REFERENCES AND NOTES

1. For reviews, see: F. F. Crim, *Annu. Rev. Phys. Chem.* **35**, 657 (1984); H. Reisler and C. Wittig, *ibid.* **37**, 307 (1986).
2. R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.* **55**, 894 (1951); R. A. Marcus, *J. Chem. Phys.* **20**, 359 (1952); W. Forst, *Theory of Unimolecular Reactions* (Academic Press, New York, 1973).
3. G. Z. Whitten and B. S. Rabinovitch, *J. Chem. Phys.* **38**, 2466 (1963).
4. E. Abramson, R. W. Field, D. Imre, K. K. Innes, J. L. Kinsey, *ibid.* **83**, 453 (1985); W. F. Polik, D. R. Guyer, C. B. Moore, *ibid.* **92**, 3453 (1990); A. Geers, J. Kappert, F. Temps, W. Wiebrecht, *Ber. Bunsenges. Phys. Chem.* **94**, 1219 (1990); Y. S. Choi and C. B. Moore, *J. Chem. Phys.* **94**, 5414 (1991).
5. C. E. Dykstra, *Annu. Rev. Phys. Chem.* **32**, 25 (1981); C. W. Bauschlicher, S. R. Langhoff, P. R. Taylor, *Adv. Chem. Phys.* **77**, 103 (1990).
6. I.-C. Chen and C. B. Moore, *J. Phys. Chem.* **94**, 263 (1990).
7. ______, *ibid.*, p. 269.
8. The character of the excited state is mostly that of highly vibrationally excited ground singlet because of the overwhelming density of ground singlet states at these energies. The harmonic densities of vibrational states are 1.2×10^4 (S_0), 15 (S_1), and 60 (T_1) per cm^{-1} at 28,250 cm^{-1} above the S_0 zero point level.
9. W. D. Allen and H. F. Schaefer III, *J. Chem. Phys.* **89**, 329 (1988).
10. An upper limit for the density of CH_2CO states can be calculated by assuming that the first two rate constant steps represent two hindered rotor levels, which are each triply degenerate as a result of the electron spin. If this is the case, the density of CH_2CO states is 4.5×10^4 per cm^{-1} at 28,360 cm^{-1}, which is about four times the harmonic count.
11. S. J. Klippenstein and R. A. Marcus, *J. Chem. Phys.* **93**, 2418 (1990); W. H. Green, Jr., A. J. Mahoney, Q.-K. Zheng, C. B. Moore, *ibid.* **94**, 1961 (1991).
12. Supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under contract DE-AC03-76SF00098.

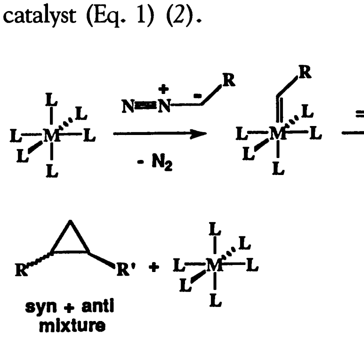
6 February 1992; accepted 21 April 1992

Mechanism of the Rhodium Porphyrin–Catalyzed Cyclopropanation of Alkenes

Jana L. Maxwell, Kathlynn C. Brown, David W. Bartley, Thomas Kodadek*

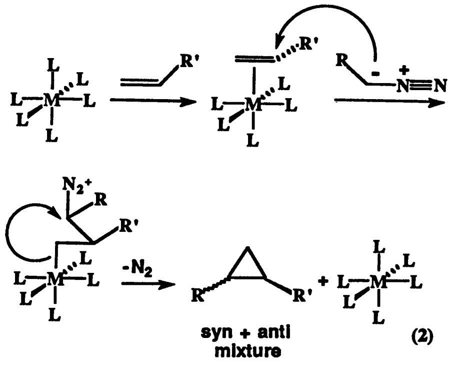
The rhodium porphyrin–catalyzed cyclopropanation of alkenes by ethyl diazoacetate (EDA) is representative of a number of metal-mediated cyclopropanation reactions used widely in organic synthesis. The active intermediate in these reactions is thought to be a metal carbene complex, but evidence for the involvement of metal-olefin π complexes has also been presented. Low-temperature infrared and nuclear magnetic resonance spectroscopies have been used to characterize a rhodium porphyrin–diazoalkyl adduct that results from the stoichiometric condensation of the catalyst and EDA. Optical spectroscopy suggests that this complex is the dominant steady-state species in the catalytic reaction. This compound decomposes thermally to provide cyclopropanes in the presence of styrene, suggesting that the carbene is indeed the active intermediate. Metal-alkene π complexes have also been detected spectroscopically. Kinetic studies suggest that they mediate the rate of carbene formation from the diazoalkyl complex but are not attacked directly by EDA.

