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(Porphyrinato)osmium(II) Ylide Complexes from the Addition of Pyridine Derivatives to (Porphyrinato)osmium(II) Alkylidene Complexes: Spectroscopic Properties and Reactivity toward Cyclopropanation

Jean-Pierre Djukic, Victor G. Young, Jr., and L. Keith Woo*[,1]

Department of Chemistry, Gilman Hall, Iowa State University, Ames, Iowa 50011-3111

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Addition of 4-substituted pyridine derivatives (4-R-C_5H_4N; R = Me, *i*-Pr, NMe_2) to the tetratolylporphyrinato (TTP) osmium carbene complex (TTP)Os=CH(CO_2Et) affords stable osmium ylide complexes, *trans*-(4-R-C_5H_4N)(TTP)Os–CH(CO_2Et)(4-R-C_5H_4N). Dynamic NMR studies of the 4-picoline and 4-(dimethylamino)pyridine adducts show that the free energies for the barrier to rotation around the C_α–N axis are respectively 14 ± 1 kcal/mol at 298 ± 5 K and 13.0 ± 0.5 kcal/mol at 268 ± 2 K. The barrier to rotation around the C–NMe_2 axis of the (dimethylamino)pyridine ylide fragment is 13.0 ± 0.5 kcal/mol at 240 ± 2 K. Addition of 4-picoline (4-pic) to (TTP)Os=CH($SiMe_3$) leads to the equilibrium formation of *trans*-(4-pic)(TTP)Os=CH($SiMe_3$) and the osmium ylide complex *trans*-(4-pic)-(TTP)Os–CH($SiMe_3$)(4-pic). ^1H NMR spin saturation transfer experiments confirm the existence of this equilibrium. Disubstituted carbene complexes (TTP)Os=CR_2 do not yield osmium ylide complexes upon treatment with 4-picoline. Prolonged treatment of (TTP)-Os=C(CO_2Et)$_2$ with 4-picoline affords mainly (TTP)Os(4-pic)$_2$. The bis(picoline) complex (TTP)Os(4-pic)$_2$ crystallizes in the monoclinic space group $P2_1/n$ with 1.74 molecules of benzene ($C_{60}H_{50}N_6Os{\cdot}1.74C_6H_6$, $a = 10.800(2)$ Å, $b = 21.332(2)$ Å, $c = 12.868(1)$ Å, $\beta = 108.89(1)°$, $V = 2805$ Å^3, $Z = 2$, $R = 3.08\%$, $R_w = 3.80\%$). Key metrical parameters include an Os–N_{pic} distance of 2.078(3) Å and a torsional angle between the plane of the axial ligand and the closest Os–$N_{pyrrole}$ bond of 40.1(3)°. Treatment of the osmium ylide complexes with styrene yields cyclopropane derivatives with high stereoselectivities and conversions ranging from 65 to 95%. The trans/cis ratios for these reactions range from 23 to 28.

Introduction

The alkylidene complexes L_nM=CRR′ have a wide range of applications in organometallic synthesis. This class of compounds is particularly useful in many carbene transfer and cyclization reactions. Among the most studied applications are alkenylations of carbene complexes,[2] annulation of arenes by cocyclization with an exogenous alkyne,[3] insertions into metal–hydrogen bonds,[4] and the [2 + 1] cycloaddition of metal carbenes to alkenes or cyclopropanation reactions.[5] Furthermore, metal carbene complexes are believed to be involved in several chemical and biochemical transformations as transient species. Important examples include Ziegler–Natta polymerization,[6] olefin metathesis,[7] suicide inhibition of cytochrome P-450 by halogenoalkanes,[8] and catalytic cyclopropanation of alkenes by diazoalkanes.[9] Thus, many isolable carbene complexes have been used in modeling transition-metal-catalyzed processes.[5,10] We have recently reported that (porphyrinato)osmium(II) alkylidene complexes can react stoichiometrically with either diazoalkanes or olefins to yield respectively alkenes or cyclopropane derivatives.[11] Moreover, we have shown that these carbene complexes are able to

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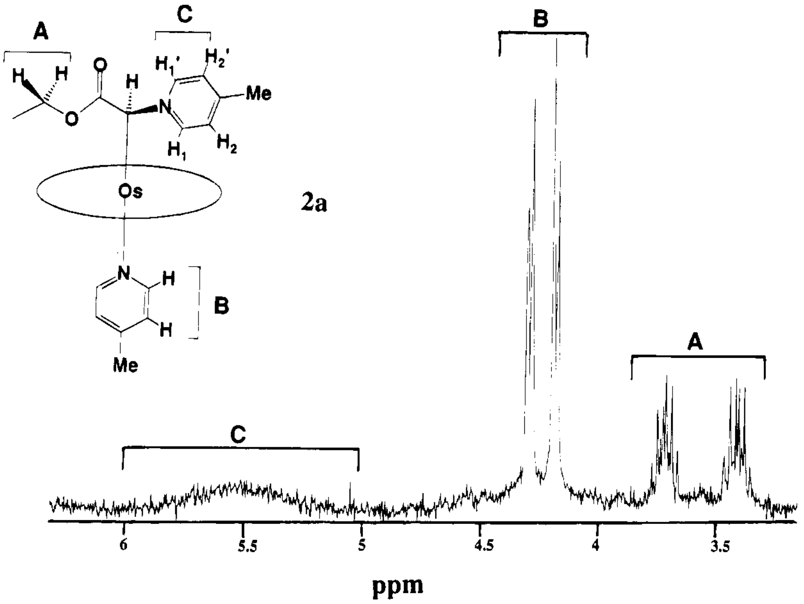
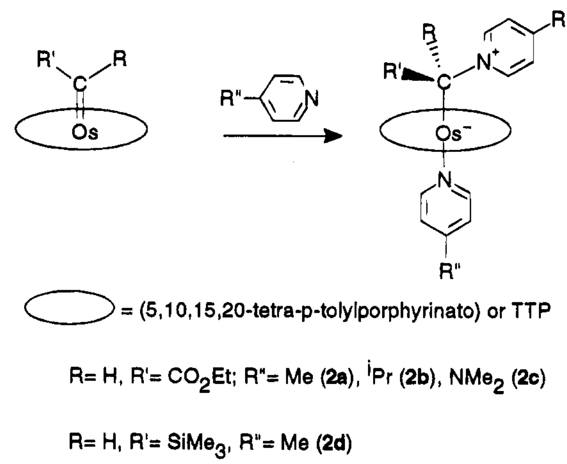


Figure 1. Expanded region of the ^{1}H NMR spectrum of the osmium ylide complex **2a** acquired at room temperature.

catalyze cyclopropanation reactions in the presence of a diazoalkane and an olefin.[12] The high efficiency and stereoselectivity obtained in both catalytic and stoichiometric reactions have led us to undertake a thorough mechanistic study.[13] Herein, we report the preparation and spectroscopic characterization of the first examples of (porphyrinato)osmium(II) ylide complexes obtained from the reaction of (porphyrinato)osmium(II) alkylidene complexes with pyridine derivatives. Formation of metal ylide complexes was first reported by Fischer and co-workers.[14] When pentacarbonylmetal carbene complexes are treated with phosphines[15] or hindered tertiary amines[16] (XR_3, X = P, N), a 1/1 zwitterionic adduct can be formed. Although the formation of most metal ylide complexes results from the irreversible addition of XR_3, cases of reversible processes have been reported.[17] Metal ylide formation has also been used to trap unstable transition-metal carbene intermediates involved in cyclopropanation reactions.[18]

Results and Discussion

Reaction of 4-Substituted Pyridine Derivatives with (TTP)Os=CHCO$_2$Et[19] (1a). Addition of an excess of 4-picoline to a freshly prepared sample of the tetratolylporphyrinato osmium carbene complex (TTP)Os=CHCO$_2$Et[11] (**1a**) in toluene produces a new zwitterionic complex, *trans*-(4-pic)(TTP)Os—CH(CO$_2$Et)(4-pic) (**2a**) (eq 1). Two picoline ligands have coordinated to the complex, one at the axial metal site and one at the carbene carbon, forming a tetrahedral carbon center. We first noticed that 4-picoline could affect the ^{1}H NMR properties of (porphyrinato)osmium(II) monosubstituted carbene complexes while studying their behavior with respect to strong σ ligands. Whereas triphenylphosphine, a strong base such as DABCO, and THF do not alter significantly the chemical structure or the spectroscopic properties of the carbene complex **1a**, addition of 4-picoline dramatically induces structural changes. The first indication of such change is manifested by a 24.7 ppm upfield shift of the α-proton resonance. In the osmium(II) ylide complex **2a** the H_α resonance appears at −3.09 ppm, whereas it originally appeared at +21.60 ppm in the precursor **1a**. The second major difference arises in the CH_2 ester resonance (a quartet at 2.67 ppm in the starting material), which appears as two well-resolved doublets of quartets at 3.70 and 3.40 ppm in the osmium ylide complex **2a** (Figure 1). Similar spectroscopic trends have been observed by Callot and Shaeffer[20] and lately by Kodadek and co-workers[21] for



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(19) List of abbreviations used: TTP, 5,10,15,20-tetra-*p*-tolylporphyrinato; TPP, 5,10,15,20-tetraphenylporphyrinato; TMP, 5,10,15,20-tetramesitylporphyrinato; 4-pic, 4-picoline or 4-methylpyridine; 4-*i*-Pr-py, 4-isopropylpyridine; 4-NMe$_2$-py, 4-(dimethylamino)pyridine; THF, tetrahydrofuran; py, pyridine; DABCO, 1,4-diazabicyclo[2.2.2]octane.

