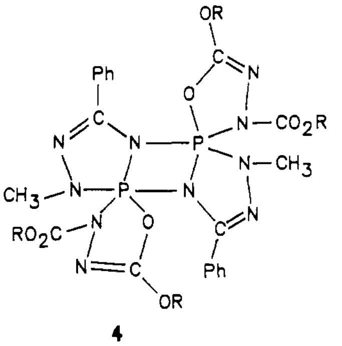
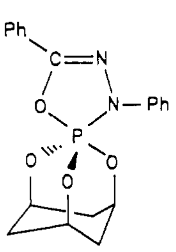


4

R = Me, Et, iPr, CH_2Ph



5

phorus-containing ligand, which is attached to the iron center by an Fe–P single bond of 2.241 (2) Å.[6] The exocyclic P–P bond distance [2.074 (3) Å] is comparable to the P–P bond [2.064 (2) Å] in I ($R^1 = R^2 = H$). The atoms Fe, P(1), P(2), and C(24) are no longer located in the same plane as is the case for educt 1 [torsion angle Fe–P(1)–P(2)–C(24) = 163.7°]. The tetracoordinate phosphorus atom P(1) is part of a planar oxadiazaphospholene ring.

The bond lengths P(1)–N(2) [1.744 (6) Å] and P(1)–O(3) [1.709 (5) Å] are attributed to single bonds (calculated values are 1.76 and 1.72 Å, respectively).[7]

In I the P—O distance was determined to be 1.703 (5) Å. The endocyclic C═N bond [1.266 (9) Å] is close to the value of the C═N double bond in **5** [1.289 (7) Å].[8] The CO bond lengths C(3)–O(3) [1.349 (10) Å] and C(3)–O(4) [1.322 (9) Å] are significantly shorter than C(7)–O(5) [1.449 (11) Å] and C(4)–O(4) [1.443 (12) Å], which agrees with the π-conjugation of oxygen lone pairs to C(3).

Acknowledgment. Our work was generously supported by the Deutsche Forschungsgemeinschaft, Bonn, Germany, the Fonds der Chemischen Industrie, Frankfurt, Germany, and BASF AG, Ludwigshafen, Germany. This assistance is gratefully acknowledged.

Supplementary Material Available: Listings giving a structure determination summary, atomic positional parameters, bond lengths and angles, and anisotropic thermal parameters (8 pages); a table of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

---

[6] Crystal data for complex **3a**: space group $P\bar{1}$, a = 9.863 (3) Å, b = 13.884 (3) Å, c = 14.484 (4) Å, α = 82.72 (2)°, β = 84.85 (3)°, γ = 81.82 (2)°, V = 1942.2 (10) Å^3, Z = 2, ρ_{calcd} = 1.246 g/cm^3, Mo Kα (graphite monochromator, λ = 0.71073 Å), ω scan data collection at room temperature (4.0° ≤ 2θ ≤ 48.0°), 6064 unique reflections, 4134 unique observed reflections ($F > 4.0\sigma(F)$) Siemens R3m/V four-circle diffractometer, structure solved by direct methods and refinement by full-matrix least squares, with use of the Siemens SHELXTL PLUS software on a Micro VAX II computer. All non-hydrogen atoms were refined anisotropically with 424 parameters (hydrogen atoms in calculated positions riding on the corresponding C atoms; U(H) = 0.08 Å^2). R = 0.093, R_w = 0.0795, $w^{-1} = \sigma^2(F) + 0.0002F^2$, maximum rest electron density 0.5 e/Å^3.

[7] Holleman-Wiberg. *Lehrbuch der Anorganischen Chemie*, 81st–90th ed.; de Gruyter: Berlin, New York, 1976; p 129.

[8] Hamilton, W. C.; Ricci, S., Jr.; Ramirez, F.; Kramer, L.; Stern, P. *J. Am. Chem. Soc.* **1973**, *95*, 6335.

