Cyclopropanation Catalyzed by Osmium Porphyrin Complexes

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Cyclopropanation Catalyzed by Osmium Porphyrin Complexes

Abstract
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 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 cyclopropanation activity. Several years ago Callot demonstrated that rhodium porphyrins catalytically cyclopropanated a variety of alkenes in the presence of ethyl diazoacetate. Kodadek and co-workers have expanded this work and have attempted to prepare synthetically useful enantioselective catalysts for the formation of cyclopropanes. Their approach has been to use rhodium complexes with optically active porphyrins to induce chirality into the product. A similar approach was used for a variety of non-porphyrin copper catalysts. Kodadek has shown that the carbon-bound diazonium complex \([(TTP)RhC(H)(C02Et)(N2W is an intermediate in the catalytic cyclopropanation of styrene with ethyl diazoacetate. In addition, kinetic studies suggest that the formation of a rhodium carbene complex is at least partially rate limiting. However, this carbene complex has not been isolated or directly observed. We report herein the use of osmium porphyrins as stereoselective cyclopropanation catalysts using ethyl diazoacetate with a variety of alkenes. In addition, our studies show that an isolable carbene complex \((TTP)Os=CHC02Et) is capable of catalytically and stoichiometrically cyclopropanating styrene.

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program. The optimized structures for BC2H2, HBC2, HBC2H2, and cyclop propane are given in Figure 2. Calculated vibrational frequencies and intensities are given in Table II for the 11-12-12-1 BC2H2 isotope. The strong calculated 1214.9-cm⁻¹ band dominates the spectrum. Table I also lists the harmonic isotopic fundamentals; multiplying by the average scale factor 0.964 gives calculated bands in agreement within a 1.0-cm⁻¹ average for seven isotopic E band frequencies. (The fit for the five hydrogen isotopes with similar anharmonicities is ±0.3 cm⁻¹.) This excellent agreement between calculated and observed isotopic frequencies confirms the identification of BC2H2. The out-of-plane deformation calculated at 733.6 cm⁻¹ is probably masked by the very strong C2H2 band at 720-750 cm⁻¹. Large basis set coupled cluster calculations predict BC2H2 to be 74 kcal/mol more stable than B+C2H.

On the other hand, the F bands are assigned to the cyclic HBC2 species; the different 28.7-cm⁻¹ boron-10, 16.5-cm⁻¹ carbon-13, and 47.0-cm⁻¹ deuterium isotopic shifts are matched (±1.7 cm⁻¹) by quantum chemical calculations for HBC2. Calculations for the similar boricene molecule HBC2 reveal similar isotopic shifts for the strong B-C2 fundamental calculated at 1215.8 cm⁻¹, 26.3-cm⁻¹ boron-10, 22.3-cm⁻¹ carbon-13, and 50.2-cm⁻¹ deuterium shifts. Clearly, each molecule has a unique arrangement of atoms and unique normal vibrational modes, which can be characterized by isotopic substitution at all atomic positions. One important conclusion reached from this study is that agreement between scaled calculated and observed isotopic frequencies for one vibrational fundamental with substitution at all atomic positions constitutes a fingerprint match for identification of the molecule, which is demonstrated here for BC2H2.

It is clearly seen that the C=C bonds in BC2H2 and HBC2H2 are longer than in C2H2 (Figure 2). Likewise the B-C bonds are shorter than typical single bonds [1.558 Å in B(C2H3)],. Similar evidence has been offered to support delocalization of the two π electrons over the three-membered ring and aromatic character for the BC2 ring in trimesitylboring. Furthermore, the BC2 rings in BC2H2 and HBC2H2 are seen to be virtually identical. Thus, the σ radical site in BC2H2 has no effect on the delocalized π bonding in the BC2 ring.

The photoysis of BC2H2 in the near ultraviolet range indicates a strong absorption band in this region, in agreement with trimesitylboring. The photoysis behavior also provides evidence for delocalized bonding as acetylene and ethylene absorbers at shorter wavelengths.

The appearance of BC2H2 on diffusion and reaction of B atoms at 18 K in solid argon follows similar behavior for BO2. These exothermic reactions proceed without activation energy. The BC2H2 radical is the simplest boricene species yet observed and characterized. Further studies are in progress in this laboratory to prepare substituted boricene radicals.

### Acknowledgment

The experimental work was supported by NSF Grant CHE 91-22556 and the theoretical work by the San Diego Supercomputer Center. J.M.L.M. is a Senior Research Assistant of the National Fund for Scientific Research Belgium (FNWO/FNRS) and acknowledges Fulbright/Hays and NATO travel grants.

#### Cyclopropanation Catalyzed by Osmium Porphyrin Complexes

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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 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 cyclopropanation activity. Several years ago Callot demonstrated that rhodium porphyrins catalytically cyclopropanated a variety of alkenes in the presence of ethyl diazocacetate. Kodak and co-workers have expanded this work and have attempted to prepare synthetically useful enantioselective catalysts for the formation of cyclopropanes. Their approach has been to use rhodium complexes with optically active porphyrins to induce chirality into the product. A similar approach was used for a variety of non-porphyrin copper catalysts. Kodak has shown that the carbon-bound diazonium complex [(TTP)RhC(H)(CO2ET)(N2)]+ is an intermediate in the catalytic cyclopropanation of styrene with ethyl diazocacetate. In addition, to each of the carbene complexes the overall photoysis process is reversed. While the BC2H2 is stable, the BC2H2• radical is not very stable.