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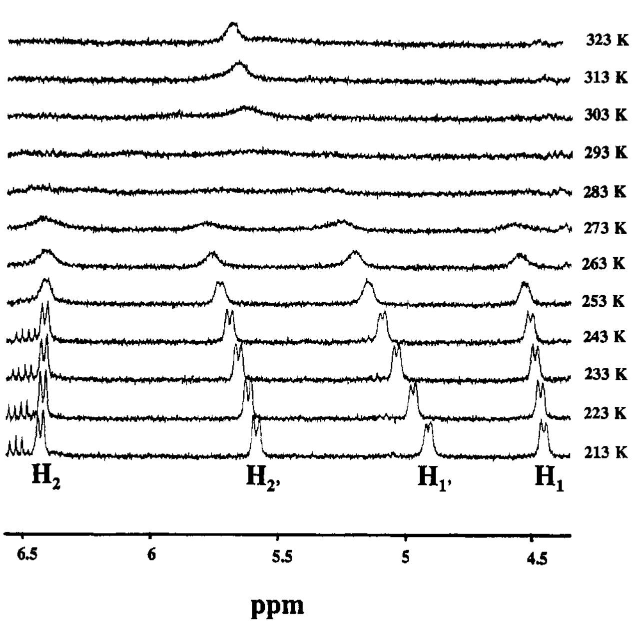

Figure 2. Temperature dependence of the ^{1}H NMR spectrum for the osmium ylide complex *trans*-(4-pic)(TTP)Os$-$CH(CO$_2$Et)(4-pic) (**2a**), pyridinium protons H$_1$, H$_2$, H$_{1'}$, H$_{2'}$. Coalescence of each related pair of signals occurs between 293 and 303 K. The free energy barrier to rotation is estimated to be 14 ± 1 kcal/mol.

several examples of alkylrhodium(III) complexes, (TTP)Rh$-$C(H)(CO$_2$Et)(X), where X is a methoxy group, a diazo group, or an iodide. The last two examples of alkylrhodium porphyrin (X = N$_2$, I$^-$) complexes have been observed at low temperatures and have been proposed as active species in cyclopropanation reactions catalyzed by rhodium(III) porphyrin halides.[22] In both cases the methylene fragment of the ester group possesses diastereotopic protons that resonate at significantly different chemical shifts. This confirms the tetrahedral geometry of the α carbon bound to the metal. Similar to our results, the α-proton resonance in the alkyl$-$Rh complexes appears at high field.

The ^{1}H NMR spectrum of **2a** clearly exhibited two new methyl signals at 1.40 (s, 3H) and 0.28 (s, 3H) ppm corresponding to the two chemically distinct picoline fragments. However, only one set of new aromatic 4-picoline proton resonances was distinguishable at ambient temperature, at 4.29 (d, 2H) and 4.18 (d, 2H) ppm; these are assigned to the *ortho* and *meta* protons of the Os-bound *trans*-4-picoline (Figure 1). A ^{1}H 2D-NOESY experiment revealed a correlation between the H$_\alpha$ ylide proton and a weak, broad signal at 5.5 ppm. Cooling the NMR sample to 213 K resulted in the decoalescence of the broad 5.5 ppm signal into four doublets at 6.43, 5.58, 4.90, and 4.46 ppm, each integrated as one proton (Figure 2). Homonuclear ^{1}H COSY and low-temperature 2D-NOESY confirm the assignment of these four signals to the ylide-bound picoline. Thus, it is clear that the ylide-bound picoline rotates rapidly about the C$_\alpha-$N axis at ambient temperature. An estimate of the free energy barrier for this rotation is 14 ± 1 kcal/mol at 298 ± 5 K (Figure 2).[23]

The ylide complex **2a** undergoes a slow decomposition to (TTP)Os(4-pic)$_2$ (**3a**) and diethyl maleate and fumarate when left in solution in toluene over 4 days. Collman et al. reported recently that addition of triphenylphosphine to the analogous ruthenium carbene complex (TTP)Ru=CHCO$_2$Et resulted in decomposition of the starting complex to give mainly diethyl maleate and fumarate and (TTP)Ru(PPh$_3$)$_2$.[24] Similar reactivity was reported several years ago by Mansuy and coworkers for (porphyrinato)iron(II) carbene complexes treated with strong σ-donor ligands.[25]

Other pyridine derivatives also react with **1a** to give osmium ylide complexes. Addition of 4-isopropylpyridine to **1a** affords the osmium ylide complex *trans*-(4-*i*-Pr-py)(TTP)Os$-$CH(CO$_2$Et)(4-*i*-Pr-py) (**2b**) which precipitates from a toluene solution when hexane is added to the reaction medium. The osmium ylide complex **2b** is slightly soluble in toluene and can be purified readily by recrystallization from a toluene$-$hexane mixture. Complex **2b** displays similar ^{1}H NMR trends compared to those observed for **2a**. The ylide$-$pyridinium *ortho* and *meta* proton resonances are not resolved at ambient temperature but can be seen clearly at 233 K. The isopropyl group of the ylide fragment possesses two diastereotopic methyl groups. At room temperature, the *i*-Pr methyl protons appear as two sharp doublets at 0.59 and 0.61 ppm (Figure 3).

Complex **2c**, *trans*-(4-NMe$_2$-py)(TTP)Os$-$CH(CO$_2$Et)(4-NMe$_2$-py), can be prepared readily by treating **1a** with 4-(dimethylamino)pyridine under conditions similar to those used for the preparation of **2b**. The corresponding zwitterionic complex is stable for several weeks as a solid under a strictly inert and anhydrous atmosphere. Similar temperature-dependent ^{1}H NMR properties arising from restricted rotation of the ylide-bound pyridyl group are evident for this complex. At 213 K, the dimethylamino group exhibits two distinct resonances at 1.78 and 1.62 ppm (Figure 4). As the temperature increases, the two signals undergo a slight downfield shift and begin to coalesce at 238 K. Similarly, four well-resolved signals accounting for the aromatic protons of the ylide-bound (dimethylamino)pyridinium group can be observed at 6.24 (d, 1H), 5.05 (d, 1H), 4.70 (d, 1H), and 4.49 (d, 1H) ppm. Coalescence of related pairs of proton signals is estimated to take place around 273 K, a value lower than that observed for **2a**. Corresponding barriers to rotation are approximately 13.0 ± 0.5 kcal/mol for $\Delta G^{\ddagger}_{C4-N}$ at 240 ± 2 K and 13 ± 1 kcal/mol for $\Delta G^{\ddagger}_{C\alpha-N}$ at 268 ± 5 K.