The design of asymmetric catalysts for use in synthesis has emerged as one of the most important problems in modern organic chemistry because most biologically active compounds are chiral. Recently, there has been a great deal of interest in the development of metal-based asymmetric cyclopropanation catalysts (*1*) for the synthesis of pyrethroid insecticides, β-turn peptide mimics, and a number of other interesting compounds. We have concentrated on rhodium porphyrin catalysts and have developed moderately enantioselective systems for the cyclopropanation of alkenes by diazo esters. In order to rationally design more effective asymmetric pockets, it is important to understand in detail the mechanism of the reaction, including the nature of the reactive intermediates and the arrangement of atoms in the transition state. This will allow a rational positioning of groups in the chiral cavity to more effectively influence the approach of the prochiral substrate to the metal. Unfortunately, despite considerable investigation, many aspects of the mechanism of metal-catalyzed cyclopropanations remain unclear. Current speculation is that the catalyst reacts with the diazo compound to produce an electrophilic metal carbene that is subsequently attacked by the alkene to provide the cyclopropane and regenerate the catalyst (Eq. 1) (*2*).



(1)

However, a carbene complex has never been observed in a catalytic system (*3*). An alternative mechanism that has been discussed is nucleophilic attack of the diazo compound on a metal-alkene π complex (Eq. 2) (*4*).



(2)

Nucleophilic additions to metal-alkene complexes are common in organometallic chemistry (*5*), and π complexes have been characterized for some cyclopropanation catalysts (*4*). However, the precise role of these species is unclear. Other mechanisms are also possible. We report a mechanistic analysis of the rhodium porphyrin–catalyzed cyclopropanation of alkenes by ethyl diazoacetate (EDA) (*6*) that clarifies these matters. Our results, including the characterization of a reactive organometallic intermediate, provide strong evidence for the intermediacy of a metallocarbene and also reveal a novel role for the substrate as an axial ligand that moderates the rate of carbene formation when the catalyst has a labile ligand such as iodide.

In order to probe for the possible formation of a reactive rhodium porphyrin carbene, we investigated the stoichiometric reaction of EDA with a rhodium porphyrin in the absence of alkene. Addition of a slight excess of EDA to a CD_2Cl_2 solution of iodorhodium tetra(*p*-tolyl) porphyrin (RhTTPI) at −40°C results in a rapid, subtle color change and formation of a porphyrin-EDA adduct. The ^1H nuclear magnetic resonance (NMR) spectrum of this species exhibits a single set of resonances attributable to the protons of the EDA-derived fragment (Fig. 1). Each signal is shifted upfield relative to its position in EDA, demonstrating that these protons sit above the face of the aromatic macrocycle, which has a strong diamagnetic ring current. The proton α to the carbonyl carbon is a doublet, although a two-dimensional correlated (2-D COSY) spectrum shows that it is not coupled to any other proton. Therefore, the splitting is due to coupling

---

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712.

*To whom correspondence should be addressed.

