and (OEP)Ru=CHOMe signal 7.07 ppm, while for (OEP)Os=CHPh and (OEP)Ru=CHPh the signals are at 20.10 and 13.06, respectively. These α-H shifts are similar to those of nonporphyrin Ru and Os carbene complexes, 13.30 - 18.05 ppm.[79] The only α-proton shift reported for an iron porphyrin carbene complex, (TPP)Fe=CH(SC_6H_5) , is 13.83.[88]

A few ^{13}C chemical shifts have been reported for the carbene carbon in iron porphyrin carbene complexes. These occur in the range 210 to 340 ppm (see Table 4.1) and are within the normal chemical shift range for metal carbene complexes, 200 - 400.[79]

Limited structural data are available for metalloporphyrin carbene complexes. The iron complex (H_2O)(TPP)Fe=CCl_2 has an Fe=C distance of 1.83(3) Å.[83] The only other single-crystal X-ray structural data on a metalloporphyrin carbene complex was reported for the rhodium complex [($CNCH_2C_6H_5$)(TPP)Rh=C($NHCH_2C_6H_5$)$_2$]$^+$ PF_6^-, discussed above. Several nonporphyrin structures have been reported for osmium carbenes.[79]

Synthesis of Metal Centers With Multiple Carbene Ligands

Multiple carbene ligands on a metal center are of interest due to their potential use in making organic compounds. *Cis*-biscarbene complexes have been proposed as intermediates in the isomerization of alkenes[103] and the formation of tetrakis(trimethylsilyl)butatriene from bis(trimethylsilyl)acetylene.[104] Several theoretical papers cover the coupling of *cis*-biscarbene complexes to form alkenes[105] and preferred conformations of *cis*-biscarbene complexes.[106]

Biscarbene complexes were first reported in 1967,[107] only four years after Fischer's seminal work on metal monocarbene complexes.[108] These first biscarbene complexes were mercury salts formulated as $[Hg(C(NR^1R^2)OR^3)_2][BF_4]_2$. The carbene complexes were prepared by treating mercury(II) acyl complexes, $Hg(C(O)NR^1R^2)_2$, with $R^3{}_3OBF_4$. Similar mercury biscarbene complexes were prepared by treating mercury(II) acetate with a mixture of methylisonitrile and primary amines. The following year, Wanzlick and Schonherr prepared mercury salts containing two cyclic carbene ligands, $[Hg(N,N\text{-diphenyl-2-imidazolidene})_2]_2^+$.[109] Although the mercury compounds were the first to be formulated as biscarbene complexes, Chugaev's salt first reported in 1925,[110] was later found to be a platinum biscarbene complex, Figure 4.3, with a Pt=C distance of 1.948(5) Å.[111]

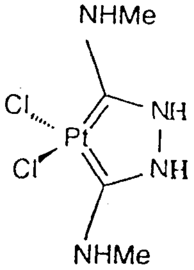
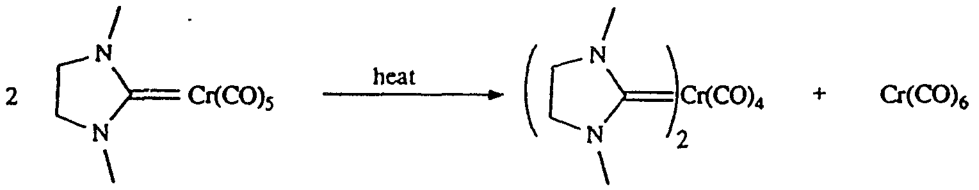


Figure 4.3. Chugaev's Salt

The first undisputed transition metal biscarbene was reported by Ofele in 1970.[112] Bis(N,N-dimethyl-2-imidazolidene)chromiumtetracarbonyl was prepared by the photo-induced disproportionation of N,N-dimethyl-2-imidazolidenechromiumpentacarbonyl. Several years later, the thermal disproportionation of Cr, Mo, and W monocarbene complexes was reported to produce the biscarbene complexes and the hexacarbonyl compounds, eq. 4.1.[113]



(4.1)

All but a few of the complexes containing multiple carbene ligands prepared since 1970 fall into several general synthetic categories; 1) addition of an electron rich alkene to a metal center, 2) addition of an imidazole to a metal complex, 3) nucleophilic attack on a coordinated isonitrile, 4) nucleophilic attack on a coordinated carbonyl, 5) α-H abstraction and 6) addition of a terminal alkyne followed by nucleophilic attack on Cl. Each of these methods will be discussed below.

Lappert has widely used the addition of an electron rich alkene to metal carbonyl or phosphine complexes to produce multiple carbene ligands on a metal center.[114] Tetraaza-substituted alkenes, Figure 4.4, were used to prepare mono-, bis-, tris-, and tetrakis-carbene complexes. Multiple carbene complexes have been prepared for Cr, Mo, W, Mn, Fe, Ru, Os, Co, Rh, Ir, Ni, Pt, and Au. Chiral biscarbene complexes have also been prepared using this method.[1141] Ofele has recently synthesized *trans*-bis(N-methylbenzothiazolinyl carbene complexes) from the appropriate alkene, Figure 4.4, and Mo(CO)$_6$ or W(CO)$_6$.[115]

A mercury(II) biscarbene salt, prepared by Schonherr and Wanzlick[116] by the addition of N,N'-diphenylimidazolium cation to mercury(II) acetate, [Hg(N,N-diphenyl-2

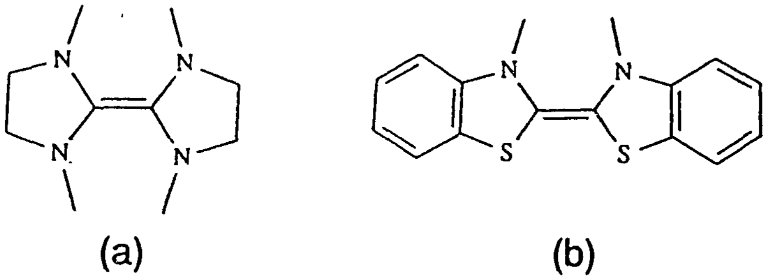


Figure 4.4. Electron rich alkenes. a)1,1',3,3'-tetraalkyl-2,2'-bi-imidazolidinylidene b) bis(N-methylbenzothiazolinylidene)

-imidazolidene)$_2$][ClO$_4^-$]$_2$, has a Hg=C bond length of 2.059(19) Å. This distance is only slightly shorter than the σ-bond distance of 2.10 Å in Hg(p-C$_6$H$_4$Br)$_2$. Thus only slight π-back donation occurs from mercury to the carbene carbon.

Ofele[117] also used substituted imidazole cations (Im$^+$) and [M$_2$(CO)$_{10}$]$^{-2}$ M = Cr, Mo, and W to prepared a series of biscarbene complexes. A one electron oxidation using Cp$_2$Fe$^+$ produced the cationic carbene species [M(CO)$_4$Im$_2$]PF$_6$. X-ray structures of *cis*-Cr(CO)$_4$(Im)$_2$ and *cis*-[Cr(CO)$_4$(Im)$_2$]$^+$ were obtained. The Cr=C distance of the neutral complex (2.131(3) Å) is slightly longer than that of the cationic species (2.113(4) and 2.119(4) Å). The molybdenum and tungsten complexes are isomerized from *trans* to *cis* by electrochemical oxidation.[118] After substitution of a carbonyl by a phosphine, the molybdenum complexes exist as three isomeric forms, *trans*-mer, *cis*-mer, and fac.[119]

Nucleophilic attack on metal coordinated isonitriles is an effective method for introducing multiple carbene ligands to a metal center. The first example of a multi-carbene complex produced by this approach was Chugaev's salt mentioned above.[111] When tetrakis(methylisonitrile)platinum(II) dichloride was treated with hydrazine, a cyclic biscarbene platinum complex, Figure 4.3, was produced. The single crystal X-ray structure confirmed the presence of two carbene ligands with a Pt=C distance of 1.948(5) Å. Subsequently, a series of Pd biscarbene complexes, Pd(C(NR)Y)$_2$Cl$_2$, was prepared by treating Pd isonitrile complexes, Pd(CNR)$_2$Cl$_2$, with HY, where R was p-MeOC$_6$H$_4$, p-MeC$_6$H$_4$, C$_6$H$_5$ or p-NO$_2$C$_6$H$_4$ and Y was MeO, p-MeOC$_6$H$_4$-NH, p-MeC$_6$H$_4$-NH, C$_6$H$_5$-NH, Me$_2$N or (C$_6$H$_5$)(Me)N.[120] In the same year, Miller and Balch prepared Pt and Pd tetrakis(carbene) complexes by the reaction of the dicationic tetrakis(methylisonitrile) metal complexes and methylamine.[121] A crystal structure of Pt(C(NHMe)$_2$)$_4^{+2}$ indicated that the Pt-C distances (2.046(7) and (2.047(7) Å)[122] are long compared to Pt-C distances in platinum isonitrile (1.96(1) Å)[123] and carbonyl (1.78 Å)[124] complexes. Furthermore, the C-N bond (1.310(3) Å) in the tetrakis complex suggested that limited π-back bonding occurs in this type of metal carbene complex.

Homoleptic hexacarbene rhodium and cobalt complexes have been prepared by intramolecularly incorporating the nucleophile into the isonitrile ligand. The hexacarbene complexes were produced from $CoCl_2$ or $RhCl_3 \cdot 3H_2O$ and $CNCH_2CHROH$, R = H or Me, Figure 4.5.[125] ^{13}C chemical shifts for the carbene carbon are between 200 and 220 ppm and are within the normal range for carbene ligands. A poorly resolved crystal structure of the cobalt complex when R = H clearly shows the six carbene ligands. The same method was used to generate bis- and tetrakis-carbene complexes of Ni, Pd, and Pt.[126] Similarly, treatment of $[NiCpCO]_2$ with four equivalents of $CNCH_2CH_2OH$ and NH_4PF_6 generated a biscarbene nickel compound, Figure 4.5.[127]

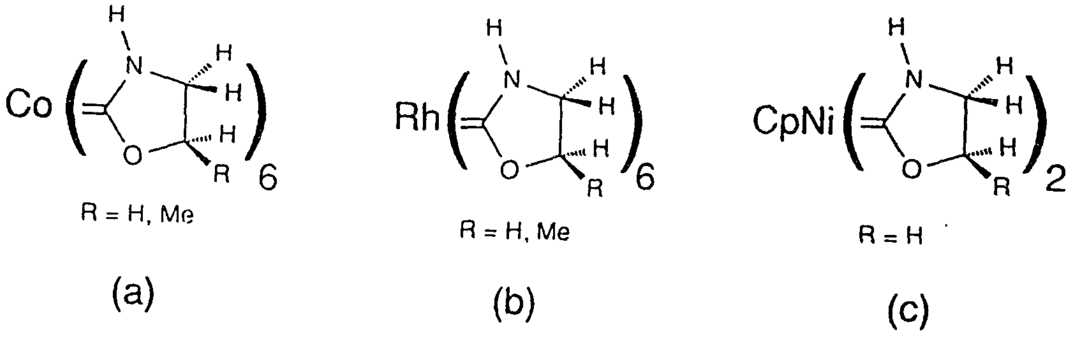


Figure 4.5. Examples of complexes containing multiple carbene ligands

Nucleophilic attack at coordinated carbonyls has not been successful as a general method for the formation of multiple carbene ligands at a metal center. This is primarily due to the susceptibility of the initial carbene towards further nucleophilic attack, eq. 4.2[128] and 4.3.[129] Nonetheless, Fischer was able to prepare biscarbene complexes of Cr and W,

$(CO)_4M(C(OEt)PMe_2)_2$, by the reaction of the hexacarbonyl complexes with lithium dimethylphosphide followed by alkylation.[130] Similarly, using lithium diisopropylamide generated the Mo and W *cis*-biscarbene $(CO)_4M(C(OEt)N^iPr_2)_2$.[131] The ^{13}C resonances of the carbene carbons occur at 240.8 (Mo) and 237.1 (W) ppm. The W=C bond lengths are 2.300(9) and 2.304(10) Å.

$$(CO)_5Cr{=}C(OMe)Ph + RNH_2 \rightarrow (CO)_5Cr{=}C(NHR)Ph + HOMe \tag{4.2}$$

$$[Cp(NO)(PPh_3)Re{=}CH_2]^+ + MeLi \rightarrow Cp(NO)(PPh_3)ReCH_2Me + Li^+ \tag{4.3}$$

Use of dilithium reagents minimizes the problem of secondary nucleophilic attack at an initially formed carbene ligand. For example, Fischer prepared cyclic biscarbene complexes, Figure 4.6, by treating the hexacarbonyls of Cr, Mo, and W with o-$Li_2C_6H_4$ followed by alkylation.[132] These complexes exhibited ^{13}C NMR α-C resonances of 337.97 (Cr), 329.52 (Mo), and 312.31 (W) ppm. In addition, an X-ray structure of the chromium analog was obtained. The Cr=C distances are 2.000(7) and 2.004(7) Å.[132] Similar complexes of Cr and W were prepared using 1,2-dilithium-1,2-diphenylethane.[133]

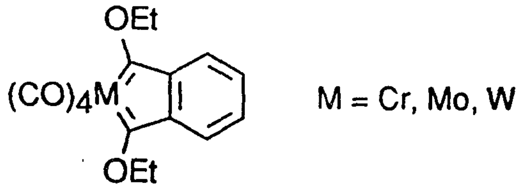


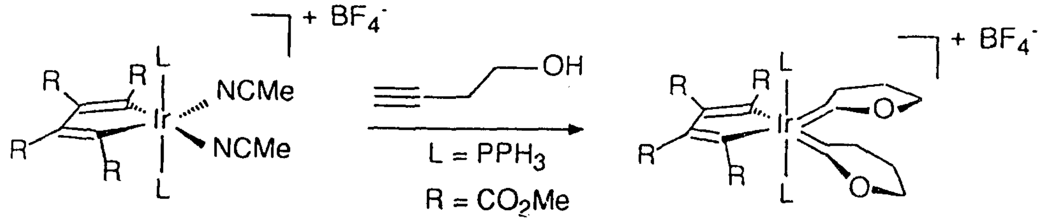
Figure 4.6. Cyclic biscarbene complexes prepared by E. O. Fischer

Similar to the method in which monocarbene complexes of early transition metals have been isolated, Schrock has prepared tantalum and niobium bisalkylidene complexes. Some of this work has been reviewed.[75b] The bisalkylidene complexes $M(=CH^tBu)_2(Np)L$, M = Ta or Nb; L = PMe_3 or PMe_2Ph can be synthesized by treating $M(=CH^tBu)(Np)_3$ with the appropriate phosphine.[134] A series of alkyl bisalkylidene complexes can be prepared from $Ta(Np)_4Cl$. The addition of trimethylphosphine generates $Ta(=CH^tBu)_2(PMe_3)_2Cl$ which readily reacts with LiR to produce $Ta(=CH^tBu)_2(PMe_3)_2R$, where R may be Me, Et, Bu, Np or Mes.[135] Proton and carbon NMR spectroscopy indicate that the two carbene ligands are not equivalent in $Ta(=CH^tBu)_2(Np)L$. An X-ray structure of $Ta(=CH^tBu)_2(PMe_3)_2(Mes)$ (**6**) reveals that the carbene ligands occupy equatorial sites and that both metal carbon bonds are short, 1.955(7) and 1.932(7) Å,[136] compared to the Ta=C bond (2.030(6) Å) in $Cp_2Ta(=CH^tBu)Cl$.[137] The Ta-C(α)-C(β) angles are 154.0(6)° and 168.9(6)°. This is similar to M=C-C angles of monoalkylidene structures and suggests that agostic interactions involving the α-H are occurring. The agostic interactions are further supported by low C-H coupling constants, proton NMR shifts of α-H's,[75b] and a theoretical study,[138].