Organometallic Chemistry of Porphyrins: Spectroscopic and Chemical Characterization of a Rhodium Porphyrin–Ethyl Diazoacetate Adduct

Jana Maxwell and Thomas Kodadek*

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

Received September 24, 1990

Summary: Iodorhodium(III) tetra-*p*-tolylporphyrin and ethyl diazoacetate (EDA) yield a 1:1 adduct possessing a metal–carbon bond. The ^{13}C and ^1H NMR spectra of this species suggest that it is a novel iodoalkyl complex resulting from formal insertion of the carbene fragment into the Rh–I bond. This and related species are of interest with regard to their potential roles in the rhodium porphyrin catalyzed cyclopropanation of alkenes by EDA.

Callot and co-workers have reported that Rh(III) porphyrins efficiently transfer carbene fragments derived from diazo esters to simple olefins.[1] These porphyrin-catalyzed cyclopropanations are unusual in a number of ways. They provide predominantly syn products when macrocycles with bulky substituents are employed, demonstrating that the carbene transfer step occurs within the porphyrin pocket and is not the result of the formation of free organic carbenes. More typical catalysts generally produce the anti isomer as the major product. In addition, the metal is in the 3+ oxidation state rather than the usual 2+ of common catalysts such as $Rh_2(OAc)_4$. We[2] and Callot[1] have also demonstrated that the porphyrin catalysts exhibit interesting substrate shape selectivity. For example, cis-disubstituted alkenes are somewhat more reactive than the trans isomers and tetrasubstituted alkenes are very poor substrates, allowing selective cyclopropanation of monosubstituted double bonds, a preference that may be useful synthetically. Finally, the small amount of work done in the area of porphyrin organometallic chemistry[3] has shown that the unique geometry and electronic properties of the macrocycle can lead to unusual reaction pathways.[4,5] Therefore, we have undertaken a mechanistic study of this reaction, including an analysis of the organometallic chemistry that ensues when EDA and rhodium porphyrins are allowed to react in the absence of alkene.

Iodorhodium tetra-*p*-tolylporphyrin (Rh(TTP)I; 0.1 mol %) efficiently catalyzes the reaction between styrene and ethyl diazoacetate (EDA) (10:1 molar ratio) at room temperature, providing a 98% yield (based on EDA) of the syn and anti cyclopropanes in 50 min. In order to address the chemical nature of the active intermediate in this system, we examined the stoichiometric reaction between Rh(TT-

---

[1] Callot, H. J.; Metz, F.; Piechoki, C. *Tetrahedron* **1982**, 2365.

[2] Maxwell, J.; O'Malley, S.; Brown, K.; Kodadek, T. *J. Am. Chem. Soc.*, submitted for publication.

[3] Brothers, P. J.; Collman, J. P. *Acc. Chem. Res.* **1986**, *19*, 209.

[4] Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333.

[5] Collman, J. P.; McElwee-White, L.; Brothers, P. J.; Rose, E. *J. Am. Chem. Soc.* **1986**, *108*, 1332.

0276-7333/91/2310-0004$02.50/0

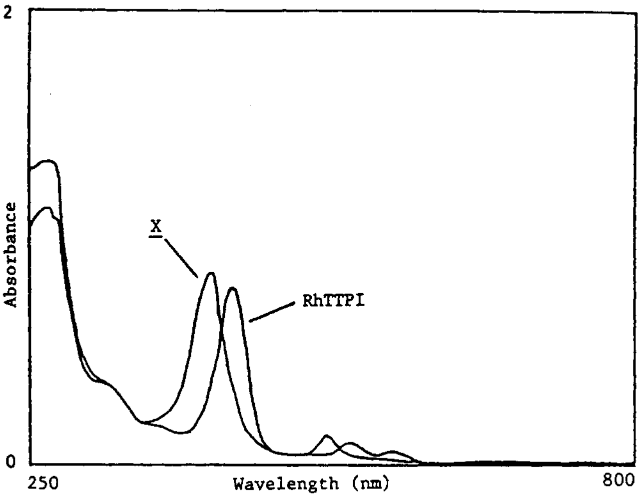


Figure 1. Optical spectra of Rh(TTP)I and adduct X.

