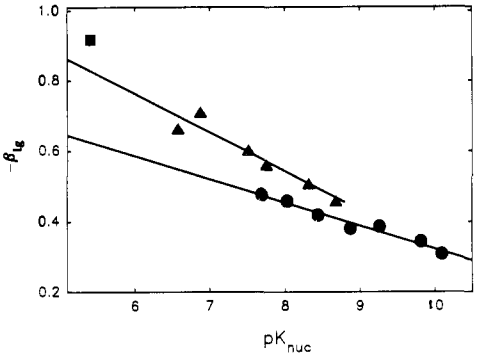

Figure 8. The dependence of the Brønsted β_{lg} on the pK_a of the phenolate nucleophile for the reactions of phenyl formates with meta- or para-substituted phenolate anions (circles), meta- or para-substituted *o*-chlorophenolate anions (triangles), and 2,3,5,6-tetrafluorophenolate anion (square).

^{15}N isotope effect does not provide rigorous proof of a concerted mechanism, because there may be a decrease in the C–N bond order in a transition state for rate-determining attack of the nucleophile to form a tetrahedral intermediate. However, there is no detectable isotope effect in the reaction with hydroxide ion, which presumably represents rate-limiting nucleophilic attack.[18]

Figure 8 shows that the reactions of phenyl formates show a larger change in transition-state structure with increasing pK_a of the nucleophile, and this change is different for meta- and para-substituted phenolate anions (circles) and meta- and para-substituted *o*-chlorophenolate anions (triangles). The change in $-\beta_{lg}$ is consistent with $p_{xy} = 0.07$ for the reactions of meta- and para-substituted phenolate anions (circles) and $p_{xy} = 0.11$ for the reactions of meta- and para-substituted *o*-chlorophenolate anions and 2,3,5,6-tetrafluorophenolate ions (triangles). This difference provides additional evidence that the structures of the transition states for the reactions of the two classes of phenolate ions are different.

Buncel and Hoz have shown that the rate constants for reactions of substituted phenolate ions with phenyl acetates in a series of different solvents follow a correlation with σ, not σ^-. This shows that there is not a measurable amount of electron donation by resonance into the aromatic system of the leaving phenolate ion in the transition state of the reaction.[19] However, this result does not show that the reaction is not concerted, because this resonance may not develop to a measurable extent until the bond to the leaving group is largely broken. It is likely that there is *imbalance* between the amount of C–O cleavage and the development of electron delocalization.[17]

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Identification of the Active Catalyst in the Rhodium Porphyrin-Mediated Cyclopropanation of Alkenes

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Contribution from the Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712. *Received July 24, 1992*

Abstract: Iodorhodium porphyrins are extremely active catalysts for the cyclopropanation of alkenes by diazo esters. Mechanistic studies of this reaction have resulted in the spectroscopic characterization of several potential organometallic intermediates in the reaction, including a novel metal diazonium complex resulting from alkylation of the rhodium center by ethyl diazoacetate. This compound is thought to decompose to a metal carbene that subsequently transfers the carbene fragment to the substrate. While our studies have led to a satisfactory general picture of the reaction mechanism, the axial ligation state of the metal under typical catalytic conditions remains unclear. We show here that the predominant active species is an iodoalkylrhodium complex that results from attack of the metal carbene by iodide. Iodination of the carbene is competitive with cyclopropanation even though the substrate is present in a vast excess. The partition ratio (cyclopropanation events/iodination events) is approximately 100:1.

Callot and co-workers reported that iodorhodium porphyrins are efficient catalysts for the cyclopropanation of alkenes by diazo esters.[1] The porphyrin-catalyzed reactions exhibit an unusual propensity to provide mostly the syn diastereomer when bulky macrocycles are used. We have been interested in developing asymmetric versions of this system using chiral porphyrin ligands, since optically pure syn cyclopropyl esters are not readily accessible with current methodology. Unfortunately, the enantioselectivities obtained to date are not synthetically useful.[2,3] In order to rationally design more selective catalysts, we recently initiated a detailed investigation of the reaction mechanism, with an emphasis on the characterization of intermediates in the catalytic cycle. In particular, stoichiometric reaction between iodorhodium tetra-*p*-tolylporphyrin (RhTTPI) and ethyl diazoacetate (EDA) led to the spectroscopic characterization of the diazonium complex **2** (see Scheme I) at low temperatures.[4] When this species was allowed to warm in the presence of an alkene, a 68% yield of cyclopropanes was obtained with concomitant evolution of 1 equiv of nitrogen.[4] When the diazonium complex is warmed in the absence of alkene, the previously characterized[5,6] iodoalkyl complex **4** is produced in quantitative yield.[4] These observations strongly implicate the intermediacy of metallocarbene **3** as the reactive intermediate (Scheme I). Cyclopropanes and iodoalkyl complex **4** represent the two possible products of nucleophilic attack on the carbene carbon, in the first case by an alkene and in the latter by iodide. In addition to the diazonium complex, both mono- and bis-alkene π complexes of RhTTPI have been observed (Scheme I). A kinetic analysis of the reaction suggests that these complexes are not attacked directly by ethyl diazoacetate but rather compete with the carbene precursor for ligation to rhodium. Another possibility is that the nature of a coordinated alkene might affect

