Synthesis of Osmium meso-Tetra-p-tolylporphyrin Carbene Complexes (TTP)Os=CRR' (R, R' = p-Tolyl; R = H, R' = SIMe3, CO2Et): Stereoselective, Catalytic Production of Olefins

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Synthesis of Osmium meso-Tetra-p-tolylporphyrin Carbene Complexes
(TTP)Os=CRR' (R, R' = p-Tolyl; R = H, R' = SIMe3, C02Et):
Stereoselective, Catalytic Production of Olefins

Abstract
A series of osmium meso-tetra-p-tolylporphyrin carbene complexes, (TTP)Os=CRR' [R, R' = p-tolyl (1); R = H, R' = SIMe3 (2), CO-t (3)], have been prepared by treating [Os(TTP)]2 with the appropriate diazoalkane (N2CRR'). The carbene complexes, 1-3, and the osmium complexes [Os(TTP)]2, Os(TTPCOXpy), and Os(TTPXpy)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 N2C(p-C8H4- CH3)2 but not from N2CHSIMe3.

Disciplines
Chemistry

Comments
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 AlCl₃ rapidly catalyzes ring-opening metathesis polymerization of cyclooctene at 25 °C either under N₂ or in the air, forming high-molecular-weight poly(1-octenylene) within minutes. The activity of this system is akin to that of TPW(CH₂CH₂)p(OCl/AICl₃, which we have previously reported. A mixture of 5 and AlCl₃ showed limited activity for the acyclic diene metathesis polymerization of 1,9-decadiene over a 12-h period at 90 °C.

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Supplementary Material Available: Text giving synthetic details for the preparation of 2, 4, and 5 and complete ¹H NMR and ¹³C 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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Summary: A series of osmium meso-tetra-p-tolylporphyrin carbone complexes, [(TTP)Os=CRR' (R, R' = p-Tolyl; R = H, R' = SiMe₂, CO₂Et)], have been prepared by treating [Os(TTP)], with the appropriate diazocompounds (N₂CR). The carbone complexes, 1–3, and the osmium complexes [Os(TTP)₂] (TTP)Os=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 28:1. Olefin also can be produced from N₂C(p-C₆H₄-CH₃)₂ but not from N₂CHSiMe₃.

Although the organometallic chemistry of metallopolyporphyrins has developed rapidly over the past few years, work in this area involving osmium porphyrin complexes has received less attention. Moreover, while various metallopolyporphyrins catalyze the production of olefins, cyclopropanes, and the oxidative carbonylation of amines, use of osmium porphyrins for catalytic reactions has been limited thus far to oxidations of alkenes. We have recently begun studies on organometallic osmium porphyrin compounds. Subsequent to our preparation of the first osmium porphyrin silylene complexes, 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 (η³-R₂Si=CR), the porphyrin silylene complex (TTP)Os=SiEt₂THF was treated with dip-tolylidiazomethane. However, the reaction resulted in displacement of the silylene ligand and formation of the carbene complex (TTP)Os=C(p-C₆H₄CH₂)₂. A more direct method for preparing these compounds involves treating [Os(TTP)₂] with the appropriate diazoalkane, as shown in eq. 1. In a typical reaction, (TTP)Os=C(p-C₆H₄CH₂)₂ + N₂C(R)₂ → (TTP)Os=CR + N₂ (1)

C₆H₄-CH₂)₂ (1) was prepared under N₂ by adding a benzene solution (3 mL) of di-p-tolylidiazomethane (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

(1) 1990-1995 Presidential Young Investigator.
(8) Abbreviations: TTP is meso-tetra-p-tolyporphyrino, THF is tetrahydrofuran, and py is pyridine.
Recrystallizing crystals from a toluene solution of complex 2 led to a product with a high melting point. The crystalline material was obtained by crystallization from ethanol to produce 10 mg (96%) of brown solid. Analytical data for complex 1 is characteristic of a typical carbene complex.

The (trimethylsilyl)carbene complex 2 required slow addition of ethyl diazoacetate to a solution of [Os(TTP)]₂ in order to minimize the catalytic production of olefins (vide infra). This procedure is similar to one reported by Collman for the ruthenium analog. 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)OsO₂ and 4,4'-dimethylbenzophenone over the course of several days as monitored by 1H NMR. However, complex 1 shows no reactivity toward Me₃Si, acetone, ethanol, or hexamethylsilylcyclopropane over a period of several days at ambient temperature.

When aniseric 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. 13C NMR and GC analyses indicate that olefin formation occurs with a Z/E ratio of 26:1. The high stereoselective formation of diethyl maleate is also catalysed by the carbene complexes 1-3 and the monomeric complexes (TTP)Os(CO)(py) and (TTP)Os(OEt)₂. Table I summarizes yields and product ratios. These are the highest olefin stereoselectivities for the decomposition of diazo compounds reported to date. The largest diethyl maleate/diethyl fumarate ratio (15:1) from ethyl diazoacetate was observed independently by Collman and Venburg using a ruthenium porphyrin catalyst. Qualitatively, reactions catalyzed by [Os(TTP)], 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 N₂CH₂CO₂Et may be added to catalyst solutions with virtually quantitative conversion to olefin and no loss in stereoselectivity. Os(TTP)(py)₃ and (TTP)Os(OEt)₂ 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 N₂C(p-C₆H₄-Ch₃)₂CO₂Et in THF, formation of tetrahydroethylene occurs quantitatively on the time scale of minutes. However, no olefin is observed by 1H NMR when N₂CH₂SiMe₃ 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=CH₂SiMe₃ and (TTP)Os=C(p-C₆H₄-CH₃)₂CO₂Et are treated with N₂CH₂CO₂Et, 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=CH₂SiMe₃ or (TTP)Os=C(p-C₆H₄-CH₃)₂, respectively. This suggests that the catalytic reactions may involve an intermediate.