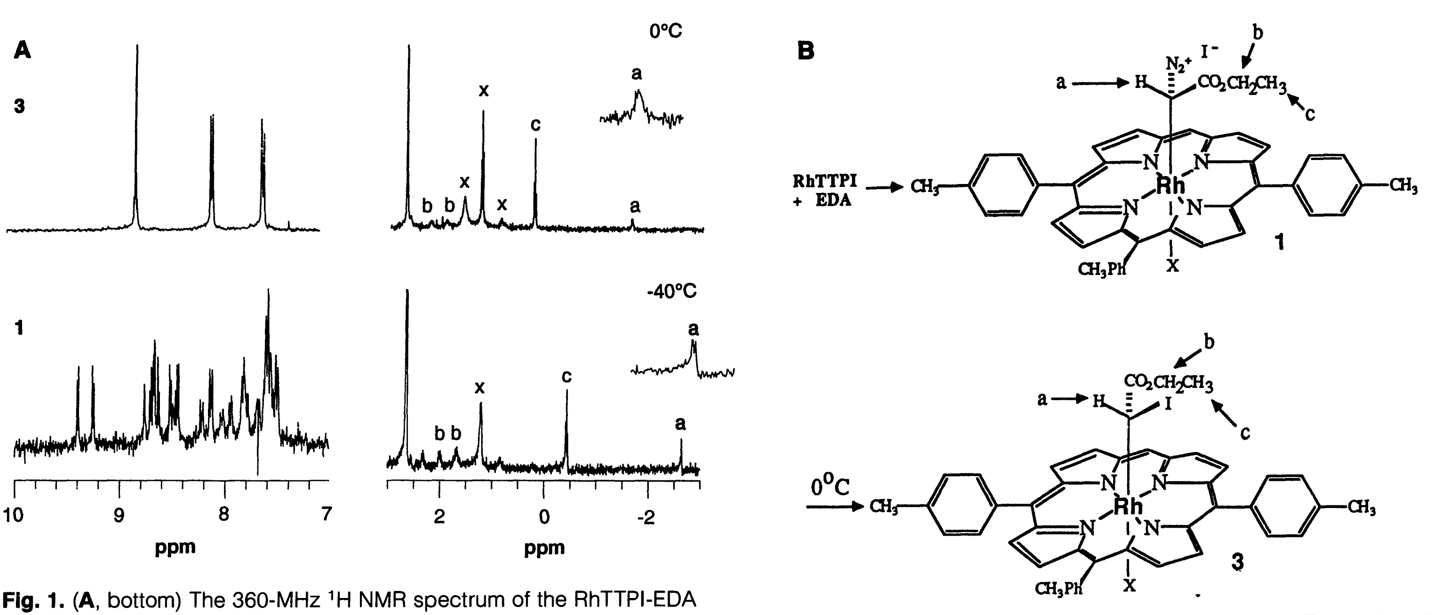
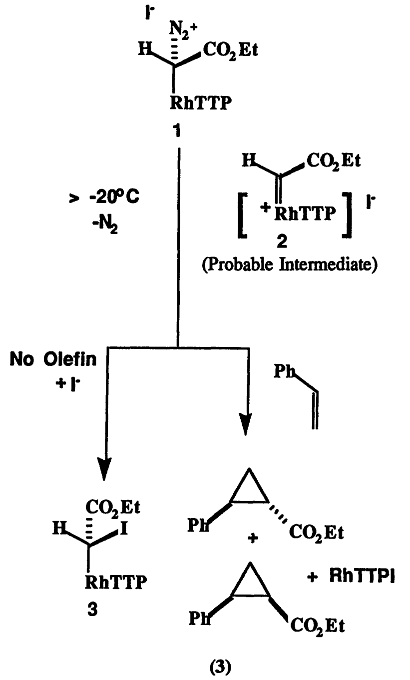


Fig. 1. (**A**, bottom) The 360-MHz ^{1}H NMR spectrum of the RhTTPI-EDA adduct at −40°C in CD_2Cl_2. The proposed structure, **1**, is shown in (**B**). Resonances due to impurities are denoted by "x". When **1** is warmed to 0°C, the upper spectrum in (A) is observed. This compound has been characterized as the iodoalkylrhodium porphyrin **3** (*9, 10*). Expansion of both spectra shows that the methine proton (a) is a doublet due to coupling with ^{103}Rh.