Another general method for the preparation of biscarbene complexes involves the addition of two equivalents of an alkyne to a metal center followed by nucleophilic attack at the coordinated triple bond. This route was first used in 1979 to synthesize $Cl_2Pt(C(Me)O^iPr)_2$ from $H_2PtCl_2 \cdot 6H_2O$ and TMSC≡CH in isopropanol.[139] An X-ray structure reveals that the Pt=C bond lengths of 1.92(2) and 1.97(2) Å are shorter than typical Pt=C bonds.

O'Connor used buta-3-yn-1-ol and Ir(III) complexes to generate the bis-cyclic oxacarbene iridium cations shown in eq. 4.4.[140] This reaction may be carried out stepwise, allowing the incorporation of two different carbene ligands on the same metal center.[141]

Chiral iridium biscarbene complexes have been prepared in this manner. The α-carbon ^{13}C NMR resonances for these complexes are between 283 and 286 ppm. The Ir=C bond lengths were found to be 2.033(8) and 2.059(7) Å by a single crystal X-ray diffraction study.



(4.4)

Recently Dixneuf and co-workers have prepared the metallocumulene bis(alkenylallenylidene)ruthenium complex, *trans*-$(dppm)_2Ru[(=C=C=C(OMe)(CH=CPh_2)]_2$.[142] Treating *cis*-$(dppm)_2$ruthenium dichloride with $HC{\equiv}C\text{-}C{\equiv}C\text{-}CPh_2OTMS$ generates the stable (diynyl)ruthenium complex, *trans*-$(dppm)_2Ru(\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CPh_2OTMS)_2$. Treating the diynyl ruthenium complex with tetrafloroboric acid etherate in methanol produces *trans*-$(dppm)_2Ru[=C=C=C(OMe)(CH=CPh_2)]_2$.

Summary

A variety of metal carbene complexes have been reviewed, including metalloporphyrin carbene complexes and metal centers containing more than one carbene ligand. Porphyrin carbene complexes have been prepared from only the iron triad metals Fe, Ru, Os, and Rh. Observation of a ^{13}C resonance between 200-400 ppm in the carbon NMR is a diagnostic tool for identifying the presence of a carbene ligand in the porphyrin complex.

Multiple carbene ligands present on the same metal center may be prepared by a variety of methods. Lappert's method of addition of an electron rich alkene to metal carbonyl or phosphine complexes has proven particularly useful for a variety of metals. Nucleophilic attack on a metal bound ligand is effective for ligands such as CO, CNR, and alkynes. As many as six carbenes have been complexed to a single metal center. Abstraction of an α-H from early transition metal alkyls is also capable of producing biscarbene complexes.

CHAPTER 5: SYNTHESIS OF OSMIUM PORPHYRIN CARBENE COMPLEXES

Introduction

The isolation of the first osmium silylene porphyrin complexes and preparation of the first η^2-disilene porphyrin complexes suggested that the synthesis of an η^2-silene osmium porphyrin complex should be possible. As an entry into this chemistry, (TTP)Os=SiEt$_2$·THF was examined as a starting material for the preparation of osmium porphyrin η^2-silene complexes. When (TTP)Os=SiEt$_2$•THF was treated with ditolyldiazomethane a ditolylcarbene osmium porphyrin complex was produced. Under conditions of excess ditolyldiazomethane, bis(ditolylcarbene)osmium porphyrin was prepared. A variety of metalloporphyrin carbene complexes have been prepared using other diazo reagents.

Experimental

General

All manipulations of reagents and products were carried out under a nitrogen atmosphere using a VACUUM/ATMOSPHERES glove box equipped with a model MO40H Dri-Train gas purification system or on a vacuum line using standard Schlenk techniques. All solvents were dried and distilled from purple solutions of sodium/benzophenone. ^{1}H NMR spectra were recorded on Nicolet 300 MHz or Varian VXR 300 MHz spectrometers. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN, Oneida Research Services, Whitesboro, NY, or Desert Analytics, Tucson, AZ. Ethyl diazoacetate and trimethylsilyldiazomethane were purchased from Aldrich degassed by freeze-pump-thaw cycles and distilled under reduced pressure. Other diazo reagents were prepared by the oxidation of the hydrazone[143] by yellow mercury(II) oxide in toluene or hexane. **WARNING** - several of the diazo reagents used here are reported to detonate spontaneously. $N_2C(CH_3)(C_6H_5)$, $N_2CH(p\text{-}C_6H_4\text{-}CH_3)$ and $N_2CH(Mes)$ were not isolated but used in situ. Concentrations of $N_2CH(p\text{-}C_6H_4\text{-}CH_3)$ and $N_2CH(Mes)$ were determined by treating the diazo compound with benzoic acid and titrating the acid with NaOH.[144] $[Os(TTP)]_2$ was prepared by the literature procedure.[63]

Synthesis

$(TTP)Os{=}C(p\text{-}C_6H_4\text{-}CH_3)_2$ (5).

A benzene solution (3 mL) of di(*p*-tolyl)diazomethane (8.3 mg, 37.4 μmol) was added to a stirred solution of $[Os(TTP)]_2$ (32.0 mg, 18.6 μmole) in benzene (6 mL). After 1 h, the solution was passed through a neutral alumina column (1 cm dia. x 10 cm long) and impurities were eluted with benzene. The carbene complex was washed from the column with benzene/THF (20:1, V:V). Removal of the solvent under reduced pressure yielded 37.6 mg (96%) of brown solid. Analytical data: ^1H NMR (C_6D_6): 8.15 (s, 8H, β-H), 8.01 (d, 4H, $p\text{-}C_6H_4\text{-}CH_3$), 7.88 (d, 4H, $p\text{-}C_6H_4\text{-}CH_3$), 7.29 (dd, 8H, $p\text{-}C_6H_4\text{-}CH_3$), 6.03 (d, 4H, $o\text{-}{=}CC_6H_4CH_3$), 4.26 (d, 4H, $m\text{-}{=}CC_6H_4CH_3$), 2.38 (s, 12H, $p\text{-}C_6H_4\text{-}CH_3$), 1.69 (s, 6H, ${=}CC_6H_4CH_3$) ppm; ^{13}C NMR (C_6D_6): 265.5 ppm (s, Os=*C*); UV-vis (C_6H_6) 410 (soret), 522, 548 nm; MS{EI} found (calcd.) 1055 (1055) $[M+H]^+$, 964 (964) $[M+H\text{-tolyl}]^+$. Analytically pure material was obtained by crystallization from ethanol to produce $(TTP)Os{=}C(C_6H_4CH_3)_2 \cdot 2EtOH$. ^1H NMR (C_6D_6) confirms the presence of two molecules of ethanol per porphyrin, which appear at 3.24 (dq, 4H, CH_2), 0.88 (t, 6H, CH_3), 0.31 (t, 2H, OH). Anal. calcd. (found) for $OsC_{67}H_{62}N_4O_2$: C, 70.25 (69.99); H, 5.46 (5.15); N, 4.89 (4.69).

(TTP)Os=C(H)Si(CH$_3$)$_3$ (6).

A hexane solution (13.5 µL) of trimethylsilyldiazomethane (2.0 M, 27 µmole) was dissolved in 3 mL benzene. The trimethylsilyldiazomethane solution was added to a stirred solution of [Os(TTP)]$_2$ (23.3 mg, 13.5 µmole) in 6 mL benzene. After 2 h, the solvent and excess trimethylsilyldiazomethane were removed under reduced pressure. Recrystallizing the solid from 2 mL cold hexane and filtering produced 19.7 mg (76.9%) of brown product. ^{1}H NMR (C$_6$D$_6$): 28.95 (s, 1H, =C*H*SiMe$_3$), 8.01 (s, 8H, β-H), 7.93 (dd, 8H, *p*-C$_6$*H*$_4$-CH$_3$), 7.24 (d, 4H, *p*-C$_6$*H*$_4$-CH$_3$), 7.17 (d, 4H, *p*-C$_6$*H*$_4$-CH$_3$), 2.32 (s, 12H, *p*-C$_6$H$_4$-C*H*$_3$), -1.41 (s, 9H, (C*H*$_3$)$_3$Si) ppm. ^{13}C NMR (C$_6$D$_6$): 295.5 ppm (d, J$_{CH}$ = 124.4 Hz, Os=*C*). UV-vis (C$_6$H$_6$): 388, 420 (soret) nm. Anal. calcd. (found) for OsSiN$_4$C$_{52}$H$_{46}$: C, 66.07 (64.91); H, 4.91 (4.73); N, 5.93 (5.80).

(TTP)Os=CHCO$_2$Et (7).

Ethyl diazoacetate (50 µL, 0.48 mmole) in 50 mL toluene was slowly added (10 h) to a vigorously stirred toluene solution (15 mL) of [Os(TTP)]$_2$ (101.5 mg, 0.059 mmole). After the addition was completed, the solution was stirred for an additional hour. The resulting solution was concentrated to 25 mL under reduced pressure and eluted down a florisil column (1 cm dia. x 10 cm long). Impurities were removed with toluene and the product was eluted with toluene:THF (10:1). Removal of the solvent under reduced pressure afforded 87 mg (78%) of orange-brown solid. Recrystallization of the resultant solid from toluene/hexane produced 37 mg (33%) of dark crystals. ^{1}H NMR (C$_6$D$_6$): 21.60 (s, 1H, =C*H*CO$_2$Et), 8.35 (s, 8H, β-H), 8.02 (d, 4H, *p*-C$_6$*H*$_4$-CH$_3$), 7.96 (d, 4H, *p*-C$_6$*H*$_4$-CH$_3$), 7.28 (d, 4H, *p*-C$_6$*H*$_4$-CH$_3$), 7.19 (d, 4H, *p*-C$_6$*H*$_4$-CH$_3$), 2.36 (s 12H, *p*-C$_6$H$_4$-CH$_3$C*H*$_3$), 2.67 (q, 2H, =CHCO$_2$C*H*$_2$CH$_3$), 0.26

(t, 3H, =$CHCO_2CH_2CH_3$) ppm. ^{13}C NMR (C_6D_6): 211.6 ppm (d, J_{CH} = 132.8 Hz, Os=*C*). UV-vis (C_6H_6): 398, 408 (soret) nm. Anal. Calcd. (found) for $C_{52}H_{42}N_4OsO_2$: C, 66.08 (66.04); H, 4.48 (4.78); N, 5.93 (5.33).

(TTP)Os=C(H)(2,4,6-$(CH_3)_3$-C_6H_2) (8).

A toluene solution (35 mL) of 2,4,6-trimethylphenyldiazomethane (0.00663 M, 232 μmole) was slowly added (5 h) to a vigorously stirred toluene solution (6 mL) of $[OsTTP]_2$ (52.5 mg, 30.5 μmole). The resulting solution was concentrated to 20 ml under reduced pressure and eluted down a florisil column (1 cm dia. x 10 cm long). Impurities were removed with toluene and the product was eluted with toluene:THF (10:1 v/v). Removal of the solvent under reduced pressure afforded 50.6 mg (84%) of orange-brown solid. ^1H NMR (C_6D_6): 20.78 (s, 1H, =C*H*), 8.19 (s, 8H, β-H), 7.99 (d, 4H, *p*-C_6H_4-CH_3), 7.89 (d, 4H, *p*-C_6H_4-CH_3), 7.25 (dd, 8H, *p*-C_6H_4-CH_3), 5.59 (d, 2H, *m*-C_6H_2), 2.36 (s 12H, *p*-C_6H_4-CH_3), 1.77 (s, 3H, *p*-CH_3), 0.39 (s, 6H, *o*-CH_3) ppm. ^{13}C NMR (C_6D_6): 248.8 ppm (d, J_{CH} = 141.1 Hz, Os=*C*). UV-vis (C_6H_6): 418 (soret), 518, 550 nm.

(TTP)Os=C(H)(*p*-C_6H_4-CH_3) (9).

A toluene solution of p-tolyldiazomethane (20 mL, 0.0044 M, 88 μmole) was slowly added (4 h) to a vigorously stirred toluene solution (6 mL) of $[OsTTP]_2$ (41.0 mg, 23.8 μmole). The solvent was removed under reduced pressure to produce 19.3 mg of crude **9**. ^1H NMR (C_6D_6): 19.82 (s, 1H, =C*H*), 8.21 (s, 8H, β-H), 8.01 (d, 4H, *p*-C_6H_4-CH_3), 7.90 (d, 4H, *p*-C_6H_4-CH_3), 7.26 (d, 8H, *p*-C_6H_4-CH_3), 5.69 (d, 2H, =CH(*p*-C_6H_4-CH_3), 4.83 (d, 2H, =CH(*p*-C_6H_4-CH_3), 2.34 (s 12H, *p*-C_6H_4-CH_3), 0.41 (s, 3H, =CH(*p*-C_6H_4-CH_3) ppm.

(TTP)Os=C(CH_3)(C_6H_5) (10).

This complex was prepared using the method described for **9** with [OsTTP]$_2$ (15.9 mg, 9.2 μmole) and an excess of methylphenyldiazomethane. ^{1}H NMR (C_6D_6): 8.16 (s, 8H, β-H), 8.00 (d, 4H, p-C_6H_4-CH_3), 7.93 (d, 4H, p-C_6H_4-CH_3), 7.26 (dd, 8H, p-C_6H_4-CH_3), 6.54 (t, 1H, p-C_6H_5), 6.26 (t, 2H, m-C_6H_5), 4.10 (d, 2H, o-C_6H_5), 2.35 (s 12H, p-C_6H_4-CH_3), -4.36 (s, 3H, =CCH_3) ppm. ^{13}C NMR (C_6D_6): 263.9 ($^2J_{C\text{-}H}$= 7.87 Hz, Os=C) ppm. UV-vis (toluene): 410 (soret), 424 sh, 516, 540.

(TTP)Os(=C(p-C_6H_4-CH_3)$_2$)$_2$ (11).

A benzene solution (3 mL) of di(p-tolyl)diazomethane (9.4 mg, 42.3 μmol) was added to a stirred solution of [Os(TTP)]$_2$ (20.3 mg, 11.8 μmole) in benzene (6 mL). After 4.5 h the solvent was removed under reduced pressure. The ratio of **11** to **5** was 2. ^{1}H NMR (C_6D_6): 8.63 (s, 8H, β-H), 7.99 (d, 8H, p-C_6H_4-CH_3), 7.33 (d, 8H, p-C_6H_4-CH_3), 5.97 (d, 4H, m-=CC_6H_4-CH_3), 3.12 (d, 4H, o-=CC_6H_4-CH_3), 2.42 (s, 12H, p-C_6H_4-CH_3), 1.68 (s, 12H, =CC_6H_4-CH_3) ppm; ^{13}C NMR (C_6D_6): 305.5 ppm (s, Os=C).

(TTP)Os(=C(CH_3)(C_6H_5))$_2$ (12).