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

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>mass (mg)</th>
<th>µmol of Os (±0.01)</th>
<th>cis/trans (±3)</th>
<th>% olefin yield (±3)</th>
<th>turnovers</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Os(TTP)]₂</td>
<td>2.7</td>
<td>3.14</td>
<td>92</td>
<td>140</td>
<td>1</td>
</tr>
<tr>
<td>(TTP)OsC(tol)₂</td>
<td>3.4</td>
<td>3.23</td>
<td>18</td>
<td>94</td>
<td>29</td>
</tr>
<tr>
<td>(TTP)OsCH₂SiMe₃</td>
<td>3.5</td>
<td>3.70</td>
<td>99</td>
<td>128</td>
<td>1</td>
</tr>
<tr>
<td>(TTP)OsCH₂Et</td>
<td>3.6</td>
<td>3.81</td>
<td>100</td>
<td>127</td>
<td>1</td>
</tr>
<tr>
<td>(TTP)OsOEt₂</td>
<td>3.5</td>
<td>3.44</td>
<td>93</td>
<td>129</td>
<td>1</td>
</tr>
<tr>
<td>(TTP)Os(CO)(py)</td>
<td>3.7</td>
<td>3.83</td>
<td>92</td>
<td>102</td>
<td>1</td>
</tr>
</tbody>
</table>

(TTP)Os-C(tol)₂ and dodecan (0.10 mL, 44 mmol) were stirred vigorously in 5.0 mL of benzene under an N₂ atmosphere. Addition of ethyl diazoacetate (0.10 mL, 56 mmol) resulted in the rapid evolution of gas which stopped after 1 min. Olefin product ratios were determined by GC analysis.

In a typical experiment, 3.4 mg (3.32 µmol) of (TTP)Os-C(tol)₂ and dodecan (0.10 mL, 44 mmol) were stirred vigorously in 5.0 mL of benzene under an N₂ atmosphere. Addition of ethyl diazoacetate (0.10 mL, 56 mmol) resulted in the rapid evolution of gas which stopped after 1 min. Olefin product ratios were determined by GC analysis.


(17) Spectroscopically equivalent to an independently prepared sample and not isolated from solution. camphan (1.0×10 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 (35%) of dark crystals. 13C NMR (CD₂Cl₂): 21.60 (s, 1 H, -CH₂SiMe₃), 8.43 (s, 1 H, -CH₂SiMe₃), 7.03 (d, 4 H, aryl), 6.34 (d, 4 H, aryl), 5.85 (s, 1 H, -CH₂SiMe₃), 5.76 (d, 4 H, aryl), 5.01 (d, 4 H, aryl), 4.78 (d, 4 H, aryl), 2.92 (d, 3 H, -CH₂SiMe₃), 1.34 (s, 9 H, -(CH₃)₃Si).
Transition-Metal Complexes with Sulfur Ligands. 89.† Unexpected Formation of the Highly Stable Binuclear Nickel Carbene Complex \([\text{Ni}(\text{S}_2\text{C})_2]\) from Nickel(II) Salts, Diamine-Dithiolate Ligands, and \(C_1\) Components \((\text{S}_2\text{C}^2\text{\(=\)}} 1,3-\text{Imidazolidine-1,3-diylibis(2-benzenethiolate)}(2-))

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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, \([\text{Ni}(\text{S}_2\text{C})_2]\), (2), was obtained. 2 contains two \([\text{Ni}(\text{S}_2\text{C})]\) fragments whose extreme stability is traced back to the tridenticity of the carbene ligand and the nickel–thiolate bonds. 2 is stable toward concentrated \(\text{H}_2\text{SO}_4\) and boiling \(\text{HCl}\) but reacts rapidly with nucleophiles to give mononuclear \([\text{Ni}(\text{S}_2\text{C})]\) complexes (L = PMe₃, PF₃H, 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 \(CoA\).

For these reasons we investigated the reaction of \([\text{Ni}(\text{N}_2\text{H}_2\text{S}_2)])(1); \text{N}_2\text{H}_2\text{S}_2^2\text{=\(=\)}} 1,2-\text{ethanediamine-N,N'-bis(2-benzenethiolate)}(2-)) with \(CO\). 1 does not react with \(\text{CO}\) gas. When recrystallized from DMF, however, it unexpectedly yielded the red carbene dithiolate complex \([\text{Ni}(\text{S}_2\text{C})_2]\)-DMF (2-DMF; \(\text{S}_2\text{C}^2\text{\(=\)}} 1,3-\text{imidazolidine-1,3-diylibis(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 \(\text{H}_2\text{O}\) and dimerization of the resulting fragments. Systematic experiments

\[
\text{Ni}(\text{N}_2\text{H}_2\text{S}_2)
\]


\[\text{OM9107092}\]