(1) Callot, H. J.; Metz, F.; Piechocki, C. *Tetrahedron* **1982**, *38*, 2365.
(2) O'Malley, S.; Kodadek, T. *Tetrahedron Lett.* **1991**, *32*, 2445.
(3) O'Malley, S.; Kodadek, T. *Organometallics* **1992**, *11*, 2299.
(4) Maxwell, J. L.; Brown, K. C.; Bartley, D.; Kodadek, T. *Science* **1992**, *256*, 1544.
(5) Callot, H. J.; Schaeffer, J. *J. Chem. Soc., Chem. Commun.* **1978**, 937.
(6) Maxwell, J.; Kodadek, T. *Organometallics* **1991**, *10*, 4.

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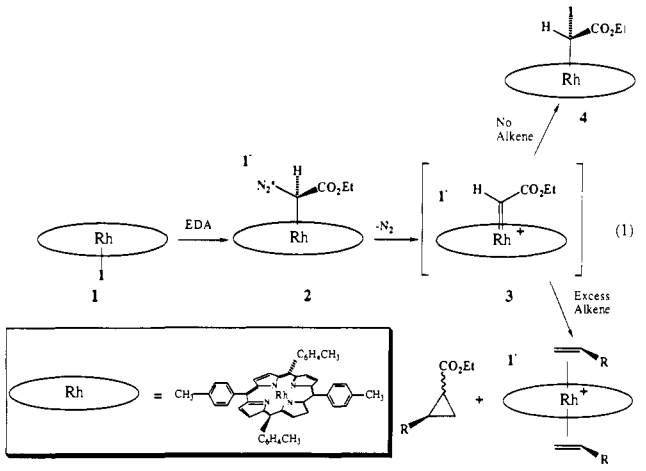
Scheme I



the rate of nitrogen ejection from **2** to form carbene **3**.[4]

While these stoichiometric reactions have provided a great deal of information, the nature of the active porphyrin species under catalytic conditions remains to be determined. An important clue was provided by the observation of a Soret band at 413 nm in an aliquot taken from a RhTTPI-catalyzed cyclopropanation reaction.[4] This signal is typical of alkylrhodium porphyrins and suggested that the steady-state intermediate might be the diazonium complex **2** and that N_2 evolution is the rate-determining step of the catalytic cycle. However, as we pointed out in our previous publication, further work was required to confirm this hypothesis. Specifically, the iodoalkyl complex **4** also exhibits a Soret band at this wavelength, raising the possibility that it might be involved in catalysis. While it initially seemed unlikely to us that iodination of the rhodium carbene would be competitive with cyclopropanation given the vast excess of alkene employed, **4** is nonetheless a known product of carbene **3** and has a remaining open coordination site trans to the iodoalkyl ligand that could support carbene formation. Furthermore, we have shown that CH_3RhTTP is a respectable cyclopropanation catalyst,[4] demonstrating that an alkyl ligand does not shut down the reaction.

We report here experiments that distinguish between these possibilities and demonstrate that iodoalkyl complex **4** is indeed the predominant catalytic species in the reaction, except in the very early stages.

Experimental Section

General Methods. RhTTPI and iodoalkyl complex **4** were synthesized as reported previously.[6] EDA and styrene were purchased from Aldrich. Styrene was passed over a plug of neutral alumina immediately prior to use. Optical spectra were recorded on an HP-8452A diode array spectrometer, and NMR spectra were recorded on a Nicolet NT-360 or General Electric QE-300 instrument. The chemical shifts were referenced to the protic impurity in CD_2Cl_2. Kinetic experiments were carried out as described previously at 25 °C.[7]

Determination of the Partition Coefficient. A 5-mL round-bottom flask equipped with a magnetic stir bar is charged with 0.9 mL of styrene (7.86 mmol), 0.25 mL of a 1.16 mM RhTTPI solution in dichloromethane (2.90×10^{-4} mmol of RhTTPI), and 1.85 mL of dichloromethane. The flask is sealed with a rubber septum and vented with a needle. The reaction is initiated by addition of 1 μL of a 2.9 M solution of ethyl diazoacetate (2.9×10^{-3} mmol, 10 equiv) via syringe with stirring. After stirring for 15 min, a 200 μL aliquot is withdrawn and added to 2 mL of dichloromethane. The sample is analyzed by optical spectroscopy, and the concentration of the iodoalkyl complex is determined by application of Beer's Law. The procedure is repeated several times with different amounts of ethyl diazoacetate (30, 50, 70, 90 or 125 equiv). The data are plotted (moles of iodoalkyl complex formed vs moles of EDA added), and the slope of the linear region gives the partition coefficient.