with ^{103}Rh (nuclear spin = 1/2, 100% abundance). The magnitude of the coupling constant (2.4 Hz) is almost identical to that observed for CH_3RhTTP (2.7 Hz), demonstrating that the porphyrin-EDA adduct has a metal-carbon bond. The methylene protons of the ester are diastereotopic, suggesting that the carbon α to the carbonyl group is a tetrahedral center. The β-pyrrolic and aromatic region of the spectrum is complex, showing that the product has lost the fourfold symmetry of the porphyrin starting material. The latter two observations are consistent with the adduct having the structure 1 (Fig. 1). This assignment is confirmed by two other experiments. When the reaction is carried out in a sealed, evacuated flask and the headspace is analyzed by gas chromatography, nitrogen evolution is not detected at −40°C (*7*). Second, the infrared spectrum of the porphyrin-EDA adduct–containing solution at −50°C exhibits a very strong band at 2338 cm^{-1}, confirming the presence of the diazo group (*8*).

The rhodium porphyrin–diazoalkyl complex 1 is unstable above about −20°C. When a solution of 1 is warmed to 0°C in the presence of 10 equivalents of styrene, a 68% yield of cyclopropanes results and 1 equivalent of nitrogen gas is released (Eq. 3). No reaction is observed at −40°C. The same result is obtained when the alkene is added before EDA. In the absence of added olefin, warming a solution of 1 above −20°C results in quantitative production of the iodoalkyl complex 3 (*9, 10*) with no observable intermediates (Fig. 1).

These data can be explained by postulating that warming adduct 1 results in ejection of molecular nitrogen to form the highly reactive carbene complex 2 (Eq. 3). In the presence of styrene, the carbene ligand is transferred rapidly to the olefin to yield cyclopropane. In the absence of substrate, I$^-$ attacks the metallocarbene at carbon to yield 3. This hypothesis is consistent with the observation that no reaction with styrene occurs below about −20°C, the temperature at which nitrogen evolution is observed in the absence of alkene. This view argues that metallocarbene formation is a necessary prerequisite for cyclopropanation and that the reaction does not occur by an S_N2-like displacement of N_2 by the alkene, which is strongly disfavored in any case because of the steric bulk of the macrocycle.



(3)

Is adduct 1 a catalytically relevant intermediate? Several lines of evidence suggest that it is. The ratio of syn to anti cyclopropyl esters produced in the stoichiometric cyclopropanation of styrene is 0.9, which is similar to that observed in the catalytic cyclopropanation of styrene under our standard conditions (1.0). Furthermore, the optical spectrum of a catalytic reaction in which styrene is used as the substrate and RhTTPI as the catalyst exhibits a Soret band at 413 nm, almost identical to that of many rhodium alkyl complexes (Fig. 2). The RhTTPI and RhTTPI-olefin complexes (see below) have different absorption maxima. This observation suggests that adduct 1 is the dominant steady-state intermediate in the catalytic reaction and that decomposition to carbene 2 is at least partially rate limiting. Therefore, although the metal carbene itself has so far escaped detection, the spectroscopic characterization and thermolysis chemistry of its immediate precursor 1 provide direct evidence for the intermediacy of such a species in a catalytic cyclopropanation reaction.

To further probe the mechanism of the reaction, we carried out kinetic analyses of the cyclopropanation of styrene and 1-decene by EDA in the presence of RhTTPI. As expected for a mechanism in which metal carbene formation is at least partially rate limiting, both reactions are first order in catalyst (not shown) and approximately first order in EDA concentration (Fig. 3) (*11*). The dependence of the rates on the alkene concentration is modest but nonetheless deviates significantly from ideal zero-order behavior. At all alkene concentrations examined, styrene is cyclopropanated more rapidly than 1-decene. These results are not expected for the simple mechanism in which RhTTPI and EDA react in the rate-limiting step to form the active carbene complex and the alkene is then cyclopropanated very rapidly. In that case, all alkenes should be cyclopropanated at the same rate, which should be independent of the substrate concentration. Therefore, the nature and concentration of the alkene must influence the rate of carbene formation.

