Compounds 2, 4, and 5 were found to be inert toward the metathesis of cyclooctene or 1,9-decadiene, even in refluxing monomer. However, a mixture of 5 and $AlCl_3$ rapidly catalyzes ring-opening metathesis polymerization of cyclooctene at 25 °C either under N_2 or in the air, forming high-molecular-weight poly(1-octenylene) within minutes.[21] The activity of this system is akin to that of $Tp'W(CHC(CH_3)_3)(O)Cl/AlCl_3$, which we have previously reported.[1] A mixture of 5 and $AlCl_3$ showed limited activity for the acyclic diene metathesis polymerization of 1,9-decadiene over a 12-h period at 90 °C.[22]

Acknowledgment is made to the National Science Foundation (Grant No. DMR-8912026) and to Shell Development Corp. for support of this research.

Supplementary Material Available: Text giving synthetic details for the preparation of 2, 4, and 5 and complete ^1H NMR and ^{13}C NMR data for 2, 4, and 5 and tables of thermal parameters, positional parameters, and bond lengths and angles as well as details of the X-ray crystal structure determination of 2 (20 pages). Ordering information is given on any current masthead page.

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[21] Polymer prepared under an N_2 atmosphere: $M_n = 98900$, $M_w/M_n = 1.2$. Polymer prepared in air: $M_n = 90000$, $M_w/M_n = 1.2$.

[22] Approximately 5% internal olefin was formed, as indicated by ^1H NMR spectroscopy of the reaction mixture.

Synthesis of Osmium *meso*-Tetra-*p*-tolylporphyrin Carbene Complexes (TTP)Os=CRR′ (R, R′ = *p*-Tolyl; R = H, R′ = SiMe$_3$, CO$_2$Et): Stereoselective, Catalytic Production of Olefins from Substituted Diazomethanes

L. Keith Woo*[,1] and Daniel A. Smith

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received November 15, 1991

Summary: A series of osmium *meso*-tetra-*p*-tolylporphyrin carbene complexes, (TTP)Os=CRR′ [R, R′ = *p*-tolyl (1); R = H, R′ = $SiMe_3$ (2), CO_2Et (3)], have been prepared by treating $[Os(TTP)]_2$ with the appropriate diazoalkane (N_2CRR'). The carbene complexes, 1–3, and the osmium complexes $[Os(TTP)]_2$, Os(TTP)(CO)(py), and $Os(TTP)(py)_2$ catalytically convert ethyl diazoacetate to diethyl maleate and diethyl fumarate in high yields and high stereoselectivity. The *Z/E* ratios range from 18:1 to 26:1. Olefin also can be produced from $N_2C(p\text{-}C_6H_4\text{-}CH_3)_2$ but not from $N_2CHSiMe_3$.

Although the organometallic chemistry of metalloporphyrins has developed rapidly over the past few years,[2] work in this area involving osmium porphyrin complexes has received less attention. Moreover, while various metalloporphyrins catalyze the production of olefins,[3] cyclopropanes,[4] and the oxidative carbonylation of amines,[5] use of osmium porphyrins for catalytic reactions has been limited thus far to oxidations of alkenes.[6] We have recently begun studies on organometallic osmium porphyrin compounds. Subsequent to our preparation of the first osmium porphyrin silylene complexes,[7] we turned our attention to the reaction of these complexes with diazo reagents. We report herein the synthesis of a series of new osmium porphyrin carbene complexes and the highly stereoselective, catalytic formation of olefins from diazo compounds.

As a potential new route for the formation of coordinated silene ligands ($\eta^2\text{-}R_2Si{=}CR_2$), the porphyrin silylene complex $(TTP)Os{=}SiEt_2{\cdot}THF$[8] was treated with di-*p*-tolyldiazomethane. However, the reaction resulted in displacement of the silylene ligand and formation of the carbene complex $(TTP)Os{=}C(p\text{-}C_6H_4\text{-}CH_3)_2$. A more direct method for preparing these compounds involves treating $[Os(TTP)]_2$[9] with the appropriate diazoalkane, as shown in eq 1. In a typical reaction, $(TTP)Os{=}C(p\text{-}C_6H_4\text{-}CH_3)_2$ (1) was prepared under N_2 by adding a benzene solution (3 mL) of di-*p*-tolyldiazomethane (8.3 mg, 37.4 μmol) to a stirred solution of $[Os(TTP)]_2$ (32.0 mg, 18.6 μmol) in benzene (6 mL). After 1 h, the solution was passed through a neutral alumina column 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

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

1, R = R′ = $p\text{-}C_6H_4\text{-}CH_3$
2, R = H, R′ = $SiMe_3$
3, R = H, R′ = CO_2Et

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[1] 1990–1995 Presidential Young Investigator.