Two limiting Lewis structures of the zwitterionic osmium ylide complex **2c** can be drawn to rationalize the ^{1}H NMR temperature dependence reported above (Scheme 1). The positive charge can be localized either on the tertiary amine nitrogen (structure **B**) or on the nitrogen atom bound to C$_\alpha$ (structure **A**). This naturally suggests a delocalization of the positive charge over the pyridinium fragment. At low temperature, the diaste-

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(23) Barrier to rotation free energy (kcal/mol) is calculated from $\Delta G^{\ddagger} = aT[9.972 + \ln(T/\delta\nu)]$ ($a = 4.575 \times 10^{-3}$).[27a]

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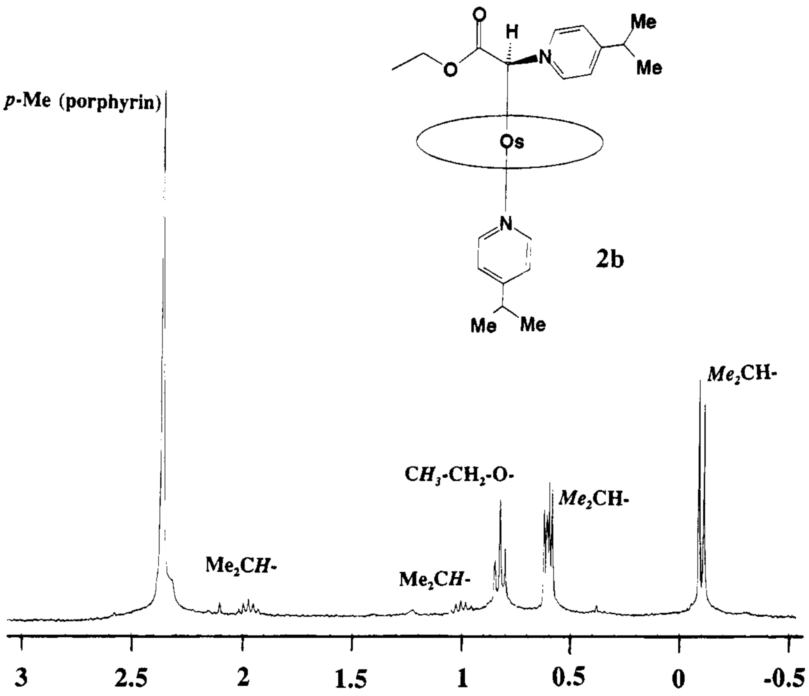


Figure 3. Expanded region of the ^{1}H NMR spectrum of the osmium ylide complex **2b** acquired at room temperature.

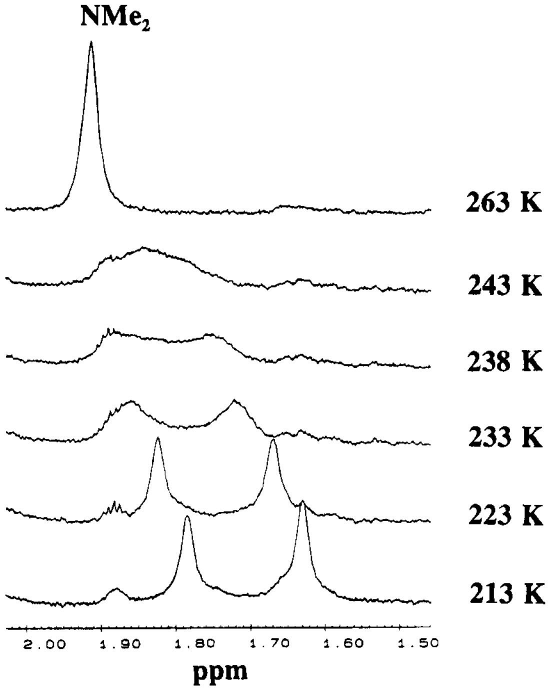
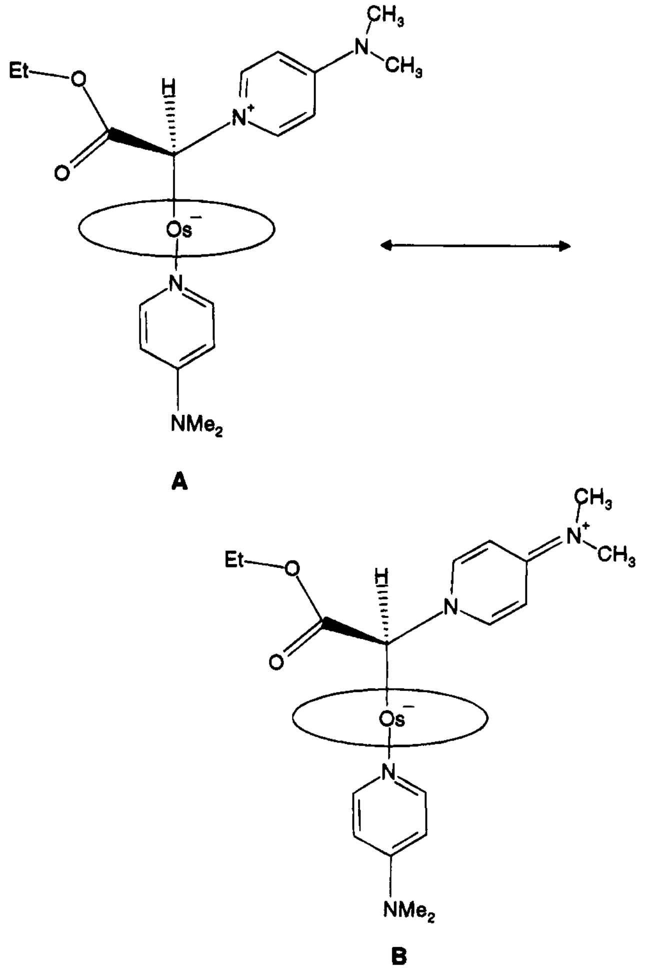


Figure 4. Temperature dependence of the dimethylamino group ^{1}H resonances of the osmium ylide complex *trans*-(4-NMe$_2$-py)(TTP)Os—CH(CO$_2$Et)(4-NMe$_2$-py) (**2c**).

Scheme 1



reotopic nature of the dimethylamino methyl groups can reasonably be interpreted by a predominant contribution of the dimethylimmonium structure **B**. Indeed, no strong steric interactions are expected to restrict the orientation of the dimethylamino group.

Reaction of 4-Methylpyridine with (TTP)Os=CH(SiMe$_3$)[26] (1b). Unlike the ester carbene complex **1a**, which forms only bis(ligand) adducts with substituted pyridines, the trimethylsilyl derivative **1b** forms a mixture of two complexes, **2d** and **4a**, on treatment with 4-picoline (Scheme 2).

The 18-electron *trans*-4-picoline adduct **4a**, *trans*-(4-pic)(TTP)Os=CH(SiMe$_3$), can be isolated as an oily

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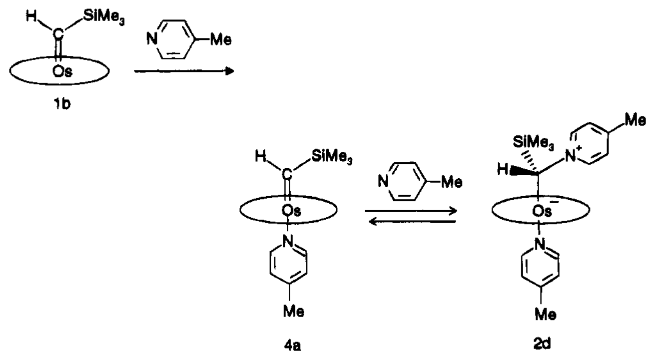
[26] Djukic, J. P.; Smith, D. A.; Young, V. G.; Woo, L. K. *Organometallics*, in press.

Scheme 2



residue when the solvent and excess picoline are removed from the reaction mixture under reduced pressure. The α-proton signal of **4a** is only shifted 0.73 ppm downfield from its original position in the 16-electron carbene complex **1b**. The trimethylsilyl methyl group resonance is also shifted downfield 0.18 ppm from its original position in pure **1b**. When an excess of picoline is present, an osmium ylide complex, *trans*-(4-pic)(TTP)-Os—CH($SiMe_3$)(4-pic) (**2d**), is the major component (**2d**/**4a** = 1.3/1). The spectrum of this adduct differs remarkably from those of **1b** and **4a** in the porphyrin ligand region between 7 and 9 ppm. A ^1H COSY experiment carried out on this portion of the spectrum of the mixture indicates that five peaks at 8.04 (d, 4H), 7.96 (d, 4H), 7.92 (s, 8H, β-pyrrolic), 7.38 (d, 4H), and 7.17 (d, 4H) ppm account for the tetra-*p*-tolyl-substituted porphyrin ring of the bis(picoline) adduct. In addition, two new resonances at −4.82 (1H) and −0.98 (9H) ppm are assigned respectively as those of the ylide α-proton and the methyl protons of $SiMe_3$. This strongly indicates that the geometry of the initial carbene carbon has changed from trigonal to tetragonal upon addition of 4-methylpyridine.