This complex was prepared in an NMR tube fwm [Os(TTP)]$_2$ (~2 mg, 1.2 μmole) and an excess of methylphenyldiazomethane in hexane. ^{1}H NMR (C_6D_6): 8.66 (s, 8H, β-H), 8.06 (d, 8H, p-C_6H_4-CH_3), 7.29 (d, 8H, p-C_6H_4-CH_3), 6.37 (t, 2H, p-C_6H_5), 6.16 (t, 4H, m-C_6H_5), 3.01 (d, 4H, o-C_6H_5), 2.40 (s, 12H, p-C_6H_4-CH_3), -3.17 (s, 6H, =CCH_3) ppm.

X-ray Structure Determination of 5·Toluene·½ Hexane

A single crystal of (TTP)Os=C(p-C_6H_4-CH_3)$_2$·C_7H_8·½ C_6H_{14} suitable for X-ray structure analysis was grown by slow evaporation of a toluene/THF/hexane solution. A brown plate-like crystal having approximate dimensions of 0.35 x 0.35 x 0.12 mm was attached to a glass fiber and mounted on an Siemens R3m/V diffractometer with graphite monochromated Cu K_α radiation (λ = 1.54178 Å) for data collection at -50 ± 1 °C. The cell constants for data collection were determined from a list of reflections found by a rotation photograph. Pertinent data collection and reduction information are given in Table 5.1. Lorentz and polarization corrections and an absorption correction using the semi-empirical method were applied. In addition, a correction based on a decay in the standard reflections of 3.4% was used. The agreement factor for the averaging of observed reflections was 2.8% (based on F).

The centric space group C2/c was initially indicated by systematic absences and intensity statistics.[145] The positions of most of the porphyrin complex atoms were determined by direct methods.[145] 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 thermal parameters. After the least-squares converged all hydrogen atoms were placed at calculated positions 0.96 Å from the attached atom with refined isotropic temperature factors. A solvent molecule of toluene was found and constrained to refine as an idealized rigid group. Two atoms near an inversion center, (C80) and C(82), were found and appear to belong to a hexane of solvation. Both molecules of solvation have more thermal motion than the porphyrin complex but appear to be fully occupied. All atoms refined with positive-definite anisotropic thermal parameters except U_{22} of C19. Therefore U_{22} of C19 was fixed at an average value derived from neighboring carbon

Table 5.1. Crystal data for (TTP)Os=C(p-C_6H_4-CH_3)$_2$·C_7H_8·½ C_6H_{14}

Formula	$OsON_4C_{77}H_{63}$·C_7H_8·½C_6H_{14}
Formula weight	1252.6
Space Group	C2/*c*
a, Å	28.003(6)
b, Å	14.385(3)
c, Å	33.748(8)
α, deg	90.0
β, deg	114.51(2)
γ, deg	90.0
V, Å	12370(5)
Z	8
d_{calc}, g/cm^3	1.345
Crystal size, mm	0.35 x 0.35 x 0.12
μ(CuK_α), mm^{-1}	4.266
Data collection instrument	Siemens SHELXTL
Radiation (monochromated in incident beam)	CuK_α (λ = 1.54178 Å)
Temperature, °C	-50(1)
Scan method	2θ-θ
Data col. range, 2θ, deg	5.0-115.0
No. data collected	18182
No. unique data, total (with $F_o^2 > 4\sigma(F_o^2)$)	8334 (7564)
Number of parameters refined	665
Trans. factors, max., min. (ψ-scans)	0.1764, 0.9775
R[a]	0.0445
R_ω[b]	0.0536
Quality-of-fit indicator[c]	2.43
Largest shift/esd, final cycle	0.013
Largest peak, e/Å^3	1.15

[a] $R = \Sigma||F_o| - |F_c|/\_|F_o|$ [b] $R_\omega = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{½}$; $\omega = 1/\sigma^2|F_o|)$

[c] Quality-of-fit = $[\Sigma\omega(|F_o| - |F_c|)^2/N_{obs} - N_{parameters}]$½

atoms for the purpose of making a reasonable thermal ellipsoid drawing. No unusually short intermolecular non-bonded contacts are observed.

X-ray data collection and structure solution were carried out at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Corp. VaxStation 3100 computer using the SHELXTL PLUS version 4.0 programs.[145]

Results

Synthesis

When a dark brown benzene solution of the paramagnetic dimer $[Os(TTP)]_2$ is treated with one equivalent of $N_2C(p\text{-}C_6H_4\text{-}CH_3)_2$ at ambient temperature, the solution becomes orange. The ^1H NMR spectrum of the material isolated from this reaction is consistent with a new diamagnetic metalloporphyrin carbene complex formulated as $(TTP)Os{=}C(p\text{-}C_6H_4\text{-}CH_3)_2$, **5**. In C_6D_6 the ditolylcarbene complex maintains a time-averaged four-fold porphyrin symmetry as indicated by a single β-pyrrole signal at 8.15 ppm and the single methyl resonance at 2.39 ppm. The appearance of resonances for the porphyrin *o*-, *o'*-, *m*-, and *m'*-tolyl protons at 8.01 (d), 7.88 (d), and 7.29 (dd) ppm is consistent with a mono-carbene complex. A six-proton singlet at 1.69 ppm and two doublets at 6.03 (4H) and 4.26 (4H) ppm are observed for the tolyl substituents of the carbene ligand. The upfield shifts of these resonances are characteristic of protons above a porphyrin ring current. Besides the normal porphyrin resonances, the ^{13}C NMR spectrum of complex **5** has a singlet at 265.5 ppm. Electron impact ionization of **5** allowed the mass spectral observation of an ion having a mass of 1055 amu, corresponding the molecular ion plus one hydrogen. Crystals suitable for a single crystal X-ray diffraction study were grown from toluene/THF/hexane. The molecular structure (*vide infra*) confirms the proposed formulation.

The carbene complexes **6-10** are prepared in a similar manner, eq. 5.1. For synthesis of the less sterically hindered carbene complexes **7-10**, slow addition of the diazo reagent is necessary to minimize alkene formation (see Chapter 6). Noteworthy in the proton NMR spectra of **6-9** are the α-H resonances from the carbene ligands. These are observed at very low field, 19.82 - 28.95 ppm, for all four complexes. The coupled ^{13}C NMR spectra for **6-8** exhibit doublets in the region 211 - 295.5 ppm with $^{1}J_{C\text{-}H}$ values ranging between 124.4 and 141.1 Hz. These values are typical for carbene complexes. A ^{13}C NMR resonance for **10** occurs at 263.9 ppm. ^{1}H NMR of α-^{13}C enrich **10** exibits 7.87 Hz coupling for the resonance at -4.36 ppm, typical of two bond coupling for an sp^2 hybridized carbon.[146]

$$\tfrac{1}{2}\,[\mathrm{Os(TTP)}]_2 + \mathrm{N_2CRR'} \rightarrow \mathrm{(TTP)Os{=}CRR'} + \mathrm{N_2} \qquad (5.1)$$

5, $R = R' = p\text{-}C_6H_4\text{-}CH_3$

6, $R = H, R' = SiMe_3$

7, $R = H, R' = CO_2Et$

8, $R = H, R' = 2,4,6\text{-}(CH_3)_3C_6H_2$

9, $R = H, R' = p\text{-}C_6H_4\text{-}CH_3$

10, $R = CH_3, R' = C_6H_5$

Biscarbene Complexes

When a benzene or toluene solution of the paramagnetic dimer [Os(TTP)]$_2$ is treated with an excess of N_2C(*p*-tolyl)$_2$ at ambient temperature the solution becomes orange. The ^{1}H NMR spectrum of the material isolated from this reaction contains **5** and a new diamagnetic metalloporphyrin carbene complex formulated as (TTP)Os[=C(*p*-C_6H_4-CH_3)$_2$]$_2$, **11**. In C_6D_6 the bis(ditolylcarbene) complex maintains a time-averaged four-fold porphyrin symmetry as indicated by a single β-pyrrole signal at 8.63 ppm and the single methyl resonance at 2.42 ppm. The appearance of only two signals for the *o*-, and *m*-tolyl protons of the porphyrin at 7.99 and 7.33 ppm indicate that mirror symmetry in the porphyrin plane is present. A twelve proton singlet is observed at 1.68 ppm and is assigned to the methyl protons of the carbene tolyl group. The *m*- and *o*-protons of the these tolyl groups are observed as two doublets at 5.97 and 3.12 ppm, respectively. The ^{13}C spectrum exhibits a new resonance at 305.5 ppm as well as the normal porphyrin resonances.

$$[\mathrm{Os(TTP)}]_2 + 2\mathrm{N_2CRR'} \rightarrow (\mathrm{TTP})\mathrm{Os}(=\mathrm{CRR'})_2 + 2\mathrm{N_2} \qquad (5.2)$$

11, $R = R' = p\text{-}C_6H_4\text{-}CH_3$

12, $R = CH_3$, $R' = C_6H_5$

The biscarbene complex **12** is prepared similarly to complex **11** using an excess of methylphenyldiazomethane, eq. 5.2. The ^{1}H NMR spectrum contains resonances for both **10** and **12**. The biscarbene complex has porphyrin β-H and tolyl signals similar to those of **11** at 8.66, 8.06, 7.29, 2.40 ppm. The two carbene methyl groups exhibit a six-proton resonance at -3.17 ppm. The phenyl protons of the carbene ligand show ^{1}H NMR signals at 3.01 (*o*-H), 6.16 (*m*-H), and 6.37 (*p*-H) ppm.

Reactions

All of the carbene complexes decompose to uncharacterized compounds on exposure to air. Treating the di(*p*-tolyl)carbene complex, **5**, with an excess of pyridine-N-oxide at ambient temperature produces (TTP)OsO_2 and 4,4′-dimethylbenzophenone over the course of several days as monitored by ^1H NMR. However, complex **5** shows no reactivity towards MeI, acetone, ethanol, or hexamethylsilacyclopropane over a period of several days at ambient temperature.

X-ray Structure of 5·THF·Toluene·½ Hexane

The molecular structure of the ditolylcarbene complex, **5**·THF·Toluene·½ Hexane was determined by single crystal X-ray diffraction. The structure is clearly established as an osmium carbene complex as shown in Figure 5.1. Crystallographic data for the structure determination and fractional coordinates for non-hydrogen atoms are listed in Tables 5.1 and 5.2. Table 5.3 gives selected bond distances and angles.

The ditolylcarbene complex, **5**·THF·Toluene·½ Hexane, crystallizes in the monoclinic space group C2/*c* with eight molecules per unit cell. As expected for a six coordinate complex, the porphyrin ligand in this molecule is nearly planar. The largest deviation occurs at N2, 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 84.6° to 94.8°. The osmium atom is slightly out of the mean porphyrin plane 0.14 Å towards the carbene ligand. The Os-O4 distance of 2.327(3) Å in **5** is similar to the Os-O distance reported for the diethylsilylene complex, (TTP)(Et_2Si·THF)Os-THF, 2.40(2) Å, discussed in Chapter 3.

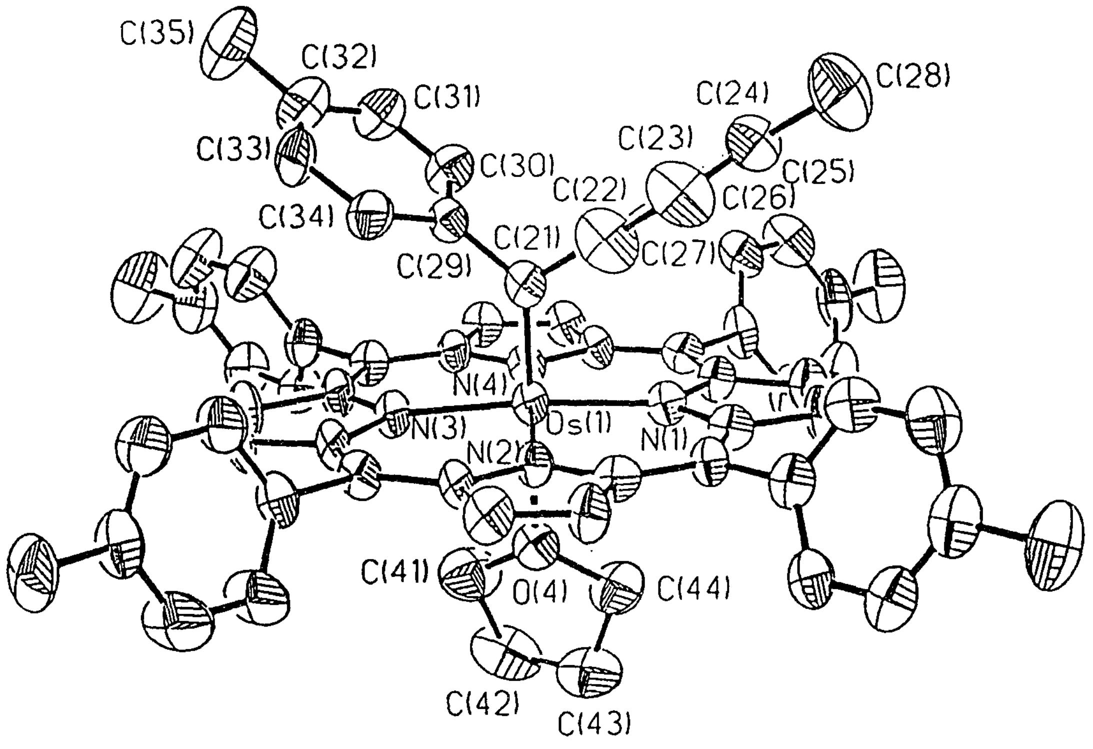


Figure 5.1. Molecular structure for (TTP)Os=C(tolyl)$_2$·THF·Toluene·½ Hexane with 50% probability thermal elipsoids and partial atom numbering scheme.

Table 5.2. Fractional atomic coordinates and equivalent isotropic displacement coefficients

Atom	x	y	z	Ueq(Å^2)
Os	0.3157(1)	0.3627(1)	0.1423(1)	0.031(1)
N1	0.3732(1)	0.2861(3)	0.1380(1)	0.034(2)
N2	0.3685(1)	0.4695(3)	0.1689(1)	0.033(2)
N3	0.2604(1)	0.4362(3)	0.1530(1)	0.034(2)
N4	0.2667(1)	0.2502(3)	0.1255(1)	0.035(2)
C1	0.3696(2)	0.1926(4)	0.1249(2)	0.038(2)
C2	0.4186(2)	0.1635(4)	0.1250(2)	0.046(2)
C3	0.4516(2)	0.2358(4)	0.1375(2)	0.047(2)
C4	0.4242(2)	0.3126(4)	0.1464(2)	0.038(2)
C5	0.4453(2)	0.4008(4)	0.1614(2)	0.035(2)
C51	0.4998(2)	0.4208(4)	0.1660(2)	0.041(2)
C52	0.5403(2)	0.4420(4)	0.2063(2)	0.047(2)
C55	0.5605(2)	0.4425(5)	0.1334(2)	0.063(3)
C54	0.6009(2)	0.4637(5)	0.1743(2)	0.056(3)
C53	0.5902(2)	0.4631(4)	0.2095(2)	0.053(3)
C56	0.5110(2)	0.4212(5)	0.1297(2)	0.055(3)
C57	0.6562(2)	0.4855(5)	0.1790(2)	0.076(3)
C6	0.4189(2)	0.4724(4)	0.1714(2)	0.038(2)
C7	0.4391(2)	0.5638(4)	0.1848(2)	0.044(2)
C8	0.4014(2)	0.6143(4)	0.1891(2)	0.045(2)
C9	0.3572(2)	0.5555(3)	0.1793(2)	0.034(2)
C10	0.3092(2)	0.5828(3)	0.1790(2)	0.038(2)
C101	0.3046(2)	0.6828(4)	0.1904(2)	0.041(2)
C102	0.3306(3)	0.7167(4)	0.2317(2)	0.079(3)
C103	0.3264(3)	0.8091(5)	0.2407(2)	0.083(3)

Table 5.2. cont.