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[8] Abbreviations: TTP is *meso*-tetra-*p*-tolylporphyrinato, THF is tetrahydrofuran, and py is pyridine.

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Table I. Catalyst Summary for the Formation of Olefins from Ethyl Diazoacetate[a]

catalyst	mass (mg) (±0.1)	μmol of Os (±0.01)	cis/trans (±2)	% olefin yield (±3)	turnovers (±5)
$[Os(TTP)]_2$	2.7	3.14	26	92	140
			25[b]	94[b]	284[b]
$(TTP)OsC(tolyl)_2$	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	100	127
			25[b]	100[b]	255[b]
			25[b]	100[b]	376[b]
$(TTP)Os(py)_2$	3.5	3.44	26	93	129
$(TTP)Os(CO)(py)$	3.7	3.83	22	93	102

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

mg (96%) of brown solid.[10] The ^{13}C chemical shift of the carbene carbon (264.6 ppm) of complex **1** is characteristic of a typical carbene complex.[11] Preliminary data from a single-crystal X-ray diffraction study confirm the assigned osmium porphyrin carbene structure for **1**.[12]

The (trimethylsilyl)carbene complex **2** was prepared in a manner similar to that for the di-*p*-tolylcarbene complex **1**.[13] Preparation of the (ethoxycarbonyl)carbene complex **3** required slow addition of ethyl diazoacetate to a solution of $[Os(TTP)]_2$ in order to minimize the catalytic production of olefins (vide infra).[14] This procedure is similar to one reported by Collman for the ruthenium analog.[2e] All three carbene complexes decompose to uncharacterized compounds on exposure to air. Treating the di-*p*-tolylcarbene complex **1** 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 **1** shows no reactivity toward MeI, acetone, ethanol, or hexamethylsilacyclopropane over a period of several days at ambient temperature.

When anaerobic benzene solutions of $[Os(TTP)]_2$ are treated with excess ethyl diazoacetate, rapid evolution of gas is observed and high yields of diethyl maleate and diethyl fumarate are obtained (Table I). Depending on reaction conditions, the final metal products consist of varying ratios of the (ethoxycarbonyl)carbene complex **3** and $[Os(TTP)]_2$. ^1H NMR and GC analyses[15] indicate that olefin formation occurs with a Z/E ratio of 26:1. The high stereoselective formation of diethyl maleate is also catalyzed by the carbene complexes **1**–**3** and the monomeric complexes (TTP)Os(CO)(py) and $(TTP)Os(py)_2$.[16] Table I summarizes yields and product ratios. These are the highest olefin stereoselectivities for the decomposition of diazo compounds reported to date.[17] The largest diethyl maleate/diethyl fumarate ratios (15:1) from ethyl diazoacetate were observed independently by Collman and Venburg using a ruthenium porphyrin catalyst.[3] Qualitatively, reactions catalyzed by $[Os(TTP)]_2$, or the carbene complexes **1**–**3**, reach completion in seconds. Catalyst activity appears to remain constant over a period of greater than 1 week. Thus, additional N_2CHCO_2Et may be added to catalyst solutions with virtually quantitative conversion to olefin and no loss in 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 olefin. 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 olefin formation. When $[Os(TTP)]_2$ is treated with excess $N_2C(p\text{-}C_6H_4\text{-}CH_3)_2$ in THF, formation of tetratolylethylene[18] occurs qualitatively on the time scale of minutes. However, no olefin is observed by ^1H 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.

When $(TTP)Os{=}CHSiMe_3$ and $(TTP)Os{=}C(p\text{-}C_6H_4\text{-}CH_3)_2$ are treated with N_2CHCO_2Et, only diethyl maleate and small amounts of diethyl fumarate 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

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(10) Analytical data for $(TTP)Os{=}C(C_6H_4CH_3)_2$: ^1H NMR (C_6D_6) 8.15 (s, 8 H, β-H), 8.01 (d, 4 H, aryl), 7.88 (d, 4 H, aryl), 7.29 (dd, 8 H, aryl), 6.03 (d, 4 H, carbene-aryl), 4.26 (d, 4 H, carbene-aryl), 2.38 (s, 12 H, CH_3), 1.69 (s, 6 H, carbene-CH_3) ppm; ^{13}C NMR (C_6D_6) 264.6 ppm (s, Os=*C*); UV–vis (C_6H_6) 410 (soret), 522, 548 nm; MS{EI} found (calcd) *m/e* 1055 (1055) $[M + H]^+$, 964 (964) $[M + H - tolyl]^+$. 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, 4 H, CH_2), 0.88 (t, 6 H, CH_3), 0.31 (t, 2 H, OH) ppm. 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).