An enormous difference exists in the chemical shifts of the α-proton resonances of (porphyrinato)metal carbene and (porphyrinato)metal alkyl complexes. The carbene α-proton in these complexes typically appears at lower fields in the range 7−30 ppm.[24b] The alkyl signals resonate at higher fields, often significantly upfield of TMS. Although this has not been fully investigated, a correlation seems to exist between the configuration of the α-carbon bound to the metal and the ^1H nuclear magnetic resonance of the α-proton. For **2d**, binding of the picoline nitrogen atom to the carbene carbon produced a major geometrical distortion and a 33 ppm shielding of the carbene α-proton resonance.

4-Picoline reversibly binds to the α-carbon of **4a** and results in an equilibrium between **4a** and **2d** in the presence of 4-picoline. The facile dissociation of 4-picoline from the α-carbon of **2d** was established by a spin saturation transfer experiment. Using the method of Forsen and Hoffman,[27] we determined the dynamic parameters of this process. The α-proton resonances of the osmium ylide and of the carbene complex **4a** serve as convenient spectroscopic probes because of their 33 ppm separation. A first set of measurements was done by saturating the H_α resonance of compound **4a** at 29.70 ppm and by monitoring the intensity decay of the related compound **2d** α-proton resonance at −4.82 ppm (Figure 5a). Complementary measurements were performed by irradiating the α-proton signal of **2d** at −4.82 ppm and by monitoring the intensity decay of the signal at +29.70 ppm (Figure 5b). The time length of the irradiation ranged from 0 to 10 s. The detailed procedure for this study is described in the Experimental Section. The chemical exchange involves three components, the mono(carbene) complex **4a**, 4-picoline, and the osmium ylide complex **2d**. Values obtained from the ^1H NMR data at 296 K for the lifetimes of the two species in equilibrium are $\tau_{2d} = 0.45(2)$ s and $\tau_{4a} = 0.36(2)$ s when a 10-fold excess of 4-picoline, with respect to **1b**, is used. According to variable-temperature ^1H NMR experiments done under the same concentration conditions, increasing the temperature of the reaction induces a decrease of **2d** in favor of **4a**, indicating the exothermic nature of ylide C—N bond formation.

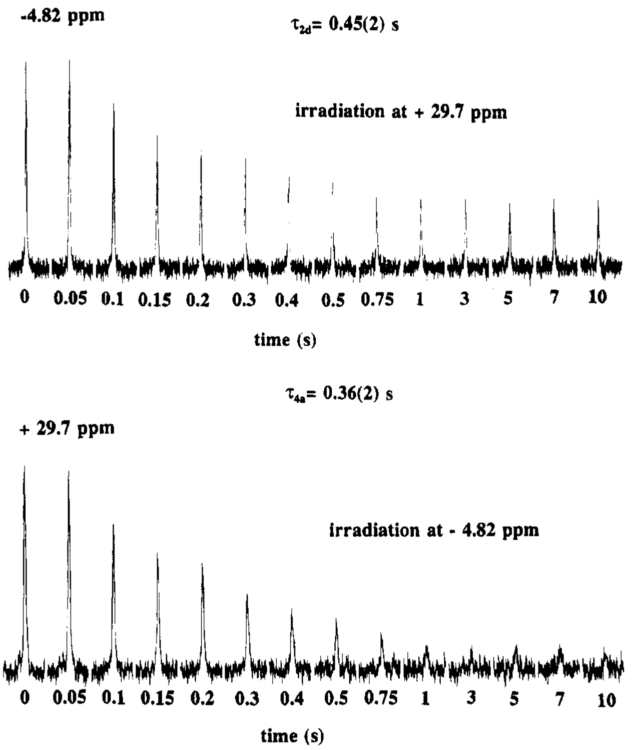


Figure 5. Study of the reversible addition of 4-pic to the 18-electron carbene complex **4a** (^1H spin saturation NMR experiment): (a, top) stacked plot of the α-proton resonance intensity decay of the osmium ylide complex *trans*-(4-pic)-(TTP)Os-CH($SiMe_3$)(4-pic) (**2d**), upon irradiation of the related α-proton resonance of **4a**; (b, bottom) stacked plot of the α-proton resonance intensity decay of the osmium−carbene complex *trans*-(4-pic)(TTP)Os=CH($SiMe_3$) (**4a**), upon irradiation of the related α-proton resonance of **2d**.

Disubstituted carbene complexes (TTP)Os=CR_2 (**1c**, R = CO_2Et; **1d**, R = *p*-tolyl) do not afford osmium ylide complexes when treated with 4-picoline. The addition of pyridine derivatives only occurs at the vacant axial metal site. The free 4-picoline ^1H resonances are broadened but not significantly shifted. Similarly, the carbene complex resonances are not significantly shifted by the presence of an excess of 4-picoline. Prolonged treatment of (TTP)Os=C(CO_2Et)$_2$ (**1c**) with 4-picoline produces (TTP)Os(4-pic)$_2$ (**3a**) (Scheme 3). A single crystal of complex **3a** has been analyzed by X-ray diffraction. Complex **3a** crystallizes with two molecules

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Scheme 3

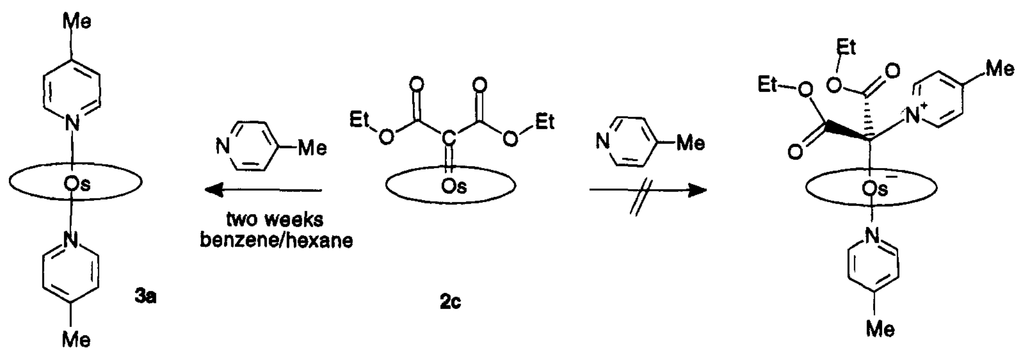

Table 1. Structure Determination Summary

empirical formula	$C_{60}H_{50}N_6Os{\cdot}1.74C_6H_6$
color; habit	brown, monoclinic
cryst size (mm)	0.50 × 0.25 × 0.22
cryst syst	monoclinic
space group	$P2_1/n$
cell dimens	
a (Å)	10.800(2)
b (Å)	21.332(2)
c (Å)	12.868(1)
β (deg)	108.89(1)
V (Å^3)	2804.9(6)
Z	2
fw	1181.2
density (calcd) (Mg/m^3)	1.399
abs coeff (mm^{-1})	4.667
F(000)	1202.19
diffractometer used	Siemens P4RA
radiation (λ, Å)	Cu Kα (1.541 78)
temp (K)	213
monochromator	highly oriented graphite crystal
2θ range (deg)	4.0–115.0
scan type	$2\theta-\theta$
no. of rflns collected	7974
no. of indep rflns	3746 (R_{int} = 1.80%)
no. of obsd rflns	3184 ($F \geq 4.0\sigma(F)$)
no. of params refined	380
final R indices (obsd data)	R^a = 2.65%, $R_w{}^b$ = 3.67%
R indices (all data)	R^a = 3.08%, $R_w{}^b$ = 3.80%
goodness of Fit^c	1.58
data-to-param ratio	8.4/1
largest diff peak (e/Å^3)	0.45
largest diff hole (e/Å^3)	−0.67