Atom	x	y	z	Ueq(Å^2)
C104	0.2996(2)	0.8732(4)	0.2088(2)	0.053(3)
C105	0.2745(3)	0.8392(4)	0.1683(2)	0.060(3)
C106	0.2765(2)	0.7463(4)	0.1584(2)	0.056(3)
C107	0.2999(2)	0.9745(4)	0.2189(2)	0.069(3)
C11	0.2650(2)	0.5259(4)	0.1681(2)	0.040(2)
C12	0.2167(2)	0.5529(4)	0.1705(2)	0.050(3)
C13	0.1837(2)	0.4815(4)	0.1572(2)	0.051(3)
C14	0.2100(2)	0.4073(4)	0.1456(2)	0.041(2)
C15	0.1892(2)	0.3188(4)	0.1306(2)	0.037(2)
C151	0.1333(2)	0.3029(4)	0.1230(2)	0.044(2)
C152	0.1214(2)	0.2384(4)	0.1483(2)	0.049(2)
C153	0.0704(2)	0.2199(5)	0.1406(2)	0.062(3)
C154	0.0289(2)	0.2636(5)	0.1072(2)	0.076(3)
C155	0.0408(2)	0.3259(5)	0.0830(2)	0.064(3)
C156	0.0922(2)	0.3462(5)	0.0895(2)	0.107(4)
C157	-0.0272(2)	0.2411(6)	0.1001(2)	0.037(2)
C16	0.2151(2)	0.2476(4)	0.1216(2)	0.043(2)
C17	0.1945(2)	0.1564(4)	0.1065(2)	0.042(2)
C18	0.2322(2)	0.1046(4)	0.1028(2)	0.036(3)
C19	0.2778(2)	0.1626(4)	0.1141(2)	0.039(2)
C20	0.3254(2)	0.1349(3)	0.1136(2)	0.041(2)
C201	0.3284(2)	0.0379(4)	0.1009(2)	0.052(3)
C202	0.2946(2)	0.0046(4)	0.0596(2)	0.038(2)
C203	0.2953(3)	-0.0881(5)	0.0492(2)	0.064(3)
C204	0.3287(3)	-0.1513(5)	0.0792(3)	0.069(4)

Table 5.2. cont.

Atom	x	y	z	Ueq(Å²)
C205	0.3619(2)	-0.1182(4)	0.1190(3)	0.067(3)
C206	0.3611(2)	-0.0254(4)	0.1305(2)	0.053(3)
C207	0.3282(3)	-0.2522(4)	0.0687(2)	0.092(4)
C21	0.2922(2)	0.4057(3)	0.0858(2)	0.036(2)
C22	0.3279(2)	0.4164(4)	0.0618(2)	0.038(2)
C23	0.3330(2)	0.3475(4)	0.0361(2)	0.050(2)
C24	0.3652(2)	0.3568(4)	0.0144(2)	0.057(3)
C25	0.3928(2)	0.4388(5)	0.0170(2)	0.057(3)
C26	0.3872(2)	0.5078(5)	0.0431(2)	0.066(3)
C27	0.3564(2)	0.4978(4)	0.0650(2)	0.060(3)
C28	0.4280(3)	0.4461(6)	-0.0066(2)	0.093(4)
C29	0.2373(2)	0.4348(4)	0.0585(2)	0.037(2)
C30	0.2010(2)	0.3728(4)	0.0321(2)	0.051(2)
C31	0.1497(2)	0.4002(5)	0.0066(2)	0.059(3)
C32	0.1341(2)	0.4901(6)	0.0074(2)	0.071(3)
C33	0.1694(2)	0.5510(5)	0.0346(2)	0.067(3)
C34	0.2215(2)	0.5251(4)	0.0597(2)	0.050(2)
C35	0.0784(2)	0.5180(6)	-0.0209(3)	0.106(4)
O4	0.3435(1)	0.3058(3)	0.2129(1)	0.045(1)
C41	0.3062(2)	0.2890(6)	0.2314(2)	0.080(3)
C42	0.3343(3)	0.2284(5)	0.2709(2)	0.081(4)
C43	0.3878(3)	0.2170(5)	0.2753(2)	0.080(3)
C44	0.3856(2)	0.2405(5)	0.2309(2)	0.068(3)
C71	0.1089(3)	0.7762(6)	0.0627(3)	0.289(4)
C70	0.1515	0.8336	0.0575	0.289(4)

Table 5.2. cont.

Atom	x	y	z	Ueq(Å^2)
C72	0.0568	0.7846	0.0324	0.289(4)
C73	0.0177	0.7319	0.0372	0.289(4)
C74	0.0306	0.6708	0.0722	0.289(4)
C75	0.0827	0.6624	0.1025	0.289(4)
C76	0.1218	0.7151	0.0977	0.289(4)
C80	0.0315	0.4496	0.1946	0.276(5)
C81	0.0109	0.4843	0.2343	0.276(5)
C82	0.0152	0.3602	0.2317	0.276(5)

Table 5.3. Selected intramolecular bond distances and angles

Bond distances in angstroms

Atom 1	Atom 2	Distance
Os	N1	2.004(4)
Os	N2	2.061(4)
Os	N3	2.027(4)
Os	N4	2.044(4)
Os	C21	1.847(5)
C21	C22	1.533(8)
C21	C29	1.487(6)

Bond angles in degrees

Atom 1	Atom 2	Atom 3	Angle
N1	Os	C21	93.6(2)
N1	Os	O4	86.7(1)
N2	Os	C21	94.8(2)
N2	Os	O4	86.6(1)
N3	Os	C21	92.1(2)
N3	Os	O4	87.5(1)
N4	Os	C21	93.9(2)
N4	Os	O4	84.6(1)
C21	Os	O4	178.5(2)
Os	C21	C29	124.6(4)
Os	C21	C22	123.2(3)
C22	C21	C29	112.2(4)

Numbers in parentheses are estimated standard deviations in the least significant digits.

The Os-C21 bond length in **5**·THF·Toluene·½ Hexane (1.847(5) Å) is short for typical osmium carbene complexes, 1.90(1) Å to 1.94(1) Å.[79] The Os-C21 distance is comparable to the Os-CO metal carbon distance of 1.83(2) Å in $Cl_2(CO)(PPh_3)_2Os=CHPh$, but is significantly shorter than the Os=C distance 1.94(1) Å.[79] This suggests unusually strong back-bonding from the metal center. The remaining bond lengths and angles in the carbene ligand are within normal ranges.

Discussion

A straight forward method for preparing osmium porphyrin carbene complexes involves treating $[Os(TTP)]_2$[63] with the appropriate diazoalkane, as shown in eq. 5.1. The yields of carbene complexes from this reaction are high (77 - 96 %). The formation of the mono-carbene complexes **5-8** is complete within 10 minutes. These complexes are sufficiently stable to be purified on neutral alumina or florisil flash columns. The resulting solids are stable for at least three months when stored in a nitrogen atmosphere.

The resonances of the α-protons in complexes **6-9** are farther downfield than those observed for non-porphyrin osmium carbene complexes, 13.81-18.05 ppm.[79] Particularly noteworthy is the α-H shift of the trimethylsilyl carbene complex **6** at 28.95 ppm. This extends the observed range of α-H shifts for osmium carbenes by about 7.5 ppm. The α-H resonances of the osmium carbene complexes are approximately 7 ppm further downfield than their ruthenium analogs.

In solution the carbene complexes **5-10** appear to be stable as five coordinate, 16-electron complexes. Although the crystal structure of **5**·**THF** shows that a THF molecule is coordinated as a sixth ligand to osmium in the solid state, in solution a coordinated THF is not observed by ^{1}H NMR. Crystals of **5** obtained from ethanol show two equivalents of alcohol are present, in solution no coordinated alcohol is observed. None of the isolated complexes show any coordinated THF after removal of the solvent.

The slow formation of biscarbene complex, **11**, from the monocarbene complex **5** upon the addition of an excess of the $N_2C(p\text{-}C_6H_4\text{-}CH_3)_2$ can be monitored by ^{1}H NMR. This *trans*-biscarbene complex has not been isolated in pure form and always contains small amounts of the mono-carbene complex **5**. In solution **11** decomposes to the monocarbene complex, **5** and tetratolylethene over the course of several days at ambient temperature. The ^{13}C NMR chemical shift at 305.5 ppm for **11** is diagnostic for carbene ligands. The presence of only one down-field resonance in the ^{13}C NMR spectrum indicates that the two carbene ligands are equivalent.

Concluding Remarks

Several new osmium porphyrin carbene complexes have been prepared and characterized. In solution these carbene complexes appear to be stable as 16-electron species. Strong π-back donation from the osmium to the carbene carbon apparently occurs as indicated by the short osmium carbon distance in **5**. The carbene complexes containing α-protons exhibit resonances at extremely low-field in the proton NMR, while the ^{13}C resonances are typical of metal carbene ligands.

CHAPTER 6: CATALYTIC PRODUCTION OF ALKENES

Introduction

Although the organometallic chemistry of metalloporphyrins has developed rapidly over the past few years,[147] work in this area involving osmium porphyrin complexes has received less attention. Moreover, while various metalloporphyrins catalyze the production of alkenes,[70] cyclopropanes[148] and the oxidative carbonylation of amines,[149] use of osmium porphyrins for catalytic reactions has been limited thus far to oxidations of alkenes.[150] Subsequent to our preparation of the osmium porphyrin carbene complexes in Chapter 5, we turned our attention to the reaction of these complexes with diazo reagents. In this chapter, the use of osmium porphyrin complexes to facilitate the highly stereoselective catalysis of diazoalkanes to alkenes will be discussed.[151]

The decomposition of diazoalkanes in the presence of metal complexes to form alkenes has been known for over 20 years.[152] Product ratios of disubstituted alkenes slightly favor the *cis*-isomer. The mechanism of this transformation is not well understood. Thus several possible pathways have been proposed including radical chains,[144,153] binuclear coupling of metal carbenes,[154,147e,f] and nucleophilic attack of a diazo reagent at a metal carbene center.[70,155,152c,d] The later two mechanisms have been previously suggested for catalytic production of alkenes by ruthenium porphyrin complexes.[70]

Experimental

General

All manipulations of reagents and products were carried out under a nitrogen atmosphere using a VACUUM/ATMOSPHERES glove box equipped with a model MO40H Dri-Train gas purification system or on a vacuum line using standard Schlenk techniques. All solvents were dried and distilled from purple solutions of sodium/benzophenone. ^{1}H NMR spectra were recorded on Nicolet 300 MHz or Varian VXR 300 MHz spectrometers. Ethyl diazoacetate and trimethylsilyldiazomethane were purchased from Aldrich degassed by freeze-pump-thaw cycles, and distilled under reduced pressure. Other diazo reagents were prepared by the oxidation of the hydrazone[143] by yellow mercury (II) oxide in toluene. **WARNING** - several of the diazo reagents are reported to detonate spontaneously, $N_2C(CH_3)(Ph)$, N_2CH(tolyl) and N_2CH(Mes) were not isolated. Concentrations of N_2CH(*p*-tolyl) and N_2CH(Mes) were determined by treating the diazo compound with benzoic acid and back titrating the acid with NaOH.[144] $[Os(TTP)]_2$ was prepared by the literature procedure.[63] GC analyses were performed using a HP 5890 Series II GC with a DB-5 capillary column (30 m, 0.32 mm, 0.25 μ) with T_i = 50 °C for 1 min followed by a temperature ramp of 10 °C/min for 10 min.

Synthesis

Diethylmaleate (13).

In a typical experiment, 3.4 mg (3.23 μmole) of (TTP)Os=C(tolyl)$_2$ and dodecane (0.10 mL, 44 mmole) were stirred vigorously in 5.0 mL of benzene under an N_2 atmosphere. Addition of ethyl diazoacetate (0.10 mL, 95 mmole) resulted in the rapid evolution of gas which stopped after 1 min. Alkene product ratios were determined by GC analysis. Assignment of the major isomer was made by comparison of the ^{1}H NMR spectrum to that of an authentic sample.

Crossover Reactions.

In a typical experiment, (TTP)Os=CHCO$_2$Et was dissolved in C_6D_6 in an NMR tube. N$_2$CHTMS was added and the reaction monitored by proton NMR. Diethyl maleate and (TTP)Os=CHTMS were formed. A summary of reactions is listed in Table 6.1.

Table 6.1. Crossover reactions to form alkenes

Initial (TTP)Os=CRR'	diazo reagent	final (TTP)Os=CRR'	alkene product
(TTP)OsCHCO$_2$Et	N$_2$CHTMS	(TTP)OsCHTMS	EtO$_2$CHC=CHCO$_2$Et
(TTP)OsCHCO$_2$Et	N$_2$C(tolyl)$_2$	(TTP)OsCHCO$_2$Et	(tolyl)$_2$C=C(tolyl)$_2$
(TTP)OsCHCO$_2$Et	N$_2$C(CH$_3$)(Ph)	(TTP)OsC(CH$_3$)(Ph)	EtO$_2$CHC=CHCO$_2$Et
(TTP)OsCHTMS	N$_2$C(tolyl)$_2$	(TTP)OsCHTMS	(tolyl)$_2$C=C(tolyl)$_2$
(TTP)OsCHTMS	N$_2$CHCO$_2$Et	(TTP)OsCHTMS	EtO$_2$CHC=CHCO$_2$Et
(TTP)OsC(tolyl)$_2$	N$_2$CHCO$_2$Et	(TTP)OsC(tolyl)$_2$	EtO$_2$CHC=CHCO$_2$Et

Results and Discussion

When anaerobic benzene solutions of [Os(TTP)]$_2$ are treated with excess ethyl diazoacetate, rapid evolution of gas is observed and high yields of diethylmaleate and diethylfumarate are obtained, Table 6.2. Depending on reaction conditions, the final metal products consist of varying ratios of the ethylcarboxyl carbene complex 7 and [Os(TTP)]$_2$. ^{1}H NMR and GC analyses indicate that alkene formation occurs with a z/e ratio of 26:1.