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(12) Manuscript in preparation. Crystallographic data for $C_{52}H_{42}N_4Os$: Space group $C2/c$; cell constants a = 28.003 (6) Å, b = 14.385 (3) Å, c = 33.748 (8) Å, β = 114.51 (2); R = 4.97%, R_w = 6.49%; $d_{Os=C}$ = 1.856 (8) Å.

(13) $(TTP)Os{=}C(H)Si(CH_3)_3$ (**2**) was prepared under N_2 by the addition of a hexane/benzene solution (3 mL) of (trimethylsilyl)diazomethane (24.6 μmol, 9×10^{-3} M) to a stirred solution of $[Os(TTP)]_2$ (23.3 mg, 13.5 μmol) in 6 mL of benzene. After 2 h, the solvent and excess (trimethylsilyl)diazomethane were removed under reduced pressure. Recrystallizing the solid from 2 mL of cold hexane and filtering produced 19.7 mg (76.9%) of brown product. ^1H NMR (C_6D_6): 28.95 (s, 1 H, $=C\mathit{H}SiMe_3$), 8.01 (s, 8 H, β-H), 7.93 (dd, 8 H, aryl), 7.24 (d, 4 H, aryl), 7.17 (d, 4 H, aryl), 2.32 (s, 12 H, CH_3), −1.41 (s, 9 H, $(CH_3)_3Si$) ppm. ^{13}C NMR (C_6D_6): 295.5 ppm (d, J_{CH} = 124.4 Hz). UV–vis (C_6H_6): 388, 420 nm. Anal. Calcd (found) for $OsSiN_4C_{52}H_{46}$: C, 66.07 (64.91); H, 4.91 (4.73); N, 5.93 (5.80).

(14) $(TTP)Os{=}CHCO_2Et$ (**3**) was prepared under N_2 by the slow addition (10 h) of ethyl diazoacetate (50 μL, 0.48 mmol) in 50 mL of toluene to a vigorously stirred toluene solution (15 mL) of $[Os(TTP)]_2$ (101.5 mg, 0.59 μmol). After the addition was completed the solution was stirred for an additional 1 h. The resulting solution was concentrated to 25 mL under reduced pressure and eluted down a Florisil column (1 cm diameter × 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. ^1H NMR (C_6D_6): 21.60 (s, 1 H, $=C\mathit{H}CO_2Et$), 8.35 (s, 8 H, β-H), 8.02 (d, 4 H, aryl), 7.96 (d, 4 H, aryl), 7.28 (d, 4 H, aryl), 7.19 (d, 4 H, aryl), 2.36 (s, 12 H, CH_3), 2.67 (q, 2 H, $=CHCO_2C\mathit{H}_2CH_3$), 0.26 (t, 3 H, $=CHCO_2CH_2C\mathit{H}_3$) ppm. ^{13}C NMR (C_6D_6): 211.6 ppm (d, J_{CH} = 132.8 Hz). UV–vis (C_6H_6): 398, 408 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).

(15) HP 5890 Series II GC using a DB-5 capillary column (30 m, 0.32 mm, 0.25 μm) with T_i = 50 °C for 1 min followed by a temperature ramp of 10 °C/min for 10 min.

(16) In a typical experiment, 3.4 mg (3.23 μmol) of $(TTP)Os{=}C(tolyl)_2$ and dodecane (0.10 mL, 44 mmol) were stirred vigorously in 5.0 mL of benzene under an N_2 atmosphere. Addition of ethyl diazoacetate (0.10 mL, 95 mmol) resulted in the rapid evolution of gas which stopped after 1 min. Olefin product ratios were determined by GC analysis.[15]

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trans-bis(carbene) complex. A moderately stable *trans*-bis(carbene) complex (TTP)Os[$=C(p\text{-}C_6H_4\text{-}CH_3)_2]_2$ (**4**) can be prepared by treating (TTP)Os$=C(p\text{-}C_6H_4\text{-}CH_3)_2$ (**1**) with additional $N_2C(p\text{-}C_6H_4\text{-}CH_3)_2$.[19] A signal at 305 ppm in the ^{13}C NMR spectrum of **4** is clearly diagnostic of the carbene ligand. However, the bis(carbene) complex **4** is always contaminated with the monocarbene complex **1** and has not yet been isolated in pure form. The olefin-forming step may involve attack of a diazo reagent at the least hindered carbene ligand of the bis(carbene) complex or may involve direct coupling between two bis(carbene) complexes in a binuclear process. Evidence for the binuclear mechanism was established by monitoring a 70:1 mixture of **4**:**1**. Over the period of days, the bis(carbene) complex **4** decomposes to produce tetratolylolefin and the mono(carbene) complex **1** (eq 2). Binuclear pathways for the formation of olefins from carbene complexes have been proposed for a number of metal complexes.[2e,f,20] Alternative processes such as oxidative pathways involving radical cations[21] cannot be ruled out at this time. Further work is in progress to address the mechanistic issues of our osmium-catalyzed processes.