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] $GOF = [\sum w(|F_o| - |F_c|)^2/(N_{observn} - N_{param})]^{1/2}$.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

atom	x	y	z	$U_{eq}{}^a$
Os	0	0	0	26(1)
N(1)	1888(3)	−69(1)	999(3)	28(1)
N(2)	−297(3)	716(1)	936(2)	30(1)
C(1)	2831(3)	−477(2)	875(3)	29(1)
C(2)	4039(4)	−370(2)	1740(3)	36(2)
C(3)	3832(4)	88(2)	2381(3)	37(2)
C(4)	2498(4)	281(2)	1924(3)	30(1)
C(5)	1902(4)	763(2)	2335(3)	30(1)
C(51)	2721(4)	1080(2)	3379(3)	34(1)
C(52)	3177(5)	1690(2)	3403(3)	52(2)
C(53)	3941(5)	1960(2)	4381(4)	59(2)
C(54)	4267(4)	1644(2)	5349(3)	49(2)
C(55)	3773(6)	1050(2)	5330(4)	65(2)
C(56)	3001(5)	774(2)	4362(3)	58(2)
C(57)	5160(5)	1930(2)	6410(4)	75(2)
C(6)	609(4)	965(2)	1859(3)	36(1)
C(7)	−9(4)	1465(2)	2281(4)	49(2)
C(8)	−1257(4)	1508(2)	1631(3)	49(2)
C(9)	−1459(4)	1039(2)	783(3)	35(1)
C(10)	−2631(4)	924(2)	−44(3)	31(1)
C(101)	−3796(4)	1299(2)	−9(3)	33(1)
C(102)	−4054(4)	1894(2)	−457(3)	41(2)
C(103)	−5105(4)	2237(2)	−377(4)	46(2)
C(104)	−5939(4)	1999(2)	148(3)	43(2)
C(105)	5695(4)	1406(2)	579(3)	46(2)
C(106)	−4648(4)	1053(2)	494(4)	43(2)
C(107)	−7077(5)	2382(2)	267(4)	66(2)
N(20)	556(3)	644(1)	−977(2)	33(1)
C(21)	1582(4)	546(2)	−1340(3)	42(2)
C(22)	1997(4)	974(2)	−1955(3)	54(2)
C(23)	1361(5)	1530(2)	−2250(4)	53(2)
C(24)	305(5)	1638(2)	−1898(4)	59(2)
C(25)	−55(5)	1193(2)	−1269(3)	47(2)
C(26)	1822(6)	2014(3)	−2915(5)	88(3)
C(31)	3202(6)	9040(3)	5609(7)	99(4)
C(32)	2502(8)	9101(4)	6276(5)	106(4)
C(33)	1230(8)	9239(4)	5869(6)	123(5)
C(34)	673(6)	9312(4)	4798(7)	112(4)
C(35)	1378(8)	9251(3)	4126(5)	103(4)
C(36)	2646(8)	9119(3)	4532(7)	99(5)

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

per unit cell. Crystal data and intensity collection parameters are given in Table 1, and fractional coordinates for the non-hydrogen atoms are listed in Table 2 Figure 6 illustrates the molecular structure and the atom-labeling scheme. Selected bond distances and angles are provided in Table 3. As expected for a six-coordinate complex, the porphyrin ligand in this complex is nearly planar. The largest deviation occurs at C(4), which is 0.027 Å out of the mean porphyrin plane. The value of the torsion angle ϕ defined by the plane of the axial ligand and the closest Os—N$_{pyrrole}$ bond, N(2)—Os—N(20)—C(25), is 40.1(3)°. The coordination sphere of the osmium atom approaches an ideal octahedral geometry with bond angles between *cis*-related ligands ranging from 89.6 to 90.4°. For reasons of symmetry, the 4-picoline ligands are coplanar. Significant divergences from coplanarity of two trans pyridine ligands are observed for complexes with sterically hindered porphyrins such as [Fe(TMP)(4-NMe$_2$-py)$_2$]ClO$_4$.[19,28] The Os—N(20) distance of 2.078(3) Å in **3a** is shorter than the distances reported in the literature for a carbonylosmium porphodimethene complex, [Os(OEPMe$_2$)CO·py] (d_{Os-Npy} = 2.223 Å),[29] and for [Os(NH$_3$)Cl$_3$(P(C$_6$H$_5$)$_3$)$_2$] (d_{Os-N} = 2.136(9) Å).[30] However, the observed Os—N$_{4\text{-pic}}$ distance in (TTP)Os(4-pic)$_2$ (**3a**) is in the range of those determined for complexes such as (TPP)Fe(py)$_2$ ($d_{Fe-N_{py}}$ = 2.039(1) Å),[31] (TPP)Fe(py)(CO)[32] ($d_{Fe-N_{py}}$ = 2.10(1) Å), and (TPP)Ru(py)$_2$ ($d_{Ru-N_{py}}$

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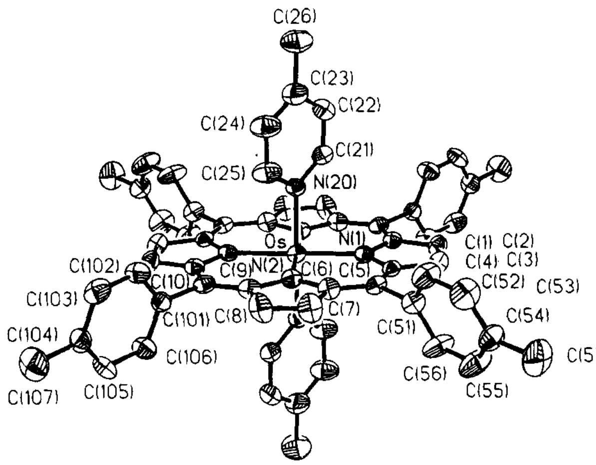
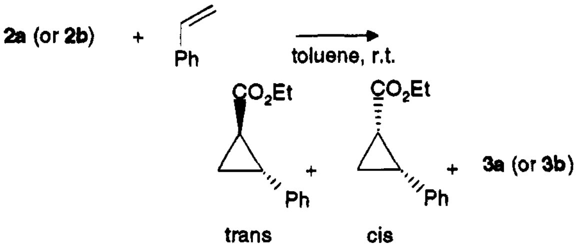


Figure 6. Thermal ellipsoid diagram of the molecular structure of (TTP)Os(4-pic)$_2$.

= 2.10 Å).[33] The ^{1}H NMR spectrum of this bis(4-picoline)osmium complex displays two doublets at 4.23 (4H) and 4.03 (4H) ppm and a sharp singlet at 0.28 (3H) ppm that account for the aromatic protons and for the methyl group of the picoline ligand. The methyl resonance of the coordinated 4-picoline is shifted 1.46 ppm upfield relative to that of free picoline.

Reactivity of Osmium Ylide Complexes 2a,b versus Styrene. Reaction of osmium ylide complexes **2a,b** with an excess of styrene affords cyclopropane derivatives with yields ranging from 65 to 95% after 1−2 days (eq 2). The stereoselectivity of the reaction is surprisingly high. In both cases the trans isomer is the major product, with a trans/cis ratio ranging from 23 to 28, according to GC/MS analyses.



(2)

2a: 61 %, cis/trans = 1/23

2b: 95 %, cis/trans = 1/28

We previously reported very high stereoselectivities for stoichiometric and catalytic cyclopropanation reactions mediated by (porphyrinato)osmium(II) carbene complexes. A trans/cis ratio of 11 was found for the production of the same cyclopropane derivatives.[12] The high trans/cis ratio observed in the cyclopropanation with the ylide complexes suggests that the stereoselective step involves displacement of the C$_\alpha$-pyridine moiety.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for (TTP)Os(4-pic)$_2$

Os−N(1)	2.034(3)	C(4)−C(5)	1.404(5)
Os−N(2)	2.034(3)	C(5)−C(51)	1.508(5)
Os−N(20)	2.078(3)	C(5)−C(6)	1.399(5)
N(1)−C(1)	1.387(5)	N(20)−C(21)	1.351(6)
N(1)−C(4)	1.379(4)	N(20)−C(25)	1.337(5)
N(2)−C(6)	1.377(4)	C(21)−C(22)	1.376(7)
N(2)−C(9)	1.389(5)	C(22)−C(23)	1.362(6)
C(1)−C(2)	1.432(5)	C(23)−C(24)	1.375(8)
C(2)−C(3)	1.344(6)	C(23)−C(26)	1.524(8)
C(3)−C(4)	1.430(6)		
N(1)−Os−N(2)	89.9(1)	N(1)−C(4)−C(5)	125.0(3)
N(1)−Os−N(20)	90.2(1)	C(3)−C(4)−C(5)	125.4(3)
N(2)−Os−N(20)	89.6(1)	C(4)−C(5)−C(51)	117.1(3)
Os−N(1)−C(1)	126.6(2)	C(4)−C(5)−C(6)	125.1(3)
Os−N(1)−C(4)	127.4(3)	C(51)−C(5)−C(6)	117.8(3)
C(1)−N(1)−C(4)	106.0(3)	C(5)−C(51)−C(52)	122.8(3)
Os−N(2)−C(6)	126.6(3)	C(5)−C(51)−C(56)	120.0(3)
Os−N(2)−C(9)	126.7(2)	Os−N(20)−C(21)	122.4(2)
C(6)−N(2)−C(9)	106.7(3)	Os−N(20)−C(25)	122.4(3)
N(1)−C(1)−C(2)	109.2(3)	C(21)−N(20)−C(25)	115.1(4)
N(1)−C(1)−C(10A)	125.4(3)	N(20)−C(21)−C(22)	123.5(4)
C(2)−C(1)−C(10A)	125.4(3)	C(21)−C(22)−C(23)	120.7(5)
C(1)−C(2)−C(3)	107.6(3)	C(22)−C(23)−C(26)	121.3(5)
C(2)−C(3)−C(4)	107.6(3)	C(23)−C(24)−C(25)	119.9(4)
N(1)−C(4)−C(3)	109.6(3)	N(20)−C(25)−C(24)	124.0(5)