The high stereoselective formation of diethylmaleate is also catalyzed by the carbene complexes, (TTP)Os=C(p-C_6H_4-CH_3)$_2$ (**5**), (TTP)Os=C(H)Si(CH_3)$_3$ (**6**), and (TTP)Os=C(H)CO_2Et (**7**) and the monomeric complexes, (TTP)Os(CO)(py) and (TTP)Os(py)$_2$. Table 6.2 summarizes yields and product ratios. These are the highest olefin stereoselectivities for the decomposition of diazo compounds reported to date.[156] Previously the largest diethylmaleate/diethylfumarate ratios (15:1) from ethyl diazoacetate were observed independently by Collman and Venburg using a ruthenium porphyrin catalyst.[70] [Os(TTP)]$_2$ also catalyzes the decomposition of N_2CH(tolyl) to 4,4'dimethylstilbene with a z/e ratio of 11:1. Again this is much higher than the previous ratios reported in the literature.[152d] Qualitatively, reactions catalyzed by [Os(TTP)]$_2$ or the carbene complexes, **5**, **6**, and **7**, reach completion in seconds. Catalyst activity appears to remain constant over a period of greater than one week. Thus, additional N_2CHCO_2Et may be added to catalyst solutions with virtually quantitative conversion to alkene and no loss in rate or stereoselectivity. Os(TTP)(py)$_2$ and (TTP)Os(CO)(py) show much slower reactivity. For example, the bis-pyridine complex requires 1 h to completely convert 0.1 mL of ethyl diazoacetate to alkene. This presumably reflects the need for a vacant coordination site in order to generate an initial carbene complex.

Steric factors appear to play an important role in the rate of alkene formation. When [Os(TTP)]$_2$ is treated with excess N_2C(p-C_6H_4-CH_3)$_2$ in THF, formation of tetratolylethylene[157] occurs qualitatively on the time scale of minutes. However, no alkene is observed by ^{1}H NMR when N_2CHSiMe$_3$ is the substrate over a period of days at ambient temperature. The lack of coupling in this case may be due to the large steric constraints of the trimethylsilyl group.

Table 6.2. Catalyst summary for the formation of olefins from ethyl diazoacetate*

catalyst	mass (mg) (±0.1)	µmole Os (±0.01)	*cis*/*trans* (±2)	% olefin yield (±3)	turnovers (±5)
$[Os(TTP)]_2$	2.7	3.14	26 25[a]	92 94[a]	140 284[a]
$(TTP)OsC(tolyl)_2$	3.4	3.23	18	94	122
$(TTP)OsCHSiMe_3$	3.5	3.70	25	99	128
$(TTP)OsCHCO_2Et$	3.6	3.81	24 25[a] 25[a]	100 100[a] 100[a]	127 255[a] 376[a]
$(TTP)Os(py)_2$	3.5	3.44	26	93	129
$(TTP)Os(CO)(Py)$	3.7	3.83	22	93	102

* Conditions: 0.100 mL (0.952 mmol) N_2CHCO_2Et, 0.100 mL dodecane, 5.00 mL C_6H_6, 22 °C. [a]Subsequent addition of 0.100 mL N_2CHCO_2Et.

A variety of cross reactions have been carried out as shown in table 6.1. When $(TTP)Os{=}CHSiMe_3$ or $(TTP)Os{=}C(p\text{-}C_6H_4\text{-}CH_3)_2$ are treated with N_2CHCO_2Et, only diethylmaleate and small amounts of diethylfumarate are produced. No evidence for the formation of mixed olefins is observed by ^1H NMR or GC. In addition, the final metal products are the original carbene complexes, $(TTP)Os{=}CHSiMe_3$ or $(TTP)Os{=}C(p\text{-}C_6H_4\text{-}CH_3)_2$, respectively. This suggests that the catalytic reactions may involve an intermediate *trans*-biscarbene complex. A moderately stable *trans*-biscarbene complex $(TTP)Os[{=}C(p\text{-}C_6H_4\text{-}CH_3)_2]_2$, **11**, has been prepared by treating $(TTP)Os{=}C(p\text{-}C_6H_4\text{-}CH_3)_2$, **5**, with additional $N_2C(p\text{-}C_6H_4\text{-}CH_3)_2$ (chapter 5). The alkene forming step may involve attack of a diazo reagent at the least hindered carbene ligand of the bis-carbene complex, Figure 6.1, or may involve direct coupling between two bis-carbene complexes in a binuclear process, Figure 6.2. Evidence for the binuclear mechanism was established by monitoring a 70:1 mixture of

$$\underset{\mathbf{11}}{(TTP)Os[=C(p\text{-}C_6H_4\text{-}CH_3)_2]_2} \rightarrow \underset{\mathbf{5}}{(TTP)Os{=}C(p\text{-}C_6H_4\text{-}CH_3)_2} + (p\text{-}C_6H_4\text{-}CH_3)_2C{=}C(p\text{-}C_6H_4\text{-}CH_3)_2 \quad (6.1)$$

11:**5**. Over the period of days, the bis-carbene complex **11** decomposes to produce tetratolylethylene and the mono-carbene complex **5**, eq. 6.1.

Concluding Remarks

Osmium porphyrin carbene complexes **5**, **6**, **7**, [(TTP)Os]$_2$, Os(TTP)(py)$_2$ and (TTP)Os(CO)(py) are all capable of catalytically forming alkenes from diazo reagents. The stereoselectivity for this process is extremely high for the diazo reagents examined. Evidence from crossover experiments indicates that a biscarbene intermediate is involved in the catalytic cycle.

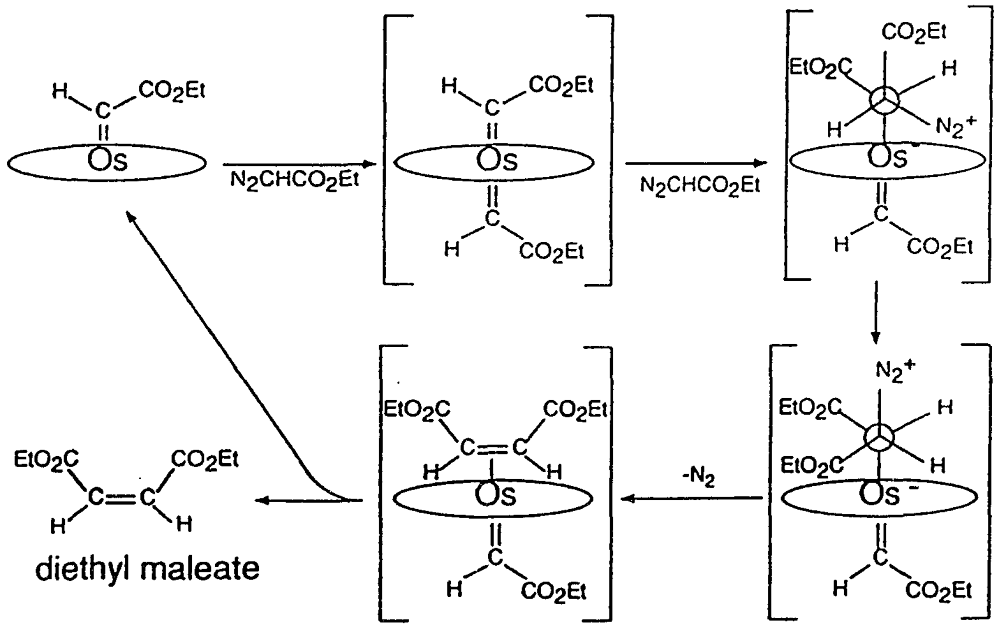


Figure 6.1. Alkene formation by diazo attack on a biscarbene complex

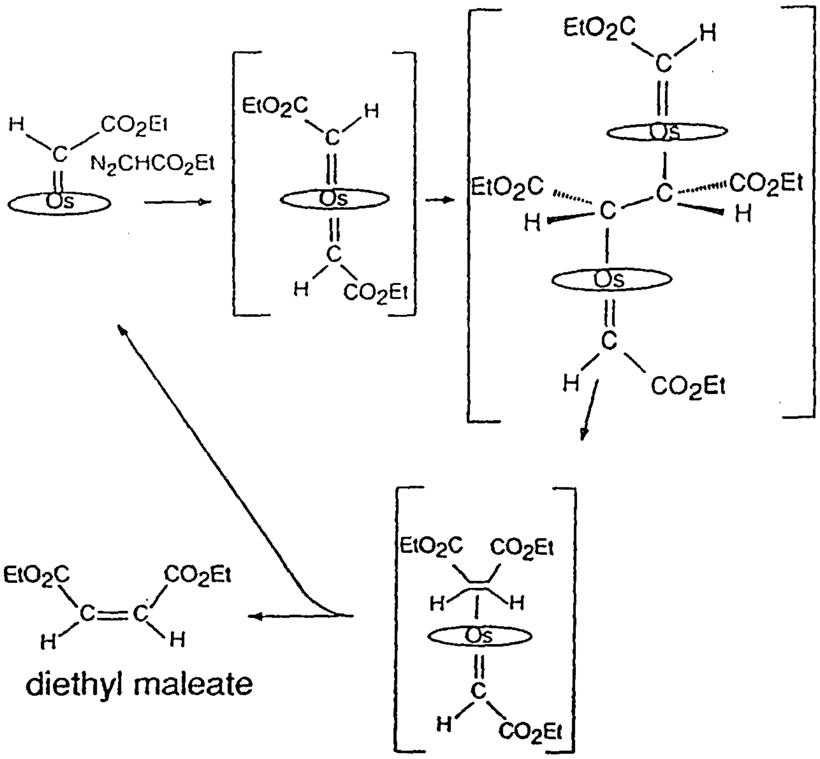


Figure 6.2. Bimolecular mechanism for alkene formation

CHAPTER 7: CATALYTIC PREPARATION OF CYCLOPROPANES

Introduction

Several excellent reviews covering catalytic[158] and stoichiometric[159] cyclopropanation reactions and mechanisms have appeared. The mechanism of cyclopropanation is currently receiving considerable attention. Since publication of the above reviews, several significant several significant studies have advanced the understanding of the mechanism. These are summarized below.

Cyclopropanation of alkenes can be accomplished catalytically or stoichiometrically. Catalytic systems typically use a diazo reagent as the carbene source and a metal-containing mediator which forms a postulated metal carbene intermediate. Transfer of the carbene fragment from the metal to an alkene produces the cyclopropane product. Despite the wide variety of catalytic cyclopropanation systems, the putative carbene complex has never been isolated or directly observed in a catalytic system. This is somewhat surprising since the second category of cyclopropanation reactions involves the stoichiometric reaction of isolated carbene complexes with an alkene to form a cyclopropane. None of the isolated carbene complexes show catalytic activity toward cyclopropanation.

Catalytic Advances

Copper catalysts are among some of the oldest cyclopropanation catalysts known.[160] Recent work has focused on developing chiral catalysts that provide enantiomerically pure cyclopropanes. Towards this end, enantiomeric excesses (ee's) as high as 99% have been achieved for cyclopropanating styrene by a diazo ester using 4,4'-disubstituted bis(oxazoline) copper(I) triflate complexes, Figure 7.1.[161] An X-ray structure of the catalyst precursor $[LCu(OTf)]_x$ reveals a chiral helical polymer,[162] with a bis(oxazoline) ligand bridging two copper(I) centers. Semicorrin copper(I) complexes, Figure 7.1, also exhibit high ee's (> 90%).[163] When styrene was used as the substrate, increasing the size of the alkyl group in the diazo reagent increased both the *anti/syn* (a/s) ratio and the ee. For example when (1R,3R,4S)-menthyl diazoacetate is used, the a/s = 5.7 and an ee greater than 90% for both the *anti* and *syn* cyclopropane isomers were acheived. However when styrene is cyclopropanated with ethyl diazoactetae, a/s = 2.7 and ee's of 68 % (*syn*) and 85% (*anti*) were observed. The best a/s ratio reported for cyclopropanation of styrene with ethyl diazoacetate is 3.3.[161]

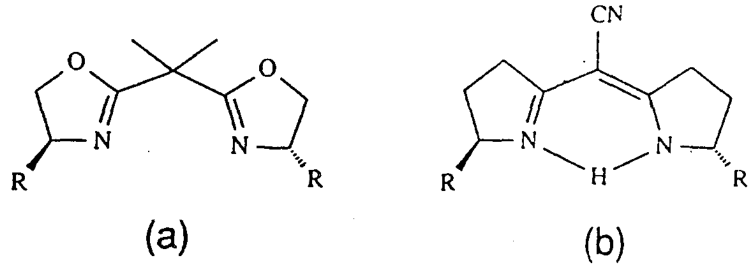


Figure 7.1. a) bisoxazoline b) semicorrin

Several years ago Callot demonstrated that rhodium porphyrins catalytically cyclopropanated a variety of alkenes in the presence of ethyl diazoacetate.[164] This was the first time a metalloporphyrin was used as a cyclopropanation catalyst. Surprisingly, the product ratio favored the *syn*-cyclopropane. Kodadek and co-workers have expanded this work and have attempted to prepare synthetically useful enantioselective catalysts for the formation of cyclopropanes.[165] Their approach has been to use rhodium complexes with optically active porphyrins to induce chirality into the product. With iodo(5α,10β,15α,20β-tetrakis[(R)-1,1'-binaphth-2-yl]-porphyrinato)rhodium(III) or iodorhodium "chiral wall" porphyrin, Figure 7.2, poor to moderate enantiomeric excesses were observed.[165b] In the same report, the catalysts (TTP)RhI and (TMP)RhI were reported to exhibit shape selectivity. Thus, 1-alkenes are preferentially cyclopropanated over internal alkenes, *cis*- are preferred to *trans*-, and disubstituted alkenes are greatly preferred to tetrasubstituted alkenes.[165b] Attempts to increase the observed ee's by increasing the steric bulk of the porphyrin ligand were unsuccessful. For example, using iodo(5α,10β,15α,20β-tetrakis[(R)-1-(1'-pyrenyl)-naphthalen-2-yl]-porphyrinato)rhodium(III) or iodorhodium "chiral fortress" porphyrin, Figure 7.2, resulted in ee's no greater than those observed for the analogous chiral wall complex.[165a] Kodadek has also shown that the diazonium complex, (TTP)Rh-C(H)(CO$_2$Et)(N$_2$)$^+$I$^-$, is the predominant steady state species in the catalytic cyclopropanation of styrene with ethyl diazoacetate.[166] In addition, kinetic studies suggest that the formation of a rhodium carbene complex is at least partially rate limiting.[166] However, this carbene complex has not been isolated or observed. Furthermore, alkenes were demonstrated to bind to the rhodium porphyrin complex. A mechanism was postulated, Scheme 7.1, in which the formation of a metal porphyrin carbene complex is activated by coordination of an alkene in the *trans* position.