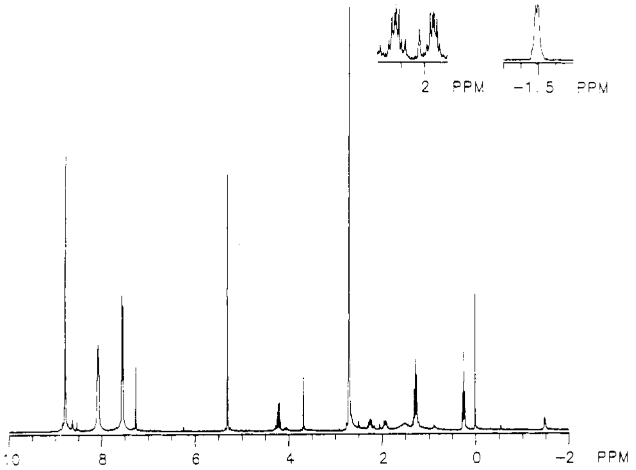


Figure 2. ^1H NMR spectrum (300 MHz) of X. The peaks at 1.3, 3.7, and 4.25 ppm are due to free EDA. The small signal at -0.55 ppm is due to a trace of a new compound that arises from decomposition of X. Insert: diastereotopic methylene protons and the proton α to the carbonyl group, which is split by rhodium.

P)I and a slight excess of EDA in the absence of olefin at room temperature (eq 1). Gas evolution is observed, and

$$\mathrm{Rh(TTP)I} + \mathrm{N_2CHCO_2C_2H_5} \xrightarrow{-\mathrm{N_2}} \mathrm{X} \qquad (1)$$

a new species, X, forms rapidly, as evidenced by the resulting optical spectrum (Figure 1). The *proton-decoupled* ^{13}C NMR spectrum of X exhibits a *doublet* at 143 ppm (see the supplementary material). The ^1H NMR spectrum of the EDA/porphyrin adduct (Figure 2) features a low-field doublet at -1.50 ppm that is *not coupled to any other protons*, as shown by a 2-D COSY spectrum (see the supplementary material). These couplings must be due to the rhodium atom (^{103}Rh, 100% abundance, $I = {}^1/_2$) and demonstrate that X has a metal-carbon bond.

Also of significance in the proton spectrum is the appearance of a single β-pyrrolic resonance at 8.78 ppm, showing that the macrocycle retains 4-fold symmetry on the NMR time scale. An apparent triplet corresponding to the methyl group of the ester is observed at 0.25 ppm, which is coupled to the *magnetically distinct* doublets of quartets at 1.90 and 2.25 ppm, respectively, as shown by a 2-D COSY spectrum. All of these signals are shifted upfield relative to their positions in EDA, suggesting that they are sitting above the macrocycle and are affected by its diamagnetic ring current. The observation of diastereotopic methylene protons indicates that the carbon α to the carbonyl carbon is a tetrahedral center.

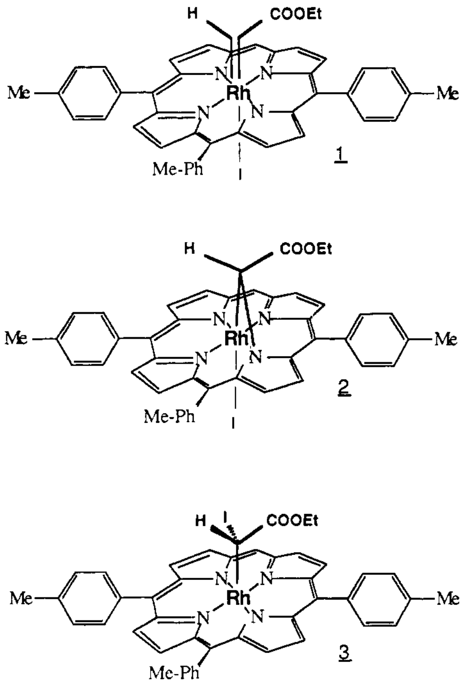


Figure 3. Possible structures for the EDA-porphyrin adduct X. The rear aryl rings are omitted for clarity.

The FAB mass spectrum exhibits a molecular ion of mass 984, consistent with the formulation RH(TTP)I-($CHCO_2CH_2CH_3$). Adduct X is stable for more than 1 h at room temperature and indefinitely when cooled to -78 °C.