Formation of the Iodoalkyl Complex 4. A solution of 7.9 mg of RhTTPI (8.80×10^{-3} mmol) in 1 mL of dichloromethane-d_2 is placed in an NMR tube. The tube is sealed with a rubber septum and cooled to −78 °C in a dry ice/acetone bath. One equivalent of ethyl diazoacetate (8.80×10^{-3} mmol, 0.9 μL) is added via syringe, and the solution is mixed by inverting the tube several times. The tube is then placed in a 0 °C ice bath for 30 min. At this time the structure is verified by NMR spectroscopy and the sample is returned to the −78 °C bath until ready for use.

Catalytic Activity of the Iodoalkyl Complex 4. A 5-mL round-bottom flask equipped with a magnetic stir bar is charged with 0.9 mL of styrene (7.86 mmol), 0.1 mL of dodecane (0.44 mmol), 0.1 mL of ethyl diazoacetate (0.95 mmol), and 1.9 mL of dichloromethane. The flask is sealed with a rubber septum, vented with a needle, and placed in a 25 °C water bath. The reaction is initiated by addition of 32.9 μL of the preformed solution of the iodoalkyl complex (2.89×10^{-4} mmol). At timed intervals, 100 μL aliquots of the reaction mixture are removed and placed in vials containing 10 μL of pyridine, which quenches the reaction. The amount of cyclopropane product in each aliquot is determined by gas chromatography using dodecane as an internal standard. The number of turnovers per minute is determined by the slope of the linear region of a plot of moles of product formed vs time. An identical experiment is performed to determine the rate of nitrogen evolution. The volume of nitrogen evolved is monitored by a gas-measuring buret and converted to moles. A similar plot is made to determine the rate. For comparison, the catalytic experiment is repeated using a solution of 7.9 mg of RhTTPI (8.80×10^{-3} mmol) dissolved in 1 mL of dichloromethane. The reactions are initiated by addition of 32.9 μL of this solution instead of the solution of the iodoalkyl complex.

Binding of Styrene by 4. The iodoalkyl complex is prepared as described previously. One equivalent of styrene (8.80×10^{-3} mmol, 1.0 μL) is added to the solution, and the NMR spectrum of the mixture is acquired. The spectrum is compared to a reference spectrum of styrene in dichloromethane-d_2.

Detection of 4 by Optical Spectroscopy. Fifteen microliters of a 1.16 mM RhTTPI solution in dichloromethane (1.74×10^{-5} mmol) is placed in a cuvette containing 50 μL of styrene (0.44 mmol, 25 000 equiv), 2 mL of dichloromethane, and a flea-sized magnetic stir bar. The cuvette is placed in the spectrophotometer and stirred. Scanning of the sample is begun at the rate of 1 spectrum per second. Within 2 s, 1 μL of a 1.74 M solution of EDA in dichloromethane is added (1.74×10^{-3} mmol, 100 equiv). Scanning is continued for a total of 90 s.

Determination of the Stability of the Iodoalkyl Complex. The iodoalkyl complex is prepared as described previously. After verification of the structure, 100 μL of styrene-d_8 (Aldrich, 0.872 mmol, 99 equiv) is added and the NMR spectrum is acquired. Ten equivalents of *tert*-butyl diazoacetate[8] (8.80×10^{-2} mmol) is added, and the tube is inverted several times to mix the contents. A needle is used to vent the tube of the evolved nitrogen. After approximately 5 min, nitrogen evolution ceases and the NMR spectrum is acquired.

Results and Discussion

Identical Behavior of Cyclopropanation Reactions Initiated with RhTTPI and 4. To test the activity of **4** as a cyclopropanation catalyst, RhTTPI was mixed with 1 equiv of EDA at 0 °C and formation of **4** was verified by NMR spectroscopy[6] (data not shown). Preformed **4** was then used as the catalyst for the cyclopropanation of styrene by EDA. Another experiment was done under identical conditions except that RhTTPI, rather than **4**, was added to initiate the reaction. The rates of the two reactions, corrected for selectivity[9] were the same within experimental error (29 vs 31 turnovers per minute, respectively. See Figure 1). Since we have shown that the nature of the axial ligand influences the rate of the reaction significantly,[4] this observation suggests that the ligation state of the catalyst in both reactions is the same. The ratio of cyclopropane and carbene dimer products was virtually identical as well. In addition, both reactions produced the same ratio of syn to anti cyclopropyl ester products (1.0).