As mentioned above, some catalytically active metals form alkene π complexes. If this is also the case for the rhodium porphyrins, the unusual kinetic parameters of the reaction could be due to axial ligation effects that allow the substrate to influence the rate of carbene formation. For example, it is possible that the alkene and EDA compete for a vacant coordination site or that the nature of an alkene ligand trans to the diazoalkyl group in intermediate 1 could accelerate the decomposition of this species to the carbene. These schemes are not mutually exclusive.

The compound RhTTPI does indeed form alkene π complexes (*12*). The ^{1}H NMR vinylic resonances of styrene alone and in the presence of one equivalent of RhTTPI are shown in Fig. 4, A and C. In the presence of the porphyrin, significant upfield shifts are observed, suggesting formation of an adduct in which the styrene protons are situated above the face of the macrocycle. Even when styrene is present in excess, a single set of vinylic resonances is observed, demonstrating that alkene binding is rapidly reversible on the NMR time scale. The binding is saturable, as shown by the titration curve in Fig. 4D. A calculated curve for a 1:1 porphyrin-alkene complex does not fit the experimental results, so we presume that a bis-alkene complex is also formed. The Soret band of RhTTPI shifts from 422 to 431 nm in the presence of excess alkene, also indicating formation of an olefin complex (Fig. 2). Similar results were obtained with aliphatic alkenes such as 1-hexene and 1-decene.

If alkene ligation does affect the rate of carbene formation from RhTTPI and EDA, then a rhodium porphyrin catalyst that forms alkene π complexes weakly should catalyze the cyclopropanation of styrene and 1-decene at nearly the same rate. To test this idea, we used CH_3RhTTP as the catalyst. The methyl ligand is not labile under the reaction conditions, and CH_3RhTTP-alkene complexes cannot be detected by ^{1}H NMR (Fig. 4B), indicating that the strong trans effect of the methyl group results in very weak alkene binding. The CH_3RhTTP-catalyzed cyclopropanations of 1-decene and styrene by EDA proceeded at 4.0 and 7.0

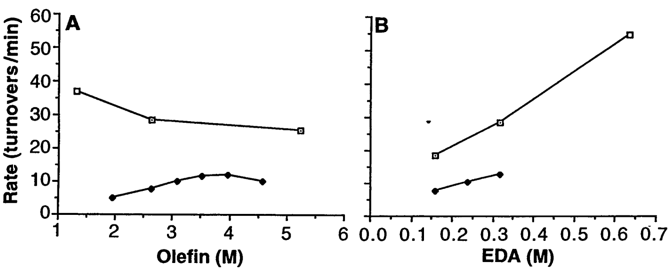
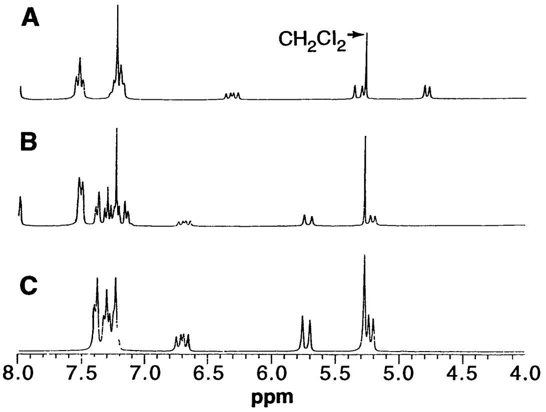


Fig. 3. The dependence of the rate of RhTTPI-catalyzed 1-decene and styrene cyclopropanation on (**A**) alkene and (**B**) EDA concentrations. The porphyrin concentration was 1.0 × 10^{-4} M in CH_2Cl_2. Each point represents the average of three runs; (◆), 1-decene, and (□), styrene.