Some chemical properties of X are also instructive. When care is taken to employ *exactly* 1 equiv of EDA in the formation of adduct X, subsequent addition of a large excess of styrene does *not* result in cyclopropane formation, demonstrating that it is not the active intermediate in the catalytic reaction. When these solutions are examined by ^1H NMR spectroscopy, significant upfield shifts for all of the vinyl protons are observed (see the supplementary material), suggesting the formation of a labile olefin π-complex[6] and indicating that metalloporphyrin X retains a vacant coordination site.

We have considered three chemically reasonable structures for the EDA/porphyrin adduct X (Figure 3). Carbene 1 was an obvious possibility, since these types of compounds are generally assumed to be the active species in metal-catalyzed cyclopropanation reactions,[7] though they have never been isolated. However, the inertness of X toward styrene and the observation of diastereotopic methylene protons tend to rule out this formulation.[8] A related possibility is the bridging carbene 2.[9] However,

---

(6) We have observed similar upfield shifts in solutions containing only Rh(TTP)I and olefin (Maxwell, J.; Kodadek, T. Unpublished observations). The vinyl signals of styrene for the Rh(TTP)I olefin π-complex are shifted upfield more strongly than they are in the X-styrene complex, indicating that the trans ligand in X is less electron withdrawing than iodide.

(7) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919.

(8) The methylene protons would be inequivalent, however, if rotation about the carbene-carbonyl bond were slow. In addition, the symmetry of the metal porphyrin orbitals would lead one to predict that the barrier for rotation about the metal-carbon double bond would be very low, allowing for rapid rotation. Therefore, we cannot completely rule out structure 1 on spectroscopic grounds. However, its lack of reactivity with styrene makes this formulation very unlikely.

(9) Several examples of the bridging carbene are known: Chevrier, B.; Weiss, R. *J. Am. Chem. Soc.* **1976**, *98*, 2985. Johnson, A. W.; Ward, D.; Batten, P.; Hamilton, A. L.; Shelton, G.; Elson, C. M. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2076.

this structure lacks the symmetry indicated by the NMR data. We have also considered the possibility that the bridging carbene might isomerize rapidly between the four possible isomeric forms. However, given the observation of diastereotopic methylene hydrogens, such a process would have to occur with retention of stereochemistry at the carbene carbon. It is difficult to see why this would be the case. Therefore, we currently favor structure **3**, an iodoalkyl complex, which best fits all of the data in hand. **3** could be imagined to arise via initial displacement of iodide by EDA, followed by loss of nitrogen and recombination of iodide at carbon. Alternatively, a direct insertion mechanism is not out of the question.[10,11] Assuming rapid rotation about the metal–alkyl bond, structure **3** is consistent with all of the spectroscopic data and rationalizes both the lack of carbene transfer to styrene and the observation of a vacant coordination site available for olefin π-complex formation. To date, we have not been able to obtain an X-ray crystal structure of adduct X to confirm this hypothesis. These efforts are continuing.

We have recently discovered that X is not the kinetic product of the reaction between EDA and the rhodium porphyrin. Mixing these species at −40 °C rather than room temperature produces a different compound that isomerizes to X above −20 °C. Studies directed toward further characterizing these interesting organometallic porphyrin complexes and elucidating their potential roles in the catalytic cyclopropanation reaction are underway.

Acknowledgment. We thank the Texas Advanced Research Program for support. T.K. also acknowledges the American Cancer Society for providing a Junior Faculty Research Award.

Supplementary Material Available: Figures showing the ^{13}C and 2-D COSY ^{1}H NMR spectra of X and the ^{1}H NMR spectrum of X + styrene (3 pages). Ordering information is given on any current masthead page.

---

(10) This would presumably require cis coordination sites, which are generally assumed not to be available in metalloporphyrin complexes. However, some complexes with two ligands on the same face of the macrocycle are known: Lecomte, C.; Protas, J. *J. Chem. Soc., Chem. Commun.* **1976**, 434. Ledon, H.; Bonnet, M. *J. Chem. Soc., Chem. Commun.* **1979**, 702. Mentzen, B. F.; Bonnet, M. C.; Ledon, H. J. *Inorg. Chem.* **1980**, *19*, 2061.