This suggests that the true catalyst in reactions initiated with RhTTPI is **4**. An alternative explanation is that **4** is unstable under the reaction conditions and somehow fragments rapidly back to

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(8) Ledon, H. J. *Org. Synth.* **1988**, *6*, 414.

(9) Carbene dimer products (*cis*- and *trans*-ethyl maleate) are also formed in the rhodium porphyrin-catalyzed reactions. This is true for most metal-catalyzed cyclopropanation reactions. The reaction selectively is defined as (2(rateΔ))/(rate N_2 + rateΔ), where rateΔ = observed rate of cyclopropanation and rate N_2 = rate of nitrogen evolution. This formula takes into account the fact that dimer formation results in the generation of 2 equiv of nitrogen whereas cyclopropanation generates 1 equiv.

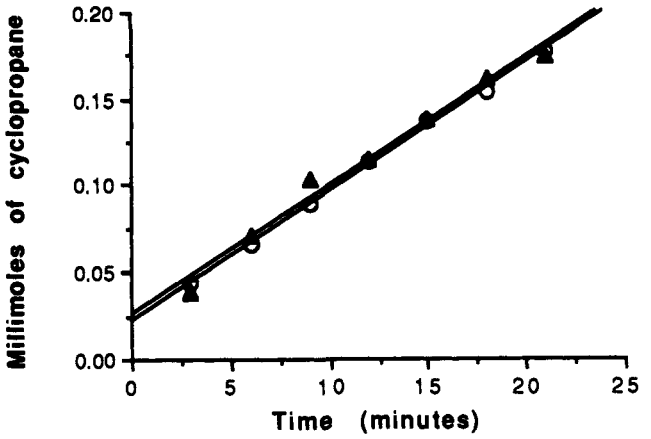

Figure 1. Rate of nitrogen evolution and cyclopropane formation are nearly identical in reactions initiated with RhTTPI (▲) or the preformed iodoalkyl complex **4** (○). Reaction conditions: RhTTPI = 9.6×10^{-5} M in CH_2Cl_2 with 3300 equiv of EDA and 27 000 equiv of styrene, 25 °C.

RhTTPI, perhaps with transfer of the carbene fragment to an alkene. However, changes in the NMR spectrum of **4** are observed only after 1 h at room temperature (data not shown). The same result was obtained when excess styrene-d_8 was also present, suggesting that fragmentation does not occur. To test the stability of the iodoalkyl complex more rigorously under catalytic conditions, we performed the following experiment. Complex **4** was formed stoichiometrically in an NMR tube from EDA and 1 equiv of RhTTPI. One hundred equivalents of styrene-d_8 and 10 equiv of *tert*-butyl diazoacetate were then added. An efficient cyclopropanation reaction ensued. If the iodoalkyl ligand in **4** is indeed labile under these conditions, then we would expect to see loss of the NMR signals due to it. The appearance of peaks due to the syn and anti carboxyethylcyclopropanes should also be observed, along with signals from a RhTTP–alkene complex and/or the *tert*-butyl analogue of **4**. Alternatively, if **4** is stable, then the only cyclopropanes produced would be those derived from reaction with the *tert*-butyl diazoacetate-derived metallocarbene. In the event, the latter result was observed (Figure 2). No loss of **4** was observed in the NMR spectrum, and no new porphyrin-derived peaks grew in. Large signals due to the *tert*-butylcyclopropyl ester products were observed. No peaks corresponding to cyclopropanes containing an ethyl ester could be detected. We conclude that **4** is stable under the reaction conditions, at least for ten turnovers. It was impractical to extend this method to probe the integrity of **4** after several hundred or thousands of turnovers, but there is no reason to believe it to be labile. In any case, even if **4** does infrequently break down in the course of a reaction, it will reform rapidly (vide infra). The above data strongly suggest that RhTTPI is actually a precatalyst and that **4** is the dominant catalytic species.