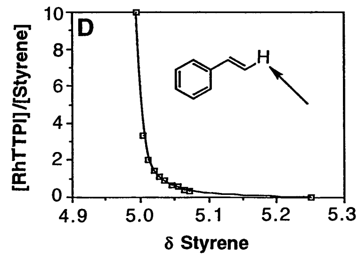


Fig. 4. Proton NMR spectroscopy reveals the formation of a RhTTPI-styrene complex. Shown are 500-MHz spectra of (**A**) RhTTPI + styrene, (**B**) CH_3RhTTP + styrene, and (**C**) styrene in $CDCl_3$. In each case the styrene and porphyrin concentrations are 2.4 × 10^{-2} M and 1.6 × 10^{-2} M, respectively. The presence of RhTTPI shifts the styrene vinylic resonances upfield, indicating formation of a complex. No shifts are observed in the presence of CH_3RhTTP, indicating that this porphyrin coordinates styrene very weakly. (**D**) The binding of styrene to RhTTPI is saturable. The plot shows the chemical shift of the vinylic proton trans to the phenyl ring at various prophyrin/styrene ratios. The experimental data are not fit by a calculated curve for a 1:1 complex, so presumably some bis-alkene complex is also formed.

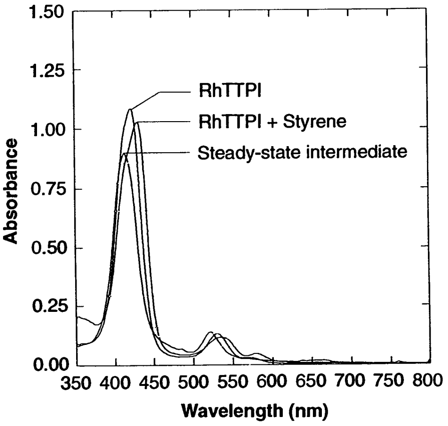
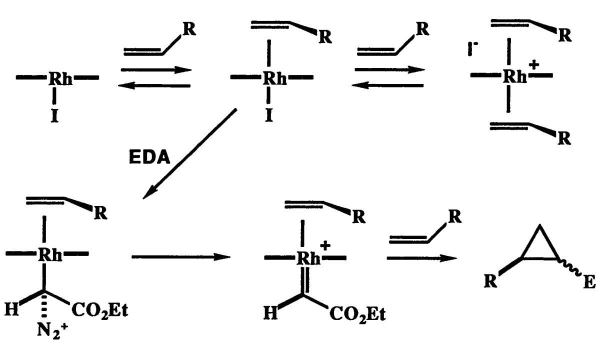


Fig. 2. Optical spectrum of RhTTPI, RhTTPI + styrene (10,000 equivalents), and RhTTPI + styrene (10,000 equivalents) + EDA (1,000 equivalents). In each case the porphyrin is 1 × 10^{-5} M in CH_2Cl_2 solvent at room temperature. The latter solution is representative of a typical catalytic cyclopropanation reaction. The spectra show that in the presence of styrene, the porphyrin forms an olefin complex but that during the catalytic reaction, this complex is not the dominant form of the catalyst. Rather, a species with λ_{max} = 413 nm is present. This value is typical of alkylrhodium porphyrins.



1-alkene

2-alkene

Fig. 5. Current mechanistic model for the RhTTPI-catalyzed cyclopropanation of alkenes by EDA. It is presumed that EDA reacts with the mono-olefin complex, because attack on the bis-olefin species would be sterically difficult. E = $CO_2CH_2CH_3$.

turnovers per minute, respectively. Under identical conditions, but with RhTTPI as the catalyst, the rates are 9.1 and 28.6 turnovers per minute, respectively, a larger difference between rates. Thus, the unusual kinetic behavior of the RhTTPI-catalyzed reactions can be attributed to the fact that the alkene acts as an axial ligand and influences the rate of metallocarbene formation (*13*). Our observation that a rhodium alkyl complex (perhaps the alkene complex of **1**) is the dominant steady-state intermediate in the catalytic reaction argues that the major effect is that of substrate acceleration of nitrogen ejection, but more work will be required to address this point rigorously. The fact that CH_3RhTTP is an efficient catalyst provides further evidence that nucleophilic attack on a metal-alkene complex (Eq. 2) is not an important reaction pathway.