Concluding Remarks

Monosubstituted (porphyrinato)osmium carbene complexes undergo nucleophilic addition of pyridine derivatives to yield the first examples of (porphyrinato)metal ylide complexes. Unlike the iron and the ruthenium carbene analogs, the addition of a strong base such as 4-(dimethylamino)pyridine does not displace the carbene fragment. The corresponding osmium ylide complexes are stable indefinitely in the solid state and can be readily characterized by spectroscopic methods. Steric interactions between the porphyrin and the ylide ligand hinder the free rotation of the pyridinium fragment. The reversible binding of 4-picoline to the carbene carbon of *trans*-(4-pic)(TTP)Os=CH(SiMe$_3$) can be rationalized by a low electrophilic character of the carbene α-carbon. Indeed, we reported previously that (TTP)Os=CH(SiMe$_3$) (**1b**) does not react with N$_2$CHSiMe$_3$ or styrene.[11] A subsequent study showed that **1b** displays structural similarities with group 5−7 electron-deficient alkylidene complexes.[26] The difference in reactivity that we previously observed for **1a** with respect to **1b** when they are treated with diazoalkanes and alkenes is still valid in reactions with these ylide derivatives. In addition, osmium disubstituted-carbene complexes such as **1c,d** seem to react poorly with pyridine ligands. No osmium ylide intermediate formation was observed by ^{1}H NMR when (TTP)Os=C(CO$_2$Et)$_2$ was treated with 4-picoline, although this complex is expected to be more electrophilic than the mono(ester) analog (TTP)Os=CHCO$_2$Et. However, the subsequent formation of a bis(4-picoline)osmium complex after several days suggests that an osmium ylide complex is likely to be a reaction intermediate. In support of this assumption is the fact that decomposition of the ylide complexes **2a−c** produces the corresponding bis(4-R-pyridine)osmium complexes (R = Me, **3a**; R = *i*-Pr, **3b**; R = NMe$_2$, **3c**) along with a mixture of diethyl maleate and fumarate. The highly selective trans/cis cyclopropanation reaction (trans/cis = 23−28) of osmium ylide complexes with styrene may provide additional information about the product-forming step. For example, a dissociative S$_N$1-like process in which the starting osmium ylide complex eliminates the C$_\alpha$-pyridine adduct to give a carbene complex is possible. However, this mechanism may produce a stereoselectivity (trans/cis = 11) similar to that obtained for the stoichiometric reaction of (TTP)Os=CH(CO$_2$Et) with styrene. Alternatively, direct at-

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[32] Peng, S. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 8032.
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tack of styrene on the ylide complex, prior to or concomitant with pyridine loss, cannot be ruled out. In this latter pathway, the steric congestion about the α-carbon is consistent with the slower rate and higher cyclopropanation stereoselectivity. Thus, this new class of ylide compounds will be useful in our continued efforts to understand the mechanistic issues of (porphyrinato)osmium-mediated cyclopropanation reactions. Indeed, several intermediates, such as metal carbene species, M=CRR′, or metal diazoalkyl species, $\mathrm{M{-}CRR'N_2^+}$, have been proposed as the active species in these reactions. The osmium ylide complexes described above are potential models of metal diazoalkyl species.

Experimental Section

All manipulations of reagents and products were carried out under a dry nitrogen atmosphere using a Vacuum Atmospheres glovebox equipped with a Model MO40H DriTrain gas purification system or on a vacuum line using Schlenk techniques. All solvents were dried and distilled from purple solutions of sodium benzophenone ketyl anion. ^{1}H NMR and ^{13}C NMR spectra (reported in parts per million downfield of $\mathrm{SiMe_4}$) were recorded on Nicolet NT300 and Varian VXR300 spectrometers. ^{1}H NMR spectra were referenced against residual proton resonances of deuterated solvents (δ (ppm): $\mathrm{CDCl_3}$, 7.24; $\mathrm{C_6D_6}$, 7.15; $\mathrm{C_7D_8}$, 2.09, 6.99). Ethyl diazoacetate was purchased from Aldrich Chemical Co. Diethyl 3-diazomalonate was obtained from the reaction of diethyl malonate with $\mathrm{CH_3SO_2N_3}$[34] at room temperature in dry dichloromethane. 4-Methylpyridine and 4-isopropylpyridine were distilled twice over sodium and degassed three times by a freeze–pump–thaw method. 4-(Dimethylamino)pyridine was dried under vacuum at 80 °C for 24 h and used without further purification. Bis[(5,10,15,20-tetra-*p*-tolylporphyrinato)osmium(II)], $\mathrm{Os_2(TTP)_2}$, was prepared from (TTP)Os(CO)(py) and $\mathrm{(TTP)Os(py)_2}$ according to a published procedure.[35] The carbene complexes $\mathrm{(TTP)Os{=}CHCO_2Et}$ (**1a**) and $\mathrm{(TTP)Os{=}CHSiMe_3}$ (**1b**) were prepared as reported earlier.[11] Fast atom bombardment mass spectra (FAB MS) were measured on a Kratos MS50 operating at a 2500 resolution power with an acceleration voltage of 8 kV and using 3-nitrobenzyl alcohol as matrix. UV–visible spectra (reported in nm) were measured using a Hewlett-Packard HP8452A diode array spectrometer. IR spectra (reported in wavenumbers (cm^{-1})) were recorded using a FTS-7 Bio-Rad Fourier transformation spectrometer. Elemental analyses were obtained from Atlantic Microlab, Norcross, GA. Gas chromatography (GC) analyses were performed with Hewlett-Packard 5890 Series II[36] and Finnigan Magnum GC-MS[37] equipment. Dodecane was used as an internal standard. Data collection and structure determination were done at the Iowa State University Molecular Structure Laboratory. Refinement calculations were performed on Digital Equipment MicroVAX 3100 and DecStation 5000 computers using the SHELXTL-Plus programs.[38]