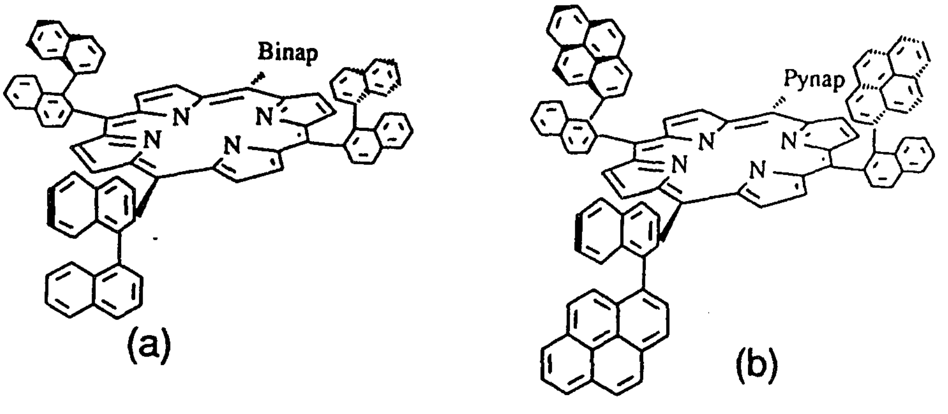
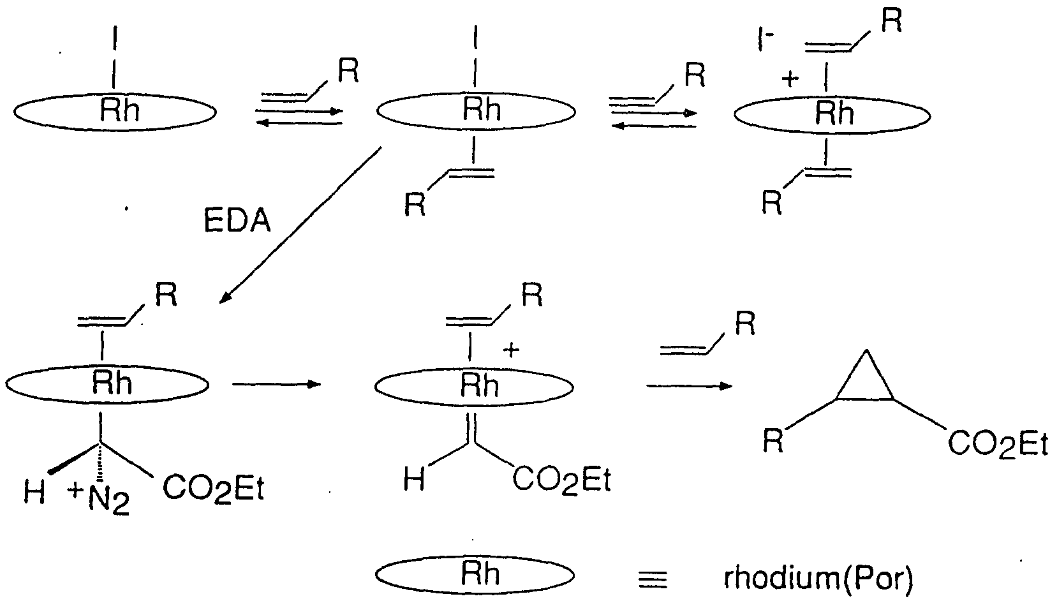


Figure 7.2. a) Chiral wall porphyrin and b) chiral fortress porphyrin

Scheme 7.1



Mechanistic Advances

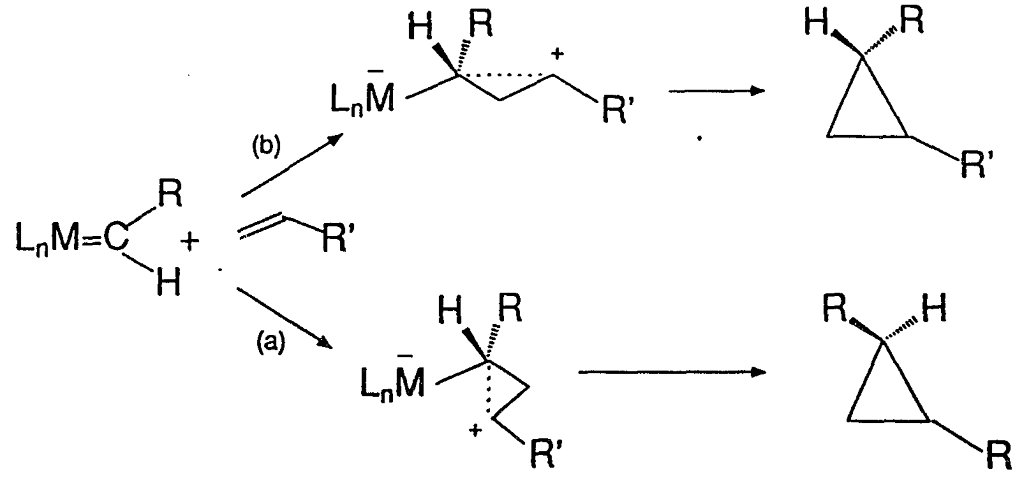
The remaining advances made since the above reviews have been in the understanding of the mechanism of cyclopropanation. It is generally accepted that a metal carbene complex participates in the catalysis, but such a species has never been observed in a catalytic cycle. As discussed above, recent evidence by Kodadek[166] suggests that the formation of a rhodium carbene complex is rate limiting when rhodium porphyrins are the catalysts. Collum also provides evidence for the formation of reactive palladium carbene complexes as possible intermediates in palladium catalyzed cyclopropanation.[167] In this case, the presence of a carbene complex was established by trapping experiments.

Two mechanisms for metal catalyzed cyclopropanation involving metal carbene complexes have been proposed. The first, Scheme 7.2, involves an initial π-complex between the metal carbene complex and the alkene. Four possible π-complexes are possible when a mono-substituted alkene is the cyclopropanation substrate. The two π-complexes with lowest energy, shown in scheme 7.2, result from minimizing the steric interactions between the alkene substituent and the metal ligands.[168] The π-complex is follwed by nucleophilic attack of the least hindered position of the alkene double bond on the carbene carbon. The incipient γ-carbon of the transition state develops a partial positive charge. This short-lived transition state collapses to the cyclopropane product by either frontside or backside attack. Frontside attack is defined as attack at the α-carbon on the same side as the metal. Backside attack refers to attack by the γ-carbon at the α-carbon on the side opposite to the M-C bond. An alternative mechanism involves the formation of a metallocyclobutane followed by reductive elimination to form the product.

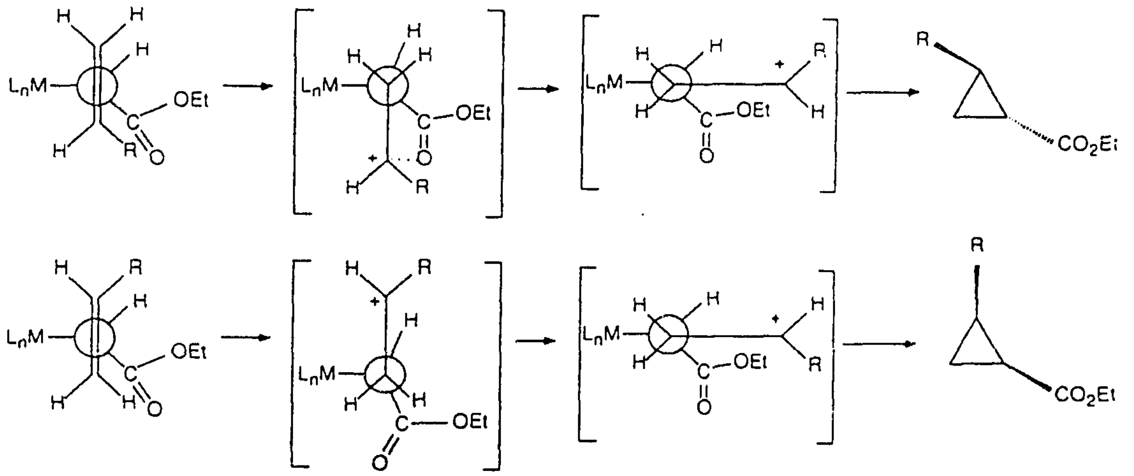
The γ-cation mechanism can account for the stereochemistry associated with cyclopropanation by alkylidene metal complexes and the trans-stereoselectivity observed in reactions with alkyl diazoesters. When alkyl diazoesters are used, stabilization of the developing positive charge on the γ-carbon by the carbonyl oxygen of the ester group adequately accounts for the observed stereoselectivity. This is only possible for the intermediate resulting in the *trans*-cyclopropane, scheme 7.3.[169] Moreover, a study of the effects of alkene substituents on cyclopropane stereochemistry[170] disfavors the metallocyclobutane mechanism.

In the most reasonable mechanism, the γ-carbon cation pathway, an unresolved issue involves the manner in which the positively charged γ-carbon transition state (Scheme 7.2) collapses, via frontside or backside attack. Brookhart has undertaken studies designed to

Scheme 7.2



Scheme 7.3



answer this question using the chiral reagent $Cp(CO)(PR_3)Fe{=}CHCH_3^+$ as an enantioselective cyclopropanation reagent.[171] The ratio of cyclopropane enantiomers exceeds that of the anticlinal to synclinal carbene complex. Thus, one isomer of the carbene complex must be more reactive towards cyclopropanation. In previous reaction studies, the synclinal rotational isomer was found to be more reactive toward nucleophiles than the anticlinal isomer, Figure 7.3. To obtain the correct cyclopropane product from the synclinal isomer, back side attack at the α-carbon is required, Scheme 7.4. From available data, Brookhart proposed a variable transition state model. The structure of the transition state depends on whether it occurs early or late in the reaction path. Less reactive metal carbene complexes, such as the more electron rich phosphine substituted iron compounds, favor late transition states. In these cases the transition state more nearly resembles the cyclopropane product and trans stereoselectivity is observed. More reactive electron deficient metal carbene centers, such as $Cp(CO)_2Fe{=}CHCH_3^+$, favor an early transition state where steric interactions arising from the initial approach of the alkene dominate the stereoselectivity. A second study using $Cp(CO)_2FeCH_2CH_2CH(OMe)Ph$ and selectively deuterated analogs demonstrate that the α-carbon is inverted during the reaction.[172] This strongly supports the mechanism involving collapse of a γ-cationic intermediate by backside attack. This has been independently confirmed by Casey in a similar series of experiments.[173] This also confirms that long lived γ-cations do not exist in the reaction. The currently accepted mechanism follows path (b) in Scheme 7.2.

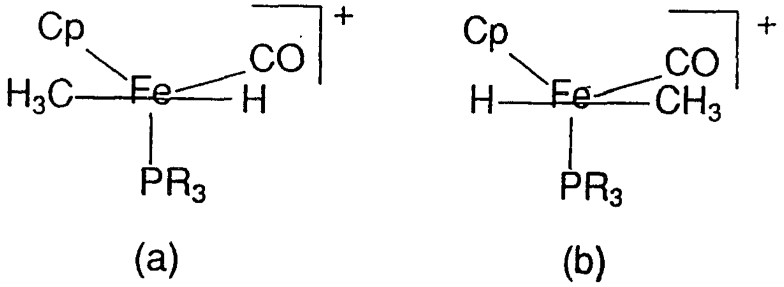
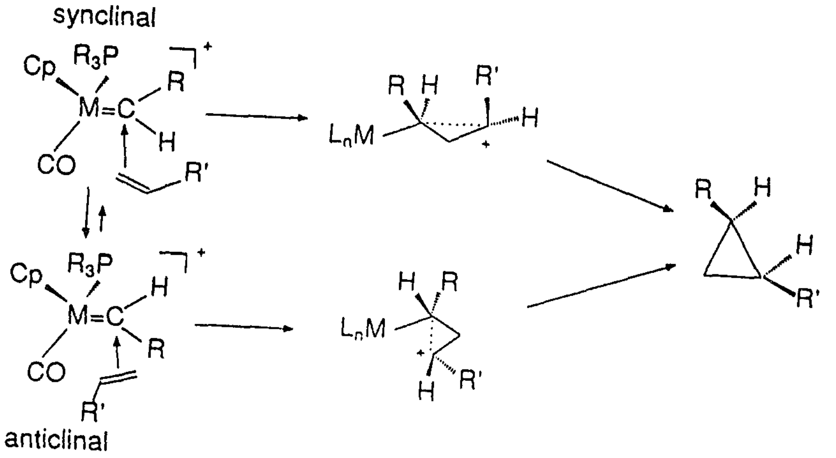


Figure 7.3. Synclinal (a) and anticlinal (b) isomers

Scheme 7.4



Experimental

General

All manipulations of reagents and products were carried out under a nitrogen atmosphere using a VACUUM/ATMOSPHERES glove box equipped with a model MO40H Dri-Train gas purification system or on a vacuum line using standard Schlenk techniques unless otherwise stated. All solvents were dried and distilled from purple solutions of sodium/benzophenone. ^1H NMR spectra were recorded on Nicolet 300 MHz, Varian VXR 300 MHz or Varian/Unity 500 MHz spectrometers. Ethyl diazoacetate and trimethylsilyldiazomethane (purchased from Aldrich) were degassed by freeze-pump-thaw cycles and distilled under reduced pressure. Other diazo reagents were prepared by the oxidation of the appropriate hydrazone[143] by yellow mercury(II) oxide in toluene. **WARNING** - several of the diazo reagents are reported to detonate spontaneously, $N_2CH(p\text{-tolyl})$ and $N_2CH(Mes)$ were therefore not isolated. Concentrations of $N_2CH(p\text{-tolyl})$ and $N_2CH(Mes)$ in toluene solutions were determined by treating the diazo compound with benzoic acid and titrating the acid with NaOH.[144] $[Os(TTP)]_2$ and (TTP)Os(CO)(Py) were prepared by literature procedures.[63] GC analyses were performed with a HP 5890 Series II GC with a DB-5 capillary column (30 m, 0.32 mm, 0.25 µ) with the following conditions: Program A - initial temperature (T_i) = 85 °C for 5 min, ramp rate (RR) = 20 °C/min, final temperature (T_f) = 250 °C or Program B - T_i = 100 °C for 2 min, RR= 10 °C/min T_f = 250 °C. GC yields were determined for alkenes (Y_A) and cyclopropanes (Y_{CP}) using dodecane as an internal standard.

Synthesis

Ethyl-2-phenyl-1-cyclopropanecarboxylic acid ester (14).

Method A. In a typical experiment, 3.4 mg (3.5 µmol) of (TTP)Os(CO)(Py) and styrene (0.22 mL, 1920 µmole) were vigorously stirred in toluene (3 mL). A toluene solution (12 mL) of N_2CHCO_2Et (0.10 mL, 952 µmole) was added dropwise over one hour. Addition of dodecane (0.10 mL, 44 mmole) was followed by GC analysis using program A: Y_A = 16(1)% Y_{CP} = 54(1)% anti/syn = 9.0(1). Anti isomer: ^{1}H NMR ($CDCl_3$): 7.3-7.0 (m, Aryl), 4.15 (q, 2H, CH_2CH_3), 2.49 (m, 1H), 1.87 (m, 1H), 1.58 (m, 1H), 1.3 (m, 1H), 1.23 (t, 3H, CH_2CH_3) ppm. Syn isomer: ^{1}H NMR ($CDCl_3$): 7.3-7.0 (m, Aryl), 3.85 (q, 2H, CH_2CH_3), 2.50 (m, 1H), 2.05 (m, 1H), 1.71 (m, 1H), 1.3 (m, 1H), 0.95 (t, 3H, CH_2CH_3) ppm. Assignment of the cyclopropane major isomer was made by comparison of the proton NMR to that of an authentic sample.[160a,174]

Method B. In a typical experiment, 3.0 mg (1.7 µmol) of $[(TTP)Os]_2$ and styrene (0.11 mL, 961 µmole) were vigorously stirred in toluene (3 mL). A toluene solution (12 mL) of N_2CHCO_2Et (0.10 mL, 952 µmole) was added dropwise over one hour. Addition of dodecane (0.10 mL, 44 mmole) was followed by GC analysis using program A: Y_A = trace

Y_{CP} = 79(2)% anti/syn = 10.2(1).

Method C. In a typical experiment, 4.3 mg (4.5 μmol) of (TTP)Os=$CHCO_2Et$ and styrene (0.10 mL, 874 μmole) were vigorously stirred in toluene (3 mL). A toluene solution (12 mL) of N_2CHCO_2Et (0.10 mL, 952 μmole) was added dropwise over one hour. Addition of dodecane (0.10 mL, 44 mmole) was followed by GC analysis using program A: Y_A = trace Y_{CP} = 63(2)% anti/syn = 8.9(6).