Determination of the Relative Reactivity of Styrene and Iodide with Carbene 3. We had previously monitored the RhTTPI-catalyzed cyclopropanation of styrene by optical spectroscopy and observed the formation of a steady-state intermediate with a Soret band at 413 nm,[4] typical of alkylrhodium porphyrins. In that experiment, the spectrum was recorded only after the catalyst had turned over several hundred times. We have now examined the optical spectrum of the porphyrin catalyst as a function of time. When EDA (100 equiv) was added to a solution containing RhTTPI and 25 000 equiv of styrene, an immediate spectral shift was observed. The new compound, whose composition is unknown, is then transformed to the ultimate steady-state intermediate, as evidenced by a blue shift of the Soret band to 413 nm with clean isobestic behavior (Figure 3). The shift is complete within 90 s, and the spectrum exhibits no change for additional 30 min. A parallel experiment in which nitrogen evolution is monitored shows that all of the EDA is consumed within 10 min. Since the diazonium complex **2** is known to be unstable at temperatures above −40 °C,[4] it cannot be responsible for the observed Soret band.

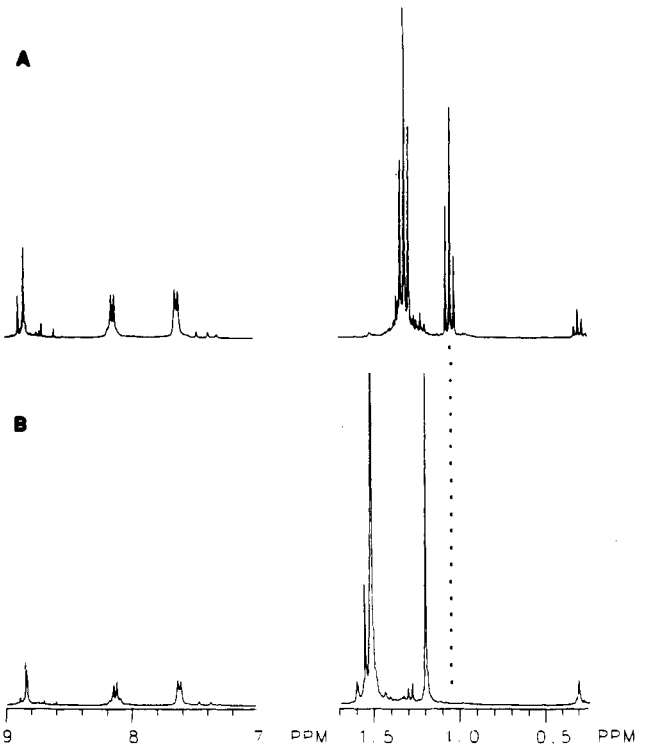

Figure 2. Rhodium iodoalkyl complex **4** is stable under catalytic conditions. (A) NMR spectrum of a reaction in which styrene-d_8 (100 equiv with respect to the catalyst) was cyclopropanated with EDA (10 equiv) using performed **4** as the catalyst. The triplet due to the methyl group of the cyclopropyl ester products is located at 1.05 ppm. A signal due to the methyl protons of iodoalkyl complex **4** (0.3 ppm) remains. (B) NMR spectrum of a reaction identical to that shown in A, except that *tert*-butyl diazoacetate was used in place of EDA. In this case, if the iodoalkyl ligand is not stable, the signals due to it should disappear and, presumably, a signal due to the ethyl ester product should be detected. We find that the signal due to the methyl group of **4** persists (0.3 ppm) and that there is no trace of the triplet due to ethyl ester products (1.05 ppm, indicated by the dotted line).

We therefore assign the steady-state intermediate as the iodoalkyl complex **4**.

A variation of this experiment was used to determine the relative reactivity of styrene and iodide with the metal carbene. Various amounts of EDA (10–125 equiv) were added to solutions of RhTTPI and styrene (10 000 equiv). After all of the EDA had been consumed, the yield of the iodoalkyl complex was determined for each reaction by optical spectroscopy (Figure 4). About 100 equiv of EDA are required to convert all of the porphyrin to the iodoalkyl complex. This partition coefficient of approximately 100 means that 1% of all metal-catalyzed decompositions of EDA result in the formation of the iodoalkyl complex under our standard conditions and most of the catalyst will acquire the iodoalkyl ligand after 100 turnovers. Since these reactions turn over thousands of times,[7] **4** is the predominant catalyst even when RhTTPI is used to initiate the reaction. While one might predict that the characteristics of reactions intiated with RhTTPI or **4** might differ somewhat at very early times, the small amounts of products produced made this point difficult to investigate and it was not pursued.