***trans*-(4-pic)(TTP)Os–CH(CO$_2$Et)(4-pic) (2a).** To a solution of complex **1a** (5.4 mg, 5.72 μmol) in a 50/50 mixture of benzene (0.5 mL) and hexane (0.5 mL) was added an excess of 4-methylpyridine (20 μL, 0.20 mmol). The reaction was monitored by UV–vis spectroscopy. The dramatic shift of the Soret band upon treatment of **1a** by the pyridine derivative indicated the quantitative formation of **2a**. The solvents were evaporated and the crude residue washed three times with ca. 2 mL of dry hexane. The resulting black powder was stable for several days at room temperature. In solution in $\mathrm{C_6D_6}$ the adduct underwent a slow decomposition that yielded complex **3a** and diethyl maleate and fumarate. Data for **2a** are as follows. MS (FAB): *m/e* 1133 $\mathrm{(M)^+}$, 947 $\mathrm{(M-2(C_6H_7N))^+}$, 874 $\mathrm{(M-2(C_6H_7N)-C_3H_5O_2)^+}$, 861 $\mathrm{((TTP)Os)^+}$. UV–vis (toluene): 418 (Soret), 510 nm. ^{1}H NMR (293 K, 300 MHz, $\mathrm{C_6D_6}$): δ 8.16–7.99 (m, 16H, $\mathrm{H}_\beta + \mathrm{H}_{\mathrm{tolyl}}$), 7.36 (d, 4H, $\mathrm{H}_{\mathrm{tolyl}}$), 7.24 (d, 4H, $\mathrm{H}_{\mathrm{tolyl}}$), 6.00–5.00 (broad signal, $\mathrm{H}_{1,2,1',2'}$), 4.29 (d, 2H, $\mathrm{H}_{trans\text{-}4\text{-pic}}$), 4.18 (d, 2H, $\mathrm{H}_{trans\text{-}4\text{-pic}}$), 3.70 (dq, 1H, $\mathrm{OC}H_2\mathrm{CH_3}$), 3.40 (m, 1H, $\mathrm{OC}H_2\mathrm{CH_3}$), 2.37 (s, 12H, $\mathrm{Me}_{\mathrm{tolyl}}$), 1.40 (s, 3H, $\mathrm{CH_3}$), 0.80 (t, 3H, $\mathrm{CH_3CH_2O}$), 0.28 (s, 3H, $\mathrm{Me}_{trans\text{-}4\text{-pic}}$), −3.09 (s, 1H, $\mathrm{Os{-}C}H_\alpha$) ppm. ^{1}H NMR (213 K, 300 MHz, $\mathrm{C_7D_8}$): δ 8.19–8.10 (m, 16H, $\mathrm{H}_\beta + \mathrm{H}_{\mathrm{tolyl}}$), 7.40 (d, 4H, $\mathrm{H}_{\mathrm{tolyl}}$), 7.26 (d, 4H, $\mathrm{H}_{\mathrm{tolyl}}$), 6.43 (d, 1H, $\mathrm{H_2}$), 5.58 (d, 1H, H2′), 4.90 (d, 1H, $\mathrm{H}_{1'}$), 4.46 (d, 1H, $\mathrm{H_1}$), 4.12 (d, 2H, $\mathrm{H}_{trans\text{-}4\text{-pic}}$), 4.10 (d, 2H, $\mathrm{H}_{trans\text{-}4\text{-pic}}$), 3.69 (td, 1H, $\mathrm{OCH_2CH_3}$), 3.44 (td, 1H, $\mathrm{OCH_2CH_3}$), 2.39 (s, 12H, $\mathrm{Me}_{\mathrm{tolyl}}$), 1.33 (s, 3H, $\mathrm{H_3}$), 0.87 (t, 3H, $\mathrm{CH_3CH_2O}$), 0.20 (s, 3H, $\mathrm{Me}_{trans\text{-pic}}$), −3.22 (s, 1H, $\mathrm{Os{-}C}H_\alpha$) ppm. Data for **3a** are as follows. UV–vis (toluene): 408 (Soret), 492 nm. ^{1}H NMR (room temp, $\mathrm{C_6D_6}$): δ 8.21 (s, 8H, H_β), 8.07 (d, 8H, $\mathrm{H}_{\mathrm{tolyl}}$), 7.24 (d, 8H, $\mathrm{H}_{\mathrm{tolyl}}$), 4.23 (d, 2H, $\mathrm{H}_{4\text{-pic}}$), 4.03 (d, 2H, $\mathrm{H}_{4\text{-pic}}$), 2.32 (s, 12H, $\mathrm{Me}_{\mathrm{tolyl}}$), 0.28 (s, 6H, $\mathrm{Me}_{4\text{-pic}}$).

***trans*-(4-*i*-Pr-py)(TTP)Os–CH(CO$_2$Et)(4-*i*-Pr-py) (2b).** To a solution of $\mathrm{Os_2(TTP)_2}$ (30 mg, 17.5 μmol) in toluene (2.5 mL) was added dropwise a solution of ethyl diazoacetate (75 μL, 0.65 mmol) in toluene (12.5 mL) for 1 h. The mixture was stirred for an additional 2 h; the dark red solution was concentrated to c.a. 5 mL and eluted down a Florisil column. The carbene complex was recovered after elution with a 10/90 mixture of THF in toluene. To that solution was added some hexane and 4-isopropylpyridine. The mixture was stirred for 10 min and decanted. Complex **2b** precipitated out as a brown-orange amorphous powder which was filtered, washed with dry hexane, and dried under vacuum (18.0 mg, 15.1 μmol, 43% yield based on the starting amount of $\mathrm{Os_2(TTP)_2}$). Solutions of **2b** in toluene decomposed slowly over 24 h to yield the corresponding complex **3b** along with diethyl maleate and fumarate. Data for **2b** are as follows. UV–vis (toluene): 408 (Soret), 438 (sh), 494, 578 nm. Anal. calcd (found) for $\mathrm{C_{68}H_{64}N_6O_2Os}$ (mass %): C, 68.78 (68.40); H, 5.51 (5.44); N, 7.07 (6.85). ^{1}H NMR (293 K, 300 MHz, $\mathrm{C_6D_6}$): δ 8.17–7.98 (m, 16H, $\mathrm{H}_\beta + \mathrm{H}_{\mathrm{tolyl}}$), 7.38 (d, 4H, $\mathrm{H}_{\mathrm{tolyl}}$), 7.24 (d, 4H, $\mathrm{H}_{\mathrm{tolyl}}$), 6.50–5.20 (broad signal, $\mathrm{H}_{1,1',2,2'}$), 4.60 (d, 2H, $\mathrm{H}_{trans\text{-}(4\text{-}i\mathrm{Pr\text{-}py})}$), 4.36 (d, 2H, $\mathrm{H}_{trans\text{-}(4\text{-}i\mathrm{Pr\text{-}py})}$), 3.72 (dq, 1H, $\mathrm{OC}H_2\mathrm{CH_3}$), 3.42 (dq, 1H, $\mathrm{OC}H_2\mathrm{CH_3}$), 2.37 (s, 12H, $\mathrm{Me}_{\mathrm{tolyl}}$), 1.97 (m, 1H, $\mathrm{CH(CH_3)_2}$), 1.02 (m, 1H, $\mathrm{CH(CH_3)_2}$), 0.82 (t, 3H, $\mathrm{CH_3CH_2O}$), 0.61 (d, 3H, $\mathrm{CH(CH_3)_2}$), 0.59 (d, 3H, $\mathrm{CH(CH_3)_2}$), −0.09 (d, 6H, $\mathrm{CH(CH_3)_2}$, *trans*-(4-*i*-Pr-py)), −3.01 (s, 1H, $\mathrm{Os{-}C}H_\alpha$) ppm. Selected ^{1}H NMR data at −40 °C (233 K, 300 MHz, $\mathrm{C_7D_8}$): δ 6.45 (d, 1H, $\mathrm{H_2}$), 6.64 (d, 1H, $\mathrm{H}_{2'}$), 5.09 (d, 1H, $\mathrm{H}_{1'}$), 4.49 (d, 1H, $\mathrm{H_1}$) ppm.

***trans*-(4-NMe$_2$-py)(TTP)Os–CH(CO$_2$Et)(4-NMe$_2$-py) (2c).** The procedure used for the preparation of **2c** was similar to that used for the preparation of **2b**. The amounts of reagents were as follows: $\mathrm{Os_2(TTP)_2}$ (19 mg, 11.1 μmol) in toluene (2.5 mL), $\mathrm{N_2CHCO_2Et}$ (50 μL, 44 mmol) in toluene (12.5 mL), 4-(dimethylamino)pyridine (5 mg, 41 μmol). **2b** was washed with hexane and filtered on a medium-porosity frit (8.6 mg, 7.2 μmol, 32% yield based on $\mathrm{Os_2(TTP)_2}$). MS (FAB): *m/e* 1191 $\mathrm{(M)^+}$, 947 $\mathrm{(M-2(C_7H_{10}N_2))^+}$, 874 $\mathrm{(M-2(C_7H_{10}N_2)-C_3H_5O_2)^+}$, 861 $\mathrm{((TTP)Os)^+}$. UV–vis (toluene): 334, 414 (Soret), 484 nm. ^{1}H NMR (room temp, $\mathrm{C_6D_6}$): δ 8.25–8.07 (m, 8 H, $\mathrm{H}_{\mathrm{tolyl}}$), 8.04 (s, 8H, H_β), 7.45 (d, 4H, $\mathrm{H}_{\mathrm{tolyl}}$), 7.33 (d, 4H, $\mathrm{H}_{\mathrm{tolyl}}$), 6.10–4.90 (broad signal, $\mathrm{H}_{1,1',2,2'}$), 4.27 (d, 2H, $\mathrm{H}_{trans\text{-py}}$), 3.94 (d, 2H, $\mathrm{H}_{trans\text{-py}}$), 3.82 (dq, 1H, $\mathrm{OC}H_2\mathrm{CH_3}$), 3.50 (dq, 1H, $\mathrm{OC}H_2\mathrm{CH_3}$), 2.36 (s, 12H, $\mathrm{Me}_{\mathrm{tolyl}}$), 1.85 (s, 6H, $\mathrm{(CH_3)_2N}$), 1.18 (s, 6H, $\mathrm{(CH_3)_2N}$), 0.85 (t, 3H, $\mathrm{OCH_2C}H_3$), −3.63 (s, 1H, $\mathrm{Os{-}C}H_\alpha$) ppm.