Our current understanding of the catalytic cycle is summarized in Fig. 5. Our experiments strongly support the metallocarbene mechanism for metal-catalyzed cyclopropanation reactions. The direct precursor to a rhodium porphyrin carbene, the diazoalkyl complex **1**, has been characterized, and its thermal decomposition chemistry has been examined. Furthermore, kinetic and spectroscopic investigations have shown that alkene π complexes play a role in the catalytic process by influencing the rate of metallocarbene formation.

REFERENCES AND NOTES

1. A. P. Marchand and N. MacBrockway, *Chem. Rev.* **74**, 431 (1974); E. Wenkert, *Acc. Chem. Res.* **13**, 27 (1980); M. P. Doyle, in *Catalysis of Organic Reactions*, R. L. Augustine, Ed. (Dekker, New York, 1985), chap. 4; E. Wenkert, *Heterocycles* **14**, 1703 (1980); H. Fritschi, U. Leutenegger, A. Pfaltz, *Angew. Chem. Int. Ed. Engl.* **25**, 1005 (1986); R. E. Lowenthal, A. Abiko, S. Masamune, *Tetrahedron Lett.* **42**, 6005 (1990); D. A. Evans, K. A. Worpel, M. M. Hinman, *J. Am. Chem. Soc.* **113**, 726 (1991); M. P. Doyle *et al.*, *Tetrahedron Lett.* **46**, 6613 (1990); M. P. Doyle *et al.*, *J. Am. Chem. Soc.* **113**, 1423 (1991); J. L. Maxwell, S. O'Malley, K. C. Brown, T. Kodadek, *Organometallics* **11**, 645 (1992).
2. M. P. Doyle, *Chem. Rev.* **86**, 919 (1988).
3. Metal carbenes that cyclopropanate alkenes stoichiometrically are known. For a review, see M. Brookhart and W. B. Studabaker, *ibid.* **87**, 411 (1987).
4. D. S. Wulfman, R. S. McDaniel, B. W. Peace, *Tetrahedron* **32**, 1241 (1976); R. G. Salomon and J. K. Kochi, *J. Am. Chem. Soc.* **95**, 3300 (1973); A. J. Anciaux, J. A. Hubert, A. F. Noels, N. Petiniot, P. Teyssie, *Tetrahedron Lett.* **1973**, 2233 (1973); A. Nakamura, T. Koyama, S. Otsuka, *Bull. Chem. Soc. Jpn.* **51**, 593 (1978); A. Nakamura, A. Konishi, R. Tsujitani, M. Kudo, S. J. Otsuka, *J. Am. Chem. Soc.* **100**, 3449 (1978).
5. J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry* (University Science, Mill Valley, CA, 1987), pp. 825–858.
6. H. J. Callot, F. Metz, C. Piechocki, *Tetrahedron* **38**, 2365 (1982).
7. When equimolar amounts of EDA and RhTTPI were mixed at 25°C in an evacuated flask and the solution was then cooled to −40°C, analysis of the headspace by gas chromatography revealed the presence of 1 equivalent of nitrogen gas.
8. The band corresponding to the diazo stretch in EDA is located at 2335 cm^{-1} (CH_2Cl_2 solution sandwiched between CaF_2 plates). This is different from the value observed with NaCl plates (2115 cm^{-1}). The position of the diazo stretch in the EDA-porphyrin complex is in the range expected for a transition metal–alkyldiazonium complex [see H. Konig, M. J. Menu, M. Dartiguenave, Y. Dartiguenave, H. F. Klein, *J. Am. Chem. Soc.* **112**, 5351 (1990), and references therein for a description of related metal-diazoalkyl species].
9. H. J. Callot and J. Schaeffer, *J. Chem. Soc. Chem. Commun.* **1978**, 937 (1978).
10. J. L. Maxwell and T. Kodadek, *Organometallics* **10**, 4 (1991).
11. Like most metal-catalyzed cyclopropanation reactions, the rhodium porphyrin–catalyzed reaction produces some carbene dimers (cis and trans isomers of $EtO_2CCH{=}CHCO_2Et$; Et, ethyl). We presume that these products result from nucleophilic attack by EDA on the metallocarbene, a reaction that competes with carbene transfer to the alkene. As the EDA concentration is increased or the alkene concentration is reduced, the ratio of dimer product to cyclopropane grows. Because formation of the carbene dimer consumes 2 equivalents of EDA, the rate of the cyclopropanation reaction will deviate somewhat from ideal first-order behavior. The differences in the apparent rates of cyclopropanation of styrene and 1-decene are not due simply to differences in selectivity (moles of cyclopropane per moles of EDA consumed). The rates presented in the text have been corrected for differences in the selectivity.
12. Porphyrin metal-alkene and metal-alkyne π complexes have been characterized for other metals. L. K. Woo, J. A. Hays, R. A. Jacobson, C. L. Day, *Organometallics* **10**, 2102 (1991); J. P. Collman, P. J. Brothers, L. McElwee-White, E. Rose, *J. Am. Chem. Soc.* **107**, 6110 (1985); J. P. Collman, C. E. Barnes, L. K. Woo, *Proc. Natl. Acad. Sci. U.S.A.* **80**, 7684 (1983).
13. Because the ester and diazo substituents of **1** are highly electron withdrawing, the $CH(N_2)^+(CO_2Et)$ ligand is expected to have a much more modest trans effect than the methyl group. Therefore, we expect that **1** can also form alkene complexes.
14. Supported by American Chemical Society–Petroleum Research Fund grant 24052-AC1. T.K. also acknowledges the American Cancer Society for a Junior Faculty Research Award. We thank T. Mallouk for the use of his gas chromatograph and infrared spectrometer and M. Darensbourg for the loan of a low-temperature infrared cell.