(11) There is precedent for apparent insertion of organic moieties into a rhodium porphyrin–halide bond: Ogoshi, H.; Setsune, J.-I.; Nanbo, Y.; Yoshida, Z.-I. *J. Organomet. Chem.* **1978**, *159*, 329.

Photochemically Enhanced Carbon–Carbon Bond-Forming Reaction between CS_2 and $[W(CO)_5CH_3]^-$. X-ray Structure of $[PPN][W(CO)_4(\eta^2\text{-}S_2CCH_3)]$

Donald J. Darensbourg,* Holly P. Wiegreffe, and Joseph H. Reibenspies

Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received July 17, 1990

Summary: The reaction between carbon disulfide and $[W(CO)_5CH_3]^-$ has been found to be greatly accelerated in the presence of UV light, with the quantitative formation of $[W(CO)_4(\eta^2\text{-}S_2CCH_3)]^-$. This complex is prepared alternatively by photolysis of the $[W(CO)_5S_2CCH_3]^-$ complex, which was prepared from the thermal reaction of $[W(CO)_5CH_3]^-$ and CS_2. The chelating dithioacetate derivative of tungsten has been characterized as its $[PPN]^+$ salt by single-crystal X-ray diffraction. A rapid photochemical reaction between carbon dioxide and $[W(CO)_5CH_3]^-$ has been observed as well, but with the exclusive production of the formate complex $[W(CO)_5O_2CH]^-$.

The carboxylation of transition-metal alkyls to yield the corresponding metal carboxylates is an important reaction in the reduction chemistry of carbon dioxide (eq 1).[1] It has previously been established that the carboxylation of metal alkyls or aryls has a much higher barrier to reaction than insertion of CO_2 into metal–hydride bonds.[2] Indeed when both phenyl and hydride functionalities appear on the same metal center, carboxylation occurs exclusively at the hydride bond (eq 2).[3]

$$[MR]^- + CO_2 \rightarrow [MO_2CR]^- \qquad (1)$$

$$trans\text{-}(H)Ni(Ph)(PCy_3)_2 + CO_2 \rightarrow trans\text{-}(HCO_2)Ni(Ph)(PCy_3)_2 \qquad (2)$$

Relevant to efforts aimed at enhancing the rate of CO_2 insertion into metal–carbon bonds, Cooper and Johnston have communicated the first photochemically activated CO_2 insertion into a transition-metal–carbon bond (eq 3).[4]

$$(Cp)_2Ti(CH_3)_2 + CO_2 \xrightarrow{h\nu} (Cp)_2Ti(CH_3)(O_2CCH_3) \qquad (3)$$

Although reaction 3 does not take place at ambient temperature in the absence of light, it does occur at elevated temperatures.[5] Similarly, Sullivan and Meyer have reported the photoinduced insertion of CO_2 into the metal–hydride bond of *fac*-Re(2,2′-bipyridine)$(CO)_3H$ to provide *fac*-Re(2,2′-bipyridine)$(CO)_3O_2CH$.[6] The reaction period for the analogous thermal process is reduced from 5 h to 10 min with irradiation. Others have reported the

---

(1) (a) Walther, D. *Coord. Chem. Ref.* **1987**, *79*, 135. (b) Behr, A. In *Catalysis in C_1 Chemistry*; Keim, W., Ed.; Reidel: Dordrecht, The Netherlands, 1983; p 169. (c) Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79. (d) Darensbourg, D. J.; Kudaroski, R. *Adv. Organomet. Chem.* **1983**, *22*, 129. (e) Ito, T. T.; Yamamoto, A. In *Organic and Bioorganic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Kodonsha: Toyoko, Japan, 1982; p 79. (f) Palmer, D. A.; van Eldik, R. *Chem. Rev.* **1983**, *83*, 651. (g) Sneeden, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 8, p 225. (h) Kolomnikov, I. S.; Grigoryan, M. Kh. *Russ. Chem. Rev