### Table I. Calculated and Observed Isotopic Frequencies (cm⁻¹) for the Strongest E Band

<table>
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<tr>
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<tbody>
<tr>
<td>v(B=C-C)</td>
<td>1107.6</td>
<td>1197.4</td>
<td>1161.9</td>
<td>1147.3</td>
<td>1172.0</td>
<td>1169.4</td>
<td>1196.0</td>
<td>1214.9</td>
<td>1242.8</td>
<td>1206.3</td>
</tr>
<tr>
<td>v(B-BC2)</td>
<td>1171.2</td>
<td>1198.1</td>
<td>1162.8</td>
<td>1149.7</td>
<td>1172.6</td>
<td>1167.4</td>
<td>1194.6</td>
<td>1171.2</td>
<td>1198.1</td>
<td>1162.8</td>
</tr>
<tr>
<td>Δ(obs-d-scaled)</td>
<td>-0.6</td>
<td>0.7</td>
<td>-0.9</td>
<td>-0.6</td>
<td>-0.6</td>
<td>2.0</td>
<td>1.4</td>
<td>-0.6</td>
<td>2.0</td>
<td>1.4</td>
</tr>
</tbody>
</table>

### Table II. Calculated (MPZ/DZP) Infrared Intensities (km/mol) and Frequencies (cm⁻¹) for 11B1²C2H2 (C2v Symmetry)

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>b₁</th>
<th>a₁</th>
<th>b₂</th>
<th>a₂</th>
<th>b₁</th>
<th>a₁</th>
<th>b₁</th>
<th>a₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency</td>
<td>733.6</td>
<td>910.6</td>
<td>925.9</td>
<td>1010.0</td>
<td>1200.9</td>
<td>1214.9</td>
<td>1506.1</td>
<td>3289.4</td>
</tr>
</tbody>
</table>


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kinetic studies suggest that the formation of a rhodium carbene complex is at least partially rate limiting. However, this carbene complex has not been isolated or directly observed. We report herein the use of osmium porphyrins as stereoselective cyclopropanation catalysts using ethyl diazoacetate with a variety of alkenes. In addition, our studies show that an isolable carbene complex ([TTP]Os=CHCO2Et) is capable of catalytically and stoichiometrically cyclopropanating styrene.

Slow addition of a toluene solution of ethyl diazoacetate (0.10 mL, 950 μmol) over 2 h to a vigorously stirred solution of [(TTP)Os]3 (3.0 mg, 1.7 μmol) and styrene (0.11 mL, 960 μmol) at 22 °C results in the formation of ethyl-2-phenyl-1-cyclopropaneacarbonyl acid ester (I) in 79(2)% yield as determined by GC. The a/s isomer ratio of cyclopropane is 1.05. Under similar conditions, the carbene complex ([TTP]Os=CHCO2Et (2) catalytically cyclopropanates styrene and ethyl diazoacetate to produce cyclopropane I in 63(2)% yield with an a/s isomer ratio of 8.96. The oxygen- and water-stable complex ([TTP]Os=CHCO2Et (3) also serves as a catalyst precursor. When a toluene solution of ethyl diazoacetate (0.10 mL, 950 μmol) was added to a vigorously stirred solution of 3 (2.8 mg, 2.8 μmol) and styrene (0.11 mL, 961 μmol), I was obtained in 65(3)% yield with an a/s = 9.5(2).

In the isoelectronic Rh porphyrin systems, carbene complexes have been proposed as the active species. From previous work we have demonstrated that the reaction of [(TTP)Os]3 and ethyl diazoacetate forms the osmium porphyrin carbene complex 2. Subsequently, cyclopropanation reactions catalyzed by [(TTP)Os]3 are likely to proceed through an osmium carbene complex. As a test for this hypothesis, (TTP)Os=CHCO2Et was treated with an excess of styrene. Cyclopropane I was formed stoichiometrically (73(5)% and identified by proton NMR and GC analysis. The a/s isomer ratio of cyclopropane I produced in this reaction was a/s = 11.5(4). The similarity of the stoichiometric and catalytic stereoselectivities strongly supports a catalytic cycle in which an osmium carbene complex is initially formed and subsequently transferred to the alkene. In addition, a new porphyrin complex was observed by 1H NMR and formulated as a π-bound styrene complex ([TTP]Os(C6H5CH=CHCH=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 base line.

Olefins such as α-methylstyrene, trans-β-methylstyrene, and 1-decene were also 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, Table I. The a/s ratios are also lower with 1-decene and α-methylstyrene. The assignment of the syn and anti isomers for the α-methylstyrene-derived cyclopropane product was confirmed by 500-MHz 2D-NOESY proton NMR. For the cyclopropanation reaction of trans-β-methylstyrene with ethyl diazoacetate, the only cyclopropane isomer with the ethyl ester group anti to the phenyl was detected.