Binding of Alkenes to 4 and Competition with EDA for the Metal. In light of these experiments, how can we rationalize that different olefins are cyclopropanated at different rates, since we have shown that carbene formation is rate-determining?[4] Previously, we had thought that the resting state of the catalyst was a bis-olefin π-complex. In this case, the substrate might affect the rate of carbene formation by either hindering attack of EDA to form the diazonium complex or by increasing the rate of nitrogen ejection to form the carbene. The latter explanation cannot be correct once **4** is formed, because the diazonium complex of **4**[10] has no vacant coordination sites for alkene binding. However,

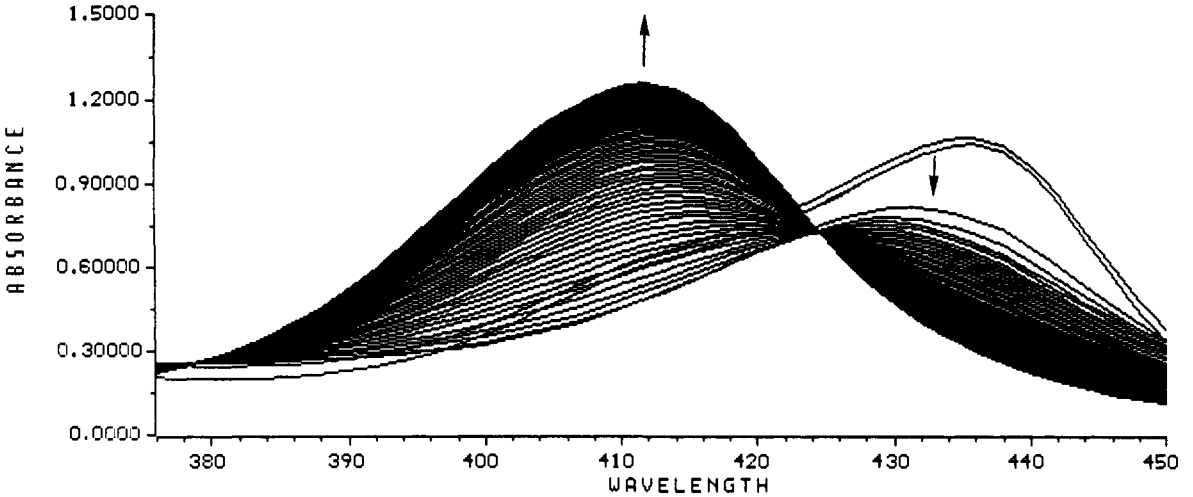

Figure 3. Optical spectrum exhibited by the RhTTPI-catalyzed cyclopropanation of styrene by EDA at various times after addition of 100 equiv of EDA to a CH_2Cl_2 solution of RhTTPI (8.7×10^{-6} M) and 25 000 equiv of styrene. Spectra were acquired at the rate of one per second. Complete formation of the $\lambda_{max} = 413$ species required about 90 s.

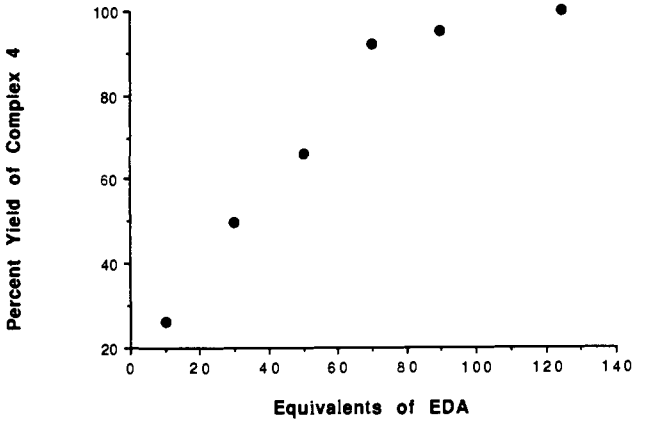

Figure 4. Determination of the partition coefficient for the formation of the iodoalkyl complex. Each reaction was initiated by addition of the indicated amount of EDA to a solution containing RhTTPI (9.6×10^{-5} M) and 27 000 equiv of styrene. An aliquot was withdrawn after 15 min and diluted 11-fold in CH_2Cl_2. Optical spectroscopy was then employed to quantitate the amount of iodoalkyl complex ($\lambda_{max} = 413$) that had formed. These data show that one molecule of **4** is formed for every 100 molecules of cyclopropanes produced. The point at which the accumulation of the $\lambda_{max} = 413$ species levels off corresponds to the porphyrin concentration.