Method D. (TTP)Os=$CHCO_2Et$ (3 mg, 3 μmole) were dissolved in C_6D_6 (0.4 mL) in an NMR tube. Styrene (1.0 μL, 8.7 μmole) was added, the tube shaken vigorously and monitored by ^1H NMR. After 4 h the reaction was 96% complete. ^1H NMR (C_6D_6): 8.62 (s, 8H, β-H), 7.94 (d, 8H, porph-aryl), 7.28 (d, 8H, porph-aryl), 6.15 (br, styrene-aryl), 2.40 (s, 12H, CH_3) ppm and signals for **14**. The NMR yield for **14** is 73(5)%. GC confirms the presence of **14**, anti/syn = 11.5(4).

1-(2,4,6-trimethylphenyl)-2-phenylcyclopropane (15).

Using method A **15** was prepared from 1.8 mg (1.9 μmol) of (TTP)Os(CO)(Py), 0.10 mL (874 μmole) styrene, and N_2CHMes (20 mL, 0.033 M in toluene, 660 μmole). GC program B: Y_A = < 1%, Y_{CP} = 100(10)%, anti/syn = 0.4(1). Assignment of the cyclopropane major isomer was made by 500 MHz 2D-NOESY proton NMR. Major isomer: ^1H NMR C_6D_6): 7.5-7.0 (m, 7H), 2.66 (s, 6H, CH_3), 2.54 (s, 3H, CH_3), 2.02 (m, 1H), 1.97 (m, 1H), 1.40 (m, 1H), 1.04 (m, 1H). Minor isomer: ^1H NMR C_6D_6): 7.5-7.0 (m, 7H), 2.45 (s, 6H, CH_3), 2.50 (s, 3H, CH_3), 1.84 (m, 1H), 1.76 (m, 1H), 1.17 (m, 1H), 1.02 (m, 1H). MS(EI) M^+ 236, 221, 143, 132, 115 (base), 91.

Using method D, with (TTP)Os=CHMes (1.5 mg, 1.5 μmole) and styrene (0.40 μL, 3.5 μmole), no cyclopropanation was observed after 21 h by proton NMR.

Using method D, with (TTP)Os=CHMes (1.5 mg, 1.5 μmole) and styrene (0.18 mL, 1570 μmole), no cyclopropanation was observed after 20 min by GC. Less than 1% of cyclopropane product was detected after 2 h by GC.

Ethyl-3-n-octyl-1-cyclopropanecarboxylic acid ester (16).

Using method A, **16** was prepared from 5.5 mg (5.7 μmol) of (TTP)Os(CO)(Py), 0.18 mL (953 μmole) 1-decene, and N_2CHCO_2Et (0.10 mL, 952 μmole). GC program B: Y_A = 31(1), Y_{CP} = 32(1)%, anti/syn = 4.3(1). GC analysis with an authentic sample of **16** confirmed the identity of the cyclopropane products. Major isomer: ^1H NMR ($CDCl_3$): 4.00 (q, 2H, CH_2CH_3), 1.39 (m, 1H), 1.3-1.1 (m, 18H), 1.03 (m, 1H), 0.77 (t, 3H, CH_2CH_3), 0.57 (m, 1H) ppm. Minor isomer: ^1H NMR ($CDCl_3$): 4.01 (q, 2H, CH_2CH_3), 1.54 (m, 1H), 1.3-1.1 (m, 18H), 0.87 (m, 1H), 0.79 (m, 1H), 0.76 (t, 3H, CH_2CH_3) ppm.

Ethyl-2-methyl-2-phenyl-1-cyclopropanecarboxylic acid ester (17).

Using method A, **17** was prepared from 4.5 mg (4.7 μmol) of (TTP)Os(CO)(Py), 0.13 mL (1000 μmole) α-methylstyrene, and N_2CHCO_2Et (0.10 mL, 952 μmole). GC program A: Y_A = 29(1), Y_{CP} = 39(1)%, anti/syn = 2.8(1). Major isomer, as determined by 500 MHz 2D-NOESY ^1H NMR, has the ethyl carboxylate group anti to the phenyl group. Major isomer: ^1H NMR ($CDCl_3$): 7.3-7.10 (m, 5H aryl), 4.15 (m, 2H, CH_2CH_3), 1.92 (m, 1H), 1.49 (s, 3H, CH_3), 1.40 (m, 1H), 1.26 (t, 3H, CH_2CH_3), 1.37 (m, 1H) ppm. Minor isomer: ^1H NMR ($CDCl_3$): 7.3-7.10 (m, 5H aryl), 3.8 (m, 2H, CH_2CH_3), 1.86 (m, 1H), 1.74 (dd, 1H), 1.43 (s, 3H CH_3), 1.10 (dd, 1H), 0.90 (t, 3H, CH_2CH_3) ppm.

Ethyl-*cis*-3-methyl-*trans*-2-phenyl-r-cyclopropanecarboxylic acid ester (18).

Using method A **18** was prepared from 3.7 mg (3.8 μmol) of (TTP)Os(CO)(Py), 0.12 mL (926 μmole) trans-β-methylstyrene, and N_2CHCO_2Et (0.10 mL, 952 μmole). GC program A: $Y_A = 43(2)$, $Y_{CP} = 13(2)\%$. ^1H NMR ($CDCl_3$): 7.4-6.7 (m, 5H aryl), 3.99 (dq, 2H, CH_2CH_3), 2.50 (dd, 1H), 1.98 (dd, 1H), 1.35 (m, 1H), 1.32 (d, 3H, CH_3), 0.97 (t, 3H, CH_2CH_3), ppm.

2-phenyl-1,1-bis-*p*-tolylcyclopropane (19).

$[(TTP)Os]_2$ (1.0 mg, 0.58 μmole), styrene (0.20 mL, 1.75 mmole), and $N_2C(tolyl)_2$ were vigorously stirred in THF (3 mL). After 4 days solvent was removed under reduced pressure. Yield was determined by proton NMR integrations of porphyrin β-pyrrole (8.18 ppm) to cyclopropane signal at 2.78 ppm, and confirmed by integration of styrene resonances at 5.6 and 5.1 ppm. $Y_{CP} = 39(1)\%$. ^1H NMR (C_6D_6): 7.4-6.8 (m, aryl), 2.75 (dd, 1H), 1.81 (dd, 1H), 1.57 (dd, 1H). MS(EI) M^+ 298 amu.

2,4-dicarboethoxy-1-phenyl[1-1-0]bicyclobutane (20).

Using method A, **20** was prepared from 3.6 mg (3.7 μmol) of (TTP)Os(CO)(Py), 50 μL (456 μmole) phenylacetylene, and N_2CHCO_2Et (0.10 mL, 952 μmole). GC program A: $Y_A = 41(1)$, $Y_{CP} = 11(1)\%$. Only one isomer observed assigned as exo-exo by ^1H NMR. ^1H NMR (C_6D_6): 7.66 (d, 2H, aryl), 7.06 (m, 3H, aryl), 3.7 (m, 4H, CH_2CH_3), 3.41 (s, 1H), 1.71 (s, 2H), 0.70 (t, 3H, CH_2CH_3) ppm.

Using method B, **20** was prepared from 4.1 mg (2.4 μmol) of $[(TTP)Os]_2$, 0.50 mL (4.56 mmole) phenylacetylene in 6 mL toluene, and N_2CHCO_2Et (1.00 mL, 9.52 mmole) 24 mL toluene. GC program A: $Y_A = 20(1)$, $Y_{CP} = 46(2)\%$. Only one isomer observed. MS(EI) M^+ 274, 245, 229, 201, 173 amu. ^{1}H NMR (C_6D_6): 7.66 (dd, 2H, aryl), 7.06 (m, 3H, aryl), 3.7 (m, CH_2CH_3, 4H), 3.41 (s, 1H), 1.71 (s, 2H), 0.70 (t, CH_2CH_3, 6H).

2,4-bis(2,4,6-trimethylphenyl)-1-phenyl[1-1-0]bicyclobutane (21).

Using method A, **21** was prepared from 3.7 mg (4.0 μmol) of (TTP)Os(CO)(Py), 0.10 mL (912 μmole) phenylacetylene, and N_2CHMes (31.6 mL, 0.045 M in toluene, 1440 μmole). GC program T_i = 100°C for 2 min, RR = 10°C/min for 3 min.(T = 130°C), RR = 20°C/min, T_f =250 to end: $Y_A = 2(1)\%$, $Y_{CP} = 77(3)\%$. MS(EI) M^+ exact mass found (calc.) 366.23454 (366.23475) amu. ^{1}H NMR (C_6D_6): 7.1- 6.8 (m, C_6H_5), 6.71 (s, 4H, *m*-C_6H_2), 3.16 (m, 1H), 2.16(s, 3H, CH_3),2.47 (s, 3H, CH_3), 2.35 (m, 2H), 2.21 (s, 3H, CH_3), 2.19 (s, 6H, CH_3), 2.11 (s, 3H, CH_3). Major isomer assigned as exo-exo based on ^{1}H NMR.

Crossover Experiment.

(TTP)Os=CHMes (7.0 mg, 7.1 μmole) and styrene (0.80 mL, 6.99 mmole) were stirred in 3 mL of toluene. A toluene solution (10 mL) of ethyl diazoacetate (7.0 μL, 67 μmole) was added dropwise over 10 min followed immediately by GC analysis. Both **14** (a/s = 9.8(2)) and **15** (a/s = 0.4) were observed.

Results

Slow addition of a toluene solution of ethyl diazoacetate over 2 h to a vigorously stirred solution of $[(TTP)Os]_2$ and styrene results in the formation of ethyl-2-phenyl-1-cyclopropanecarboxylic acid ester (**14**) in 79(2)% as determined by GC. The *anti*/*syn* (a/s)

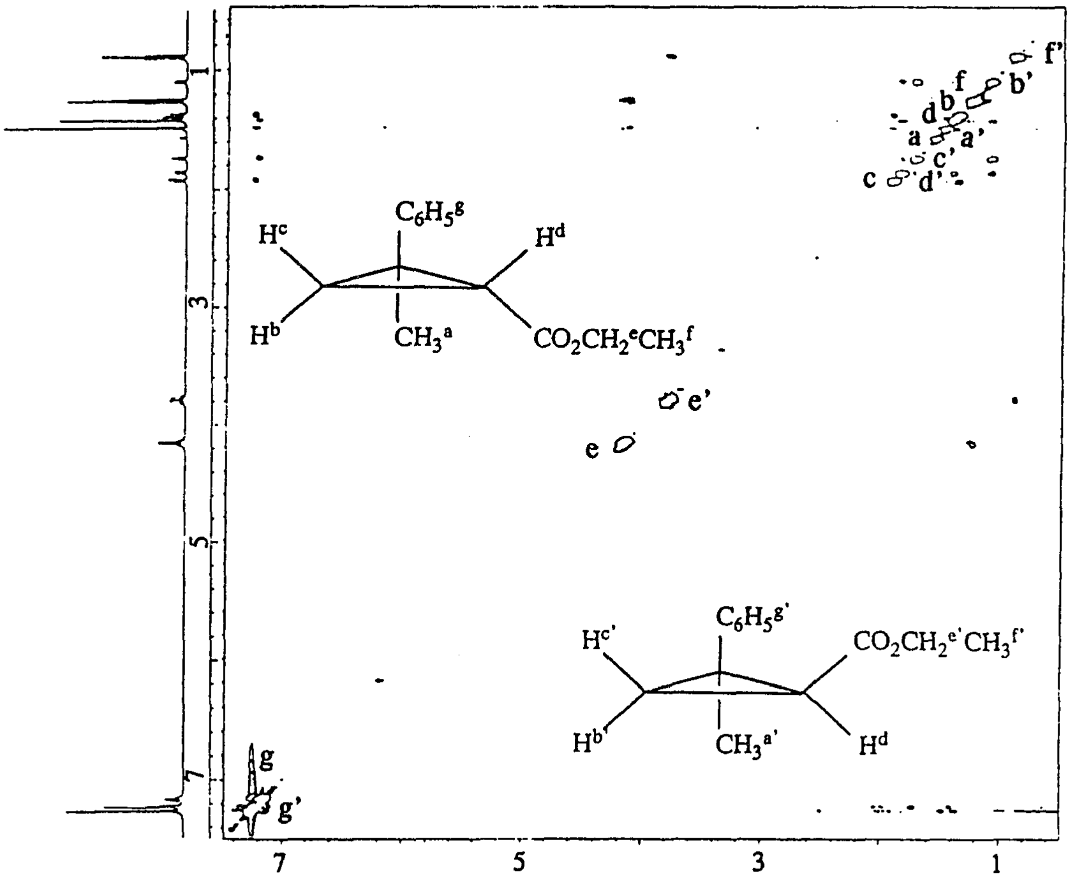


Figure 7.4. 2D-NOESY of Ethyl-2-methyl-2-phenyl-1-cyclopropanecarboxylic acid ester (17) Cross peaks (resonances off the diagonal) indicate that the two corresponding protons are proximal. The following crosspeaks were observed. *Anti* isomer: Ha-Hf, Ha-He, Ha-Hb, Hb-Hc, Hc-Hd, Hc-Hg, Hd-Hg, He-Hf. *Syn* isomer: Ha'-Hb', Ha'-Hd', Ha'-Hg', Hb'-Hc', Hb'-Hd', Hc'-Hd', Hc'-Hg', He'-Hf'.

Table 7.1. Data for cyclopropanation reactions

catalyst	substrate **A**	diazoreagent **B**	ratio [**A**/**B**]	olefin		cyclopropane	
				yield	c/t	yield	a/s
(TTP)Os(CO)(py)	styrene	N_2CHCO_2Et	2	11(2)	a	54(1)	9.0 (1)
(TTP)Os(CO)(py)	styrene	N_2CHCO_2Et	1	12(1)	a	65(3)	9.5 (2)
(TTP)Os(CO)(py)	styrene	N_2CHCO_2Et	.55	26(1)	a	44(1)	9.0 (3)
$[Os(TTP)]_2$	styrene	N_2CHCO_2Et	1	trace	a	79(2)	10.2(1)
$(TTP)OsCHCO_2Et$	styrene	N_2CHCO_2Et	1	trace	a	63(2)	8.9(6)
(TTP)Os(CO)(py)	1-decene	N_2CHCO_2Et	1	31(1)	a	32(1)	4.3(1)
(TTP)Os(CO)(py)	α-methyl styrene	N_2CHCO_2Et	1	29(1)	a	39(1)	2.8(1)
(TTP)Os(CO)(py)	trans-β-methyl styrene	N_2CHCO_2Et	1	43(2)	23	13(2)	b
(TTP)Os(CO)(py)	styrene	$N_2CH(Mes)$	1.3	trace	c	100(10)	0.42(2)
$[Os(TTP)]_2$ d	styrene	$N_2C(Tolyl)_2$	1			39(5) e	
(TTP)Os(CO)(py)	PhCCH	N_2CHCO_2Et	.5	41(1)	a	11(1) f,g	h
$[Os(TTP)]_2$	PhCCH	N_2CHCO_2Et	.5	20(1)	a	46(2) f,i	h
(TTP)Os(CO)(py)	PhCCH	$N_2CH(Mes)$	.6	2(1)	3	77(3) f	7(1)
(TTP)OsCH(Mes)	styrene					N.R.	
$(TTP)OsCHCO_2Et$	styrene					73(5)	11.5(4)

[a] cis isomer is the only one detected [b] Ethyl-trans-2-phenyl-cis-3-methylcyclopropane-r-carboxylicacid ester is the only isomer observed [c] isomer not confirmed, assumed to be cis [d] reaction conducted in THF [e] determined by NMR [f] bicyclobutanes only cyclopropane product, no cyclopropene has been observed [g] one hour addition [h] Only one isomer observed [i] ten hour addition

isomer ratio is 10.2:1 (see Table 7.1). Under similar conditions, the carbene complex (TTP)Os=$CHCO_2Et$ catalytically produces cyclopropane **14** in 63(2)% yield with an isomer ratio of a/s = 8.9(6). The oxygen and water stable complex (TTP)Os(CO)(Py) also serves as a catalyst precursor. When a toluene solution of ethyl diazoacetate was added over 2 h to a vigorously stirred solution of (TTP)Os(CO)(Py) and styrene, **14** was obtained in 65(3)% yield with a/s = 9.5(2).