A vast majority of cyclopropanation catalysts transform alkenes to cyclopropanes. However, only a few are able to doubly cyclopropanate alkenes to generate bicyclobutanes. In contrast, (TTP)Os(CO)(Py) and [(TTP)Os] catalytically produce exo,exo-2,4-dicarbethoxy-1-phenylbicyclo[1.1.0]butane as the only product from phenylacetylene and ethyl diazoacetate. The exo,exo assignment was established by the singlet at 1.7 pm in the 1H NMR for the protons on carbons 2 and 4. The exo,endo isomer should exhibit a doublet for these protons. 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 ethyl diazoacetate. This system provides the highest anti/syn isomer ratio reported to date (a/s = 10) for the catalytic cyclopropanation of styrene by ethyl diazoacetate. Unlike typical cyclopropanation catalysts which produce cyclopropanes from alkyne substrates, the osmium porphyrin catalysts generate bicyclobutanes from phenylacetylene. Moreover, we have isolated, on preparative scale, the first carbene complex (TTP)Os=CHCO2Et, which is catalytically active toward cyclopropanation. The fact that this carbene complex can stoichiometrically cyclopropanate styrene with the same stereochemistry as in the catalytic process is further evidence for it as an important species in the catalytic cycle.

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 toward nucleophilic attack by the alkene and prevents isolation of the cationic carbene complex. However, the lack of a positive charge in the osmium system allows the isolation of the osmium carbene complexes. Nonetheless, the neutral osmium complexes appear to be highly efficient cyclopropanation catalysts. Other diazo...
reagents are being examined for use in the catalytic cyclopropanation of alkenes and alkyynes. In addition, further mechanistic investigation is under way.

Acknowledgment. The authors thank The National Science Foundation (NSF-PYI Grant CHE-9057572) and the Exxon Education Foundation for the financial support of this work and Asar/Asher Johnson Mathey for donation of osmium chloride. D.N.R. was supported as a summer student by the Ames Laboratory, which is operated for the U.S. Department of Energy by Iowa State University under contract No. W-7405-ENG-82. We also thank Professor Thomas Kodadek for helpful suggestions and Ms. Kathlynn Brown for samples of several cyclopropanes used as GC standards.

Catalytic Conversion of Simple Haloporphyrins into Alkyl-, Aryl-, Pyridyl-, and Vinyl-Substituted Porphyrins

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Appending unusual organic moieties to the porphyrin periphery has often involved elaborate synthetic strategies and difficult separations of reactants from product(s). For example, typical routes to porphyrins that possess one or more differing meso or β substituents have employed condensation of the appropriate aldehyde(s) with various monopyrroles, substituted dipyrromethanes, or prefabricated 1,19-dideoxybiladienes. In addition to the considerable chromatography that is generally required, other limitations inherent in these approaches include (1) the sensitivity of the cyclization step in a porphyrin synthesis to the steric and electronic features of substituents at the methine and pyrrole positions and (2) the potential incompatibility of one or more of the components in the syntheses to conditions common to all previous porphyrin preparations, namely, protic or Lewis acid catalysis or high temperature. We report herein a powerful methodology directly applicable to a wide variety of porphyrin synthetic schemes, provided the reducing power of the organometallic species used in the reaction is insufficient to participate in an outer sphere electron transfer reaction with the porphyrin.

In a typical reaction, (5,15-dibromo-10,20-diphenylporphinato)zinc (1) or (2-bromotetraphenylporphinato)zinc (2) and an excess of the desired organometallic reagent (RZnX or BuSnR) were brought together in dry THF under nitrogen at 60 °C for 12-48 h in the presence of a catalytic amount of Pd(PPh₃)₄. Over the course of several hours, the initially nonfluorescent reaction mixture became increasingly more fluorescent, signaling the gradual transformation of the halogenated porphyrin complex to the alkyl-, vinyl-, aryl-, or pyridyl-substituted zinc porphyrin. For the organometallic reagents depicted in Scheme I, quantitative conversion of reactants to products took place within 48 h.

It is interesting to note that the oxidative addition–transmetalation–reductive elimination reaction sequence occurs much more rapidly at the porphyrin pyrrolic carbon than the analogous re-

(13) Prepared in high yield (88%) from 5,15-diphenylporphyrin under conditions analogous to those employed by Longo for the halogenation of porphyrine. Nudy, L. R.; Hutchinson, H. G.; Schieber, C.; Longo, F. R. Tetrahedron 1984, 40, 2359-2363. The selective bromination of porphyrins at free meso positions can be carried out with a wide variety of substituents present.


(15) More recent work in our lab has shown that Pd(dppf) [dppf = 1,1'-bis(diphenylphosphino)ferrocene] is a much more reactive catalyst for cross-coupling chemistry on porphyrin templates; reactions similar to those described in the text have been observed to go to completion within 1 h at room temperature with the Pd(dppf) catalyst. See: Hayashi, T.; Konishi, M.; Kumada, M. Tetrahedron Lett. 1979, 21, 1871-1874.