18 February 1992; accepted 21 April 1992

Glassy Microspherules (Microtektites) from an Upper Devonian Limestone

Kun Wang

The properties of microspherules recovered from an Upper Devonian marine limestone immediately overlain by a geochemical anomaly of siderophile and chalcophile elements are similar to those of impact-derived microtektites. These microspherules are glass, have splash-form shapes, contain spherical vesicles and lechatelierite inclusions, and show oxide compositional variations similar to those in known microtektites. These characteristics suggest that these Upper Devonian microspherules have an impact origin. A bolide impact may have occurred about 365 million years ago on the South China Plate and caused a faunal extinction on eastern Gondwana.

Recognition of ancient bolide impacts and their influence on biota is important for understanding the evolution of Earth and its biosystem. Signatures of an impact in the pre-Cenozoic rock record are difficult to recognize because of their long history. Microspherules were discovered in a marine limestone from the Upper Devonian conodont lower *Palmatolepis crepida* zone in South China (*1*). Chemostratigraphic and paleontological studies indicate that a geochemical anomaly, a negative carbon isotope excursion, and a brachiopod faunal turnover are associated with the occurrence of the microspherules in South China (Figs. 1 and 2) (*2*). Geochemical anomalies (iridium and carbon isotope) were found in the same conodont zone in Western Australia (*3*). On the basis of these results and the presence of a probable Late Devonian impact crater under Taihu Lake in South China (Fig. 1) (*4*), we propose that a bolide impact occurred about 365 million years ago on the South China Plate and probably caused a regional extinction in the Southern Hemisphere (eastern Gondwana) (*2*). In this paper, I describe glassy microspherules from South China and provide evidence that they are of impact origin.

Microspherules were recovered from a marine limestone that is immediately below a geochemical anomaly that occurs in a 3-cm-thick claystone between the Shetianqiao and Xikuangshan formations at Qidong, Hengyang, Hunan Province, South China (Figs. 1 and 2). The Qidong section, exposed in a quarry behind an elementary school about 1.5 km east of the center of the small town, was sampled when the quarry was being mined by local residents for paving stones. Samples from 25 stratigraphic horizons were collected over a 20-m span along a fresh exposure of the section. The samples were cleaned and then dissolved in 10% acetic acid. Conodonts and microspherules were picked from the 60- to 250-μm size fraction of the sieved residues. Microspherules were found only in the residues from one

---

Department of Geology, University of Alberta, Edmonton, Alberta, Canada T6G 2E3.