$$\underset{\mathbf{4}}{(\mathrm{TTP})\mathrm{Os}[=\mathrm{C}(p\text{-}\mathrm{C_6H_4\text{-}CH_3})_2]_2} \rightarrow \underset{\mathbf{1}}{(\mathrm{TTP})\mathrm{Os}=\mathrm{C}(p\text{-}\mathrm{C_6H_4\text{-}CH_3})_2} + (p\text{-}\mathrm{C_6H_4\text{-}CH_3})_2\mathrm{C}=\mathrm{C}(p\text{-}\mathrm{C_6H_4\text{-}CH_3})_2 \quad (2)$$

Acknowledgment. Financial support for this work was provided by NSF Grant CHE-9057752 and the Exxon Education Foundation. D.A.S. acknowledges the Amoco Foundation for a graduate fellowship. We are grateful to Johnson Mathey/Aesar for a generous loan of $OsCl_3$. We also thank Professor T. J. Barton and Mr. John Engel for assistance with the GC analyses.

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[19] Analytical data for (TTP)Os($=C(p\text{-}C_6H_4\text{-}CH_3)_2)_2$: ^1H NMR (C_6D_6) 8.63 (s, 8 H, β-H), 7.99 (d, 8 H, aryl), 7.33 (d, 8 H, aryl), 5.97 (d, 8 H, carbene-aryl), 3.12 (d, 8 H, carbene-aryl), 2.42 (s, 12 H, CH_3), 1.68 (s, 12 H, carbene-CH_3) ppm; ^{13}C NMR (C_6D_6) 305.5 ppm (s, Os=C).

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Transition-Metal Complexes with Sulfur Ligands. 89.[†] Unexpected Formation of the Highly Stable Binuclear Nickel Carbene Complex $[Ni(S_2C)]_2$ from Nickel(II) Salts, Diamine–Dithiolate Ligands, and C_1 Components (S_2C^{2-} = 1,3-Imidazolidine-1,3-diylbis(2-benzenethiolate)(2−))

Dieter Sellmann,* Werner Prechtel, Falk Knoch, and Matthias Moll

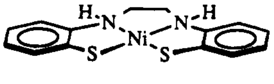
Institut für Anorganische Chemie II, University of Erlangen-Nürnberg, Egerlandstrasse 1,
W-8520 Erlangen, Germany

Received March 13, 1992

Summary: In quest of model compounds for CO dehydrogenases the interaction of nickel amine–thiolate complexes with CO and other C_1 sources was investigated, and a new type of nickel–carbene complex, $[Ni(S_2C)]_2$ (**2**), was obtained. **2** contains two $[Ni(S_2C)]$ fragments whose extreme stability is traced back to the tridenticity of the carbene ligand and the nickel–thiolate bonds. **2** is stable toward concentrated H_2SO_4 and boiling HCl but reacts rapidly with nucleophiles to give mononuclear $[NiL(S_2C)]$ complexes (L = PMe_3, PPh_3, CN^-).

Nickel complexes with thiolate and amine ligands are of interest as model compounds for the active sites of CO dehydrogenases (CODH) if they react with C_1 compounds as CO_2, CO, or CH_3 species.[1] CODH's contain nickel centers surrounded by sulfur and nitrogen donors and catalyze the CO_2/CO conversion as well as acetyl-CoA synthesis from CH_3, CO, and CoA.[2]

For these reasons we investigated the reaction of $[Ni(N_2H_2S_2)]$ (**1**; $N_2H_2S_2^{2-}$ = 1,2-ethanediamine-*N,N'*-bis(2-benzenethiolate)(2−))[3] with CO. **1** does not react with CO gas. When recrystallized from DMF, however, it unexpectedly yielded the red carbene dithiolate complex $[Ni(S_2C)]_2\cdot DMF$ (**2**·DMF; S_2C^{2-} = 1,3-imidazolidine-1,3-diylbis(2-benzenethiolate)(2−)) in minimum amounts. **2** is the formal product of CO insertion from DMF into the Ni–N bonds of **1**, followed by elimination of H_2O and dimerization of the resulting fragments. Systematic experiments



$[Ni(N_2H_2S_2)]$

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