Alkenes such as α-methylstyrene, *trans*-β-methylstyrene, and 1-decene also are cyclopropanated with ethyl diazoacetate when (TTP)Os(CO)(Py) was employed as the catalyst. However in these cases, significantly lower yields (13 - 39%) were observed. The *syn*/*anti* ratios are also lower with 1-decene and α-methyl styrene substrates. The assignments of the *syn* and *anti* isomers for **17** were confirmed by 2D-NOESY proton NMR, Figure 7.4. Somewhat surprisingly, only one product isomer was detected for the cyclopropanation reaction of *trans*-β-methylstyrene with ethyl diazoacetate. The cyclopropane product was determined to have the ethyl ester group *trans* to the phenyl and *cis* to the methyl by 500 MHz 2D-NOESY ^1H NMR.

Mesityl diazomethane and bis(*p*-tolyl)diazomethane also were found to cyclopropanate styrene using (TTP)Os(CO)(Py) as the catalyst precursor. Mesityl diazomethane was particularly effective and quantitatively produces cyclopropanes with styrene. The *anti*/*syn* ratio for the mesitylphenylcyclopropane of 0.4 was confirmed by proton NMR and GC. The assignment of the product isomers was based on a ^1H 2D-NOESY experiment conducted on a 500 MHz instrument. Cyclopropanation using bis(p-tolyl)diazomethane required several days at ambient temperature to obtain a moderate yield of cyclopropane, 39(5)%. In this case, the reaction was performed in THF using the more active catalyst [(TTP)Os]$_2$. The choice of solvent was based on prior alkene forming reactions (Chapter 6) in which product formation was strongly solvent dependent. In that case, tetratolylethylene was rapidly formed in THF, while azine and imine products were prepared over the course of several days in benzene.

When phenylacetylene is the substrate, double cyclopropanation occurs to produce [1.1.0]bicyclobutanes. Using [(TTP)Os]$_2$ as the precatalyst, rather than (TTP)Os(CO)Py) significantly improves the yield of bicyclobutane (Table 7.1). Surprisingly, the conversion of styrene and mesityl diazomethane to bicyclobutane **21** occurs in high yield, 77(3)%.

The stoichiometric reaction of the carbene complex (TTP)Os=CHCO$_2$Et and styrene produces the cyclopropane product **14**. Qualitatively this reaction is slower than the catalytic production of **14**, requiring two hours to completely convert a few milligrams of (TTP)Os=CHCO$_2$Et to the cyclopropane. The *anti/syn* ratio of 11.5(4) is similar to that observed in the catalytic reactions suggesting that the carbene complex may be an intermediate in the catalytic cycle. In addition, a new porphyrin complex was also observed by ^{1}H NMR[175] and formulated as a π-bound styrene complex (TTP)Os(C$_6$H$_5$CH=CH$_2$)$_n$, n=1 or 2. The observed styrene signals are broadened and shifted upfield indicating that a fast exchange process is occurring between coordinated and unbound styrene. Upon decreasing the ratio of styrene to osmium porphyrin, the alkene signals broaden into the baseline. Addition of pyridine to a mixture of (TTP)Os=CHCO$_2$Et and styrene resulted in fast decomposition to unidentified products. In this case, neither diethyl maleate nor cyclopropane **14** were observed.

The stoichiometric reaction of (TTP)Os=CHMes and styrene only occurs at elevated styrene concentrations. A 1000 fold excess of styrene only produces a trace (< 1%) of the desired cyclopropane after several hours. Addition of pyridine had no observed effect. A crossover experiment using (TTP)Os=CHMes, styrene and ethyl diazoacetate produced both **14** and **15** with *anti*/*syn* ratios of 9.8 and 0.4, respectively.

Discussion

The stereoselective reaction of styrene and ethyl diazoacetate to produce predominantly *anti*-ethyl-2-phenyl-1-cyclopropanecarboxylic acid ester (**14**) is effectively catalyzed by osmium porphyrin complexes in moderate to good yields. The stereoselectivity produced by osmium porphyrin catalysts, a/s = 9.5, is considerably higher than the best value reported in the literature for the cyclopropanation of styrene with ethyl diazoacetate, a/s = 3.3.[161] This is also the opposite stereoselectivity observed for the same reaction catalyzed by rhodium porphyrins reported by Callot[164] and Kodadek.[165,166] Although $[(TTP)Os]_2$ is a more active cyclopropanation catalyst than (TTP)Os(CO)(Py), the carbonyl complex is more convenient to use due to ease of preparation and handling and only suffers from a small drop in cyclopropane yields, Table 7.1. Product stereoselectivity of the two catalysts are virtually the same. A 1:1 ratio of styrene to ethyl diazoacetate results in the best yield when using (TTP)Os(CO)(Py).

The catalytic formation of cyclopropanes from alkenes and diazo reagents in the presence of (TTP)Os(CO)(Py) is a general reaction. Using the bulky diazo reagent N_2CHMes, styrene is cyclopropanated in excellent yield. The side reaction of alkene formation in this case is nearly eliminated. Only a trace (< 1%) of 1,2-bis(mesityl)ethene is present in the product mixture. As expected based on previous work, the preferred stereoisomer is *syn*-1-(2,4,6-trimethylphenyl)-2-phenylcyclopropane (**15**), an opposite stereochemistry to that of the ethyl diazoacetate derived cyclopropane product. Doyle has demonstrated that cyclopropanation using diazo esters preferentially forms the *anti*-isomer.[158a,176] In contrast, phenyl diazomethane under similar reaction conditions favors the *syn*-cyclopropane.[158a] The stereoselectivity for mesityl diazomethane and styrene is only moderate when (TTP)Os(CO)(Py) is the catalyst, a/s = 0.4. Increasing the bulkiness of the diazo reagent with two non-hydrogen substituents lowers both the yield and the rate of the reaction. Cyclopropanating styrene with $N_2C(tolyl)_2$ requires several days to reach completion. The yield of 2-phenyl-1,1-bis-*p*-tolylcyclopropane (**20**) was only 39(5)%. The remaining $N_2C(tolyl)_2$ is converted to azine and bis(tolyl)imine. Based on these results, a wide variety of diazo reagents may be effectively utilized in cyclopropanating styrene in the presence of osmium porphyrin catalysts.

Production of cyclopropanes from other alkenes and ethyl diazoacetate was also examined. Cyclopropane yields are much lower for 1-decene (32 %) than for styrene (65 %). This difference may be due to the ability of an aromatic substituent to stabilize the partial positive charge which develops at the γ-carbon of the transition state (see scheme 7.2). Based on product yields, 1,1- and 1,2-disubstituted alkenes are also less active towards cyclopropanation than styrene. The low yield (39 %) when using α-methylstyrene may reflect unfavorable steric interactions between the substrate and the metalloporphyrin carbene intermediate. Steric interactions are apparently enhanced, when *trans*-β-methylstyrene styrene is the substrate. Steric interactions apparently allow only one avenue of approach for *trans*-β-methylstyrene since only one stereoisomer is observed by GC and ^1H NMR. The observed isomer has the ethyl ester group *trans* to the phenyl and *cis* to the methyl based on 2D-NOESY ^1H NMR.

A vast majority of cyclopropanation catalysts transform alkynes to cyclopropenes. However, only a few are able to doubly cyclopropanate alkynes to generate the bicyclobutanes.[177] Surprisingly (TTP)Os(CO)(Py) and $[(TTP)Os]_2$ catalytically produce *exo-exo*-2,4-dicarboethoxy-1-phenyl[1-1-0]bicyclobutane (**20**) as the only product from phenyl acetylene and ethyl diazoacetate. The *exo-exo* assignment was made by the singlet at 1.71 ppm in the ^1H NMR for the protons on carbons 2 and 4. The *exo-endo* isomer should exhibit a doublet for these protons.[177a] Mesityl diazomethane also produces bicyclobutanes from styrene in very good yield. Two isomers are observed by GC in a ratio of 7:1. Only the major isomer is observed by proton NMR and is assigned the *exo-exo* structure based on a single signal at 2.3 for the protons geminal to the mesityl groups. The minor isomer is assumed to be *exo-endo* based on steric arguments.

The mechanism for catalytic cyclopropanation reactions, as discussed above, is believed to involve nucleophilic attack on metal carbene complexes by alkenes. Although this proposed mechanism has gained wide acceptance, carbene complexes have never been isolated from or observed in catalytic cyclopropanation reactions. Nonetheless, the metalloporphyrin carbene complexes, $(TTP)Os{=}CHCO_2Et$, (TTP)Os=CHMes, and $(TTP)Os{=}C(tolyl)_2$ could be intermediates in the osmium catalyzed reactions. Each of these complexes has been prepared and characterized by ^1H and ^{13}C NMR. $(TTP)Os{=}C(tolyl)_2$ has also been structurally characterized.

In order to test the intermediacy of osmium porphyrin carbene complexes in the catalytic cyclopropanation reactions, $(TTP)Os{=}CHCO_2Et$ was treated with an excess of styrene. Cyclopropane **14** was formed stoichiometrically over several hours and identified by proton NMR and GC analysis. The isomer ratio of **14** produced in this reaction was a/s = 11.5(4). The similarity of the stoichiometric and catalytic a/s product ratios strongly supports a catalytic cycle in which an osmium carbene complex is initially formed and subsequently transferred to an alkene.

No reaction occurred when (TTP)Os=CHMes was treated with one equivalent of styrene and monitored by proton NMR and GC. Even with a 1000-fold excess of styrene no product was detected by GC after 20 minutes. After 2 hours only a trace (<1%) of cyclopropane was observed.

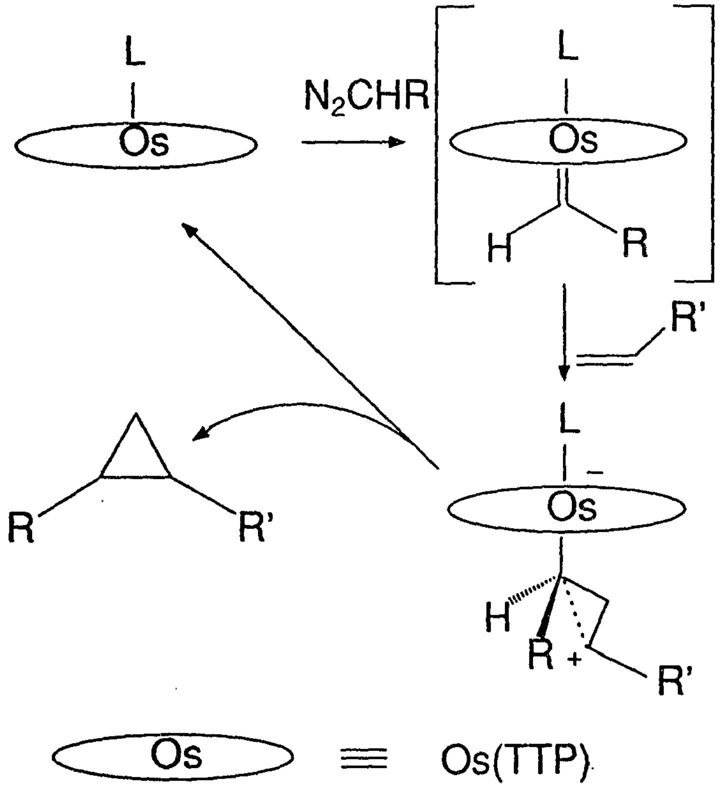
Qualitatively the rate of reaction for the stoichiometric reactions are slower than the catalytic processes. This suggests that the 16-electron osmium carbene complex is activated under catalytic conditions. For the isoelectronic rhodium porphyrin catalyzed reactions, activation by alkene coordination has been suggested by Kodadek.[166] However, in the stoichiometric osmium cyclopropanation reactions, excess alkenes qualitatively do not produce the same rate as observed in the catalytic processes. Thus, the 16-electron osmium carbene complexes are not activated by alkene coordination. Activation of the carbene complexes by addition of pyridine as a sixth ligand was also not observed. Alternatively, a bis(carbene) osmium porphyrin complex may serve as the active intermediate. This is apparently the case for the catalytic production of alkenes from diazo reagents (Chapter 6). In a crossover experiment, the addition of ethyl diazoacetate to a stirred solution of (TTP)Os=CHMes and styrene produced both cyclopropanes **14** and **15** in less than 20 minutes. This strongly supports the involvement of an activated bis(carbene) intermediate (TTP)Os(=CHCO$_2$Et)(=CHMes). Either carbene ligand may then be attacked by styrene to produce a cyclopropane. The a/s ratios of for both cyclopropanes **14** and **15** produced in the crossover reaction are comparable to those observed under catalytic conditions using

(TTP)Os(CO)(Py) as the catalyst. In the carbonyl complexes, a *trans* CO is apparently a reasonable activating ligand. A mechanism consistent with the available data has been proposed in Scheme 7.5, where L may be either a carbene ligand or a carbonyl ligand.

Conclusion

Several significant aspects have evolved from the use of osmium *meso*-tetra-*p*-tolylporphyrin complexes as catalysts for the cyclopropanation of a variety of alkenes by diazo compounds. This system provides the highest *anti/syn* isomer ratio reported to date (a/s = 10) for the catalytic cyclopropanation of styrene by ethyl diazoacetate. The activity of (TTP)Os(CO)(Py) appears to be general, catalyzing the cyclopropanation of a variety of alkenes with diazo reagents. Unlike typical cyclopropanation catalysts which produce cyclopropenes from alkyne substrates, the osmium porphyrin catalysts generate bicyclobutanes from phenyl acetylene. The first catalytically active metal carbene complex, (TTP)Os=$CHCO_2Et$, has been isolated and evidence is presented for it as an important species in the catalytic cycle. Evidence has also been presented for the intermediacy of a biscarbene osmium porphyrin in the catalytic cycle for cyclopropanation. The neutral osmium complexes reported here are isoelectronic with the cationic rhodium porphyrin complexes observed by Kodadek. The positive charge on the rhodium complexes may be an important factor which activates the carbene ligand towards nucleophilic attack by the alkene. Nonetheless, the neutral osmium complexes appear to be as active as the rhodium complexes as catalysts. Moreover, the lack of a positive charge in the osmium system appears to be an important factor which allows isolation of the osmium carbene complexes.

Scheme 7.5



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