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[34] (a) Boyer, J. H.; Mack, C. H.; Goebel, N.; Morgan, L. R., Jr. *J. Org. Chem.* **1958**, *23*, 1051. (b) Taber, D. F.; Ruckle, R. E., Jr.; Hennessy, M. J. *J. Org. Chem.* **1986**, *51*, 4077.

[35] Collman, J. P.; Barnes, C. E.; Woo, L. K. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 7684.

[36] DB-5 capillary column (30 m, 0.32 mm i.d., 0.25 μm).

[37] Varian gas chromatograph coupled to an ITS 40 ion trap mass spectrometer (capillary column DB-5MS (length 30 m, 25 mm i.d., 0.25 μm)). Mass spectra were used for characterization of cyclopropane derivatives when ionization time was in the range of 700–1500 μs.

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

***trans*-(4-pic)(TTP)Os—CH(SiMe$_3$)(4-pic) (2d)**. To a C_6D_6 (or C_7D_8 for sub-ambient-temperature experiments) solution of complex **1b** in an NMR sample tube was added 4-methylpyridine, and the solution was allowed to sit for several minutes at room temperature. The solution was then analyzed by ^{1}H NMR spectroscopy in the range of 213–343 K. At every temperature, the solution was allowed to reach the thermal equilibrium for 30 min; the shim parameters were optimized thereafter. Data for **2d** are as follows. UV–vis (toluene): 408 (Soret), 494 nm. ^{1}H NMR (295 K, C_6D_6): δ 8.02–7.83 (m, 16H, H_β + H_{tolyl}), 7.38 (d, 4H, H_{tolyl}), 7.24 (d, 4H, H_{tolyl}), 5.70 (d, 1H, H_2), 5.60 (d, 1H, $H_{2'}$), 5.50 (d, 1H, $H_{1'}$), 5.10 (d, 1H, H_1), 4.24 (d, 2H, $H_{trans\text{-}(4\text{-}pic)}$), 4.01 (d, 2H, $H_{trans\text{-}(4\text{-}pic)}$), 2.36 (s, 12H, Me_{tolyl}), 1.38 (s, Me_{ylide}), 0.33 (s, $Me_{trans\text{-}(4\text{-}pic)}$), −1.00 (s, 9H, Si($CH_3$)$_3$), −4.82 (s, 1H, Os–$CH_\alpha$).

Spin Saturation Transfer Experiment. The experiment was carried out on a Varian VXR300 spectrometer (^{1}H frequency 300 MHz) by using thoroughly degassed benzene-d_6. Complex **1b** was dissolved in 0.5 mL of C_6D_6 (C_{1b} = 0.94 mM) and added with 4-picoline ($C_{4\text{-pic}}$ = 0.01 M). The reaction mixture was allowed to sit for several hours until the chemical equilibrium was reached. The sealed NMR tube was then introduced in the probe of the spectrometer and maintained at a regulated temperature of 296 K. Two frequencies, corresponding to the α-proton of the carbene and ylide complexes, respectively, at 29.7 and −4.82 ppm, were successively irradiated by a rf pulse whose duration (d2) was arrayed as follows: d2 = 0.00, 0.05, 0.10, 0.15, 0.20, 0.30, 0.40, 0.50, 0.75, 1.00, 3.00, 5.00, 7.00, 10.0 s. A relaxation (d1 = 3.0 s)–irradiation (d2)–$\pi/2$ pulse (pw = 17.0)–acquisition (at = 3.5 s) sequence was used to carry out the spin saturation transfer experiment. Eighty transients were acquired per experiment. Values for the spin–lattice relaxation time, T_1, and the lifetimes of each species, τ, were obtained from plotting, versus d2, the intensity decay of the α-proton resonance that does not undergo irradiation.[27b] Satisfactory values were obtained by following the treatment proposed by Forsen and Hoffman: $T_1(H_\alpha(\mathbf{4a}))$ = 1.28(6) s, $\tau(H_\alpha(\mathbf{4a}))$ = 0.36(2) s; $T_1(H_\alpha(\mathbf{2d}))$ = 0.51(2) s, $\tau(H_\alpha(\mathbf{2d}))$ = 0.45(2) s, $\tau H_\alpha(\mathbf{2d})/\tau H_\alpha(\mathbf{4a})$ = 1.13.

Preparation of Complex 1c, (TTP)Os=C(CO$_2$Et)$_2$. To a THF (8 mL) solution of Os$_2$(TTP)$_2$ (15 mg, 8.7 μmol) was added dropwise a THF (20 mL) solution of $N_2C(CO_2Et)_2$ (80 mg, 0.43 mmol) at room temperature. The mixture was stirred for 2 h and the resulting solution stripped of solvent. The crude residue was dissolved in dry benzene and eluted down a Florisil column. The monocarbene complex was eluted with a 1:10 mixture of THF and benzene. The solvents were evaporated under reduced pressure and complex **1c** recrystallized from a THF–hexane solution to afford purple-black crystals (15 mg, 14.8 μmol, 85%). UV–vis (toluene): 398 (Soret) nm. IR (KBr): ν(C=O) 1705 cm^{-1}. ^{1}H NMR (C_6D_6): δ 8.45 (s, 8H, H_β), 8.24 (d, 4H, H_{tolyl}), 8.04 (d, 4H, H_{tolyl}), 8.28–8.23 (m, 8H, H_{tolyl}), 2.81 (q, 4H, OCH_2CH$_3$), 2.35 (s, 12H, Me_{tolyl}), 0.33 (t, 6H, OCH$_2$$CH_3$). MS (FAB): *m/e* 1018 (M)$^+$, 945 (M − $CO_2C_2H_5$)$^+$, 873 (M − $(CO_2C_2H_5)_2$)$^+$, 858 (M − $C(CO_2C_2H_5)_2$)$^+$.

Reaction of 2a with Styrene. To a solution of **2a** (5.7 μmol) in toluene (5 mL) was added an excess of dry styrene (10 μL, 87 μmol). The solution was stirred for 2 days and analyzed by GC–MS. Ethyl 2-phenyl-1-cyclopropanecarboxylate was formed in 61% yield based on **2a** (trans/cis = 23.0). The mass spectrum matched the features obtained for an authentic sample. MS (EI): *m/e* 190 (M)$^+$, 162 (M − C_2H_4), 144, 127, 117, 115, 91.

Reaction of 2b with Styrene. To a solution of **2b** (4.1 mg, 3.45 μmol) in toluene (3 mL) was added an excess of dry styrene (11 μL, 96 μmol). The solution was stirred for 2 days and analyzed by GC–MS. Ethyl 2-phenyl-1-cyclopropanecarboxylate was formed in 95% yield based on **2b** (trans/cis = 28.4).

Molecular Structure of the Complex (TTP)Os(4-pic)$_2$ (3a). Complex **3a** was obtained after 2 weeks from a concentrated solution of **1c** in 4-methylpyridine layered with benzene and hexane. ^{1}H NMR of the dark purple crystals that grew out of the solution indicated (TTP)Os(4-pic)$_2$ was the sole complex that remained. A suitable crystal was selected for X-ray diffraction analysis, attached to the tip of a glass fiber, and mounted on a Siemens P4RA diffractometer for a data collection at 213 K. The space group $P2_1/n$ was chosen on the basis of systematic absences and intensity statistics. This assumption proved to be correct, as determined by successful direct-methods solution and subsequent refinement. All non-hydrogen atoms were placed directly from the *E* map. All hydrogen atoms were refined as riding atoms having C–H distances of 0.96 Å with individual isotropic thermal parameters, with the exception of the methyl groups and the benzene. Half of the molecule is unique in this space group. The solvent benzene was determined to be partially occupied at 0.870. There are two benzene sites per porphyrin. All ellipsoid drawings are shown at the 50% probability level.

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Supplementary Material Available: Figures giving ^{1}H NMR data for complexes **2a–c** and FAB mass spectroscopy data for complexes **2a,c** and **1c** and tables of bond distances, angles, and positional parameters and isotropic displacement coefficients for the H atoms of **3a** (14 pages). Ordering information is given on any current masthead page.

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