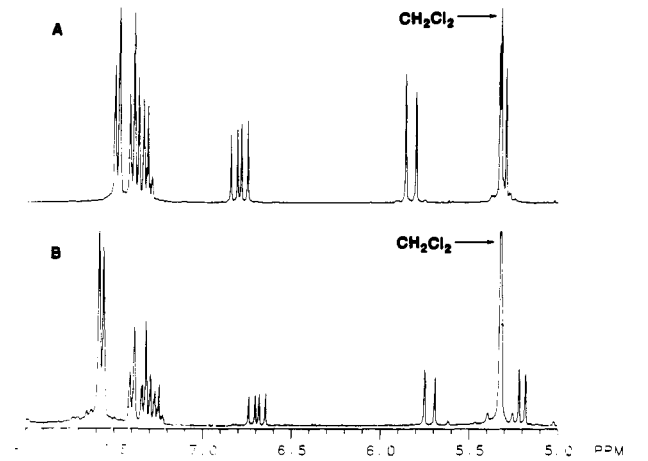

Figure 5. Proton NMR spectroscopy shows that the iodoalkyl complex **4** binds styrene. Shown are the 300-MHz spectra of (a) styrene and (b) **4** (8.9 mM) plus styrene (1 equiv) in CD_2Cl_2. Small upfield shifts in the signals for the vinylic protons can be detected in the presence of the porphyrin, indicating that the alkene feels the diamagnetic ring current of the porphyrin macrocycle (see ref 4 for a previous characterization of RhTTPI–alkene π-complexes).

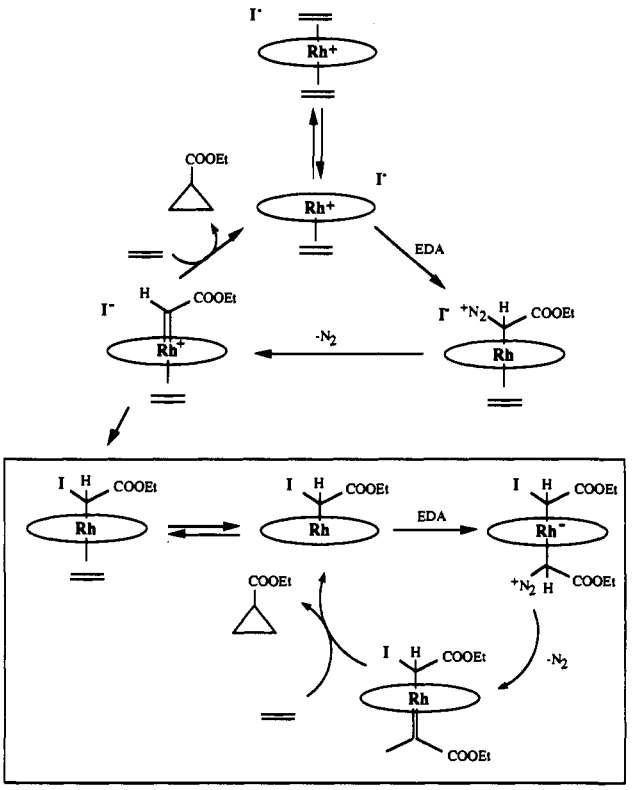

Figure 6. Proposed mechanism for the iodorhodium porphyrin-catalyzed cyclopropanation of alkenes. After about 100 turnovers under our standard conditions, almost all of the rhodium has acquired the iodoalkyl ligand and the boxed cycle predominates.

if the iodoalkyl complex coordinates olefins, the first explanation is still feasible, since different alkenes will presumably coordinate with different affinities.

When **4** is formed in an NMR tube at 0 °C and 1 equiv of styrene is added, a small, but reproducible, upfield shift of the vinylic protons is observed in the NMR spectrum (Figure 5), indicative of reversible alkene π-complex formation.[4] We are unable to derive accurate association constants from the NMR data due to the small chemical shift differences between the free and bound states. It was also impractical to employ optical spectroscopy for this purpose. Addition of alkenes to **4** resulted

(10) We have not been able to characterize a diazonium complex analogous to **2** using an alkylrhodium porphyrin in place of RhTTPI. We presume that attack of EDA on these compounds is much slower than in the case of RhTTPI and that the diazonium complex is probably less stable.

in very small shifts in the position of the Soret band of **4** (although addition of stronger ligands such as imidazole resulted in a significant red shift of the Soret (data not shown), demonstrating the availability of an open coordination site in **4**). Nonetheless, the NMR experiment qualitatively supports the conclusion that various alkenes might differentially inhibit attack of **4** by EDA by occupying a coordination site, thus leading to the modestly different rates of cyclopropanation observed in catalytic reactions.

Summary. The nature of the active catalyst in the rhodium porphyrin-mediated cyclopropanation of alkenes by EDA has been probed. The iodoalkylrhodium complex **4**, presumably produced by attack of iodide on the active metallocarbene, is formed rapidly in situ and is the predominant catalyst over the course of the reaction. Quenching of the carbene with iodide is surprisingly competitive with carbene transfer to the alkene even in the presence of a 25 000-fold excess of the alkene (100 cyclopropanation events for every iodination). Porphyrin **4** is shown to bind alkenes in a reversible fashion. Thus, competition between the alkene and EDA for the vacant coordination site provides a plausible explanation for the observation that different alkenes are cyclopropanated at different rates, even though carbene formation is rate-limiting. A similar scenario has been postulated by Salmeron and Kochi for copper triflate-catalyzed cyclopropanation reactions.[11] Our current model for the catalytic cycle is shown in Figure 6.

These findings may have some practical impact in the design of asymmetric or shape-selective porphyrin cyclopropanation catalysts. For example, it should be possible to use a bulky alkyl ligand to block the most sterically accessible face of a catalyst in which both sides are not equivalent. All subsequent cyclopropanation chemistry would then occur on the modified face of the porphyrin.

Acknowledgment. This work was supported by a grant from the Petroleum Research Fund (24052-AC1). We thank Dr. Ben Shoulders for assistance with some of the NMR experiments and Prof. Dan Ziegler for the use of his optical spectrometer. We also thank the reviewers for several helpful suggestions.

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Synthesis and Reactivity Patterns of New Proazaphosphatranes and Quasi-azaphosphatranes $ZP(MeNCH_2CH_2)_3N$

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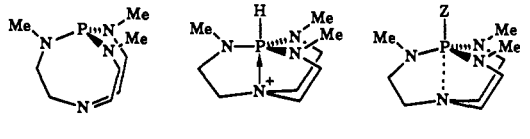
Contribution from Gilman Hall, Department of Chemistry, Iowa State University, Ames, Iowa 50011. *Received September 21, 1992*

Abstract: Partial bridgehead–bridgehead P←N transannulation in $S_2CP(MeNCH_2CH_2)_3N$ (**4**) stabilizes this unusual CS_2 adduct, facilitating the synthesis of a series of $RS(S)CP(MeNCH_2CH_2)_3N^+$ cations from the reaction of **4** with RX (**5**, R = Me; **6**, R = CH_2=$CHCH_2$; **7**, R = Et; **8**, R = *n*-Pr; **9**, R = *n*-Bu; **10**, R = *i*-Pr). The relative rates of formation of **5–10** are in accord with S_N2 attack of sulfur on the α carbon of RX. The structure determination of **5**(I) by X-ray means revealed that formation of cation **5** from **4** is accompanied by shortening of the transannular interaction from 3.008 to 2.771 Å. We also report the synthesis of a series of regioisomeric products of the reaction of $S{=}P(MeNCH_2CH_2)_3N$ (**11**) with RX, namely, $RSP(MeNCH_2CH_2)_3N^+$ (R = Me, Et, *n*-Bu) and $S{=}P(MeNCH_2CH_2)_3NR^+$ (R = Me, Et). The slow decomposition of **4** to **11** in solution is also described.

Introduction

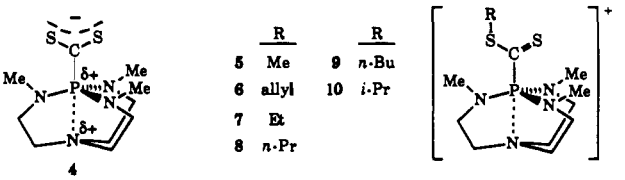
The bicyclic proazaphosphatrane **1** has been shown to be a remarkably strong base, reacting with a proton to give the stable azaphosphatrane **2**.[1-3] Cation **2** features a transannular P←N



1 2 3

covalent bond that forms via inversion of the bridgehead nitrogen.[1-3] We have also recently demonstrated that **1** forms quasi-azaphosphatranes **3**, in which the $P{-}N_{ax}$ bond distance is intermediate between the sum of the P and N van der Waals radii (3.35 Å) and the covalent transannular bond distance in **2**, depending on the nature of Z.[4]

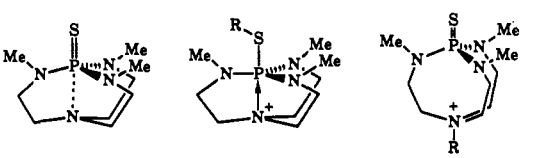
As part of our continuing exploration of the chemical consequence of partial transannulation in these systems, we report herein the synthesis of a series of quasi-azaphosphatrane cations **5–10**



4

	R		R
5	Me	9	*n*-Bu
6	allyl	10	*i*-Pr
7	Et		
8	*n*-Pr		

and rationalize the relative rates with which these products are formed from **4**[4] and the RX reagents. We also report that the proazaphosphatrane **11** described earlier[2,5] reacts with MeI to give



11 **12a**, R = Me; **13a**, R = Et; **14a**, R = *n*-Bu **12b**, R = Me; **13b**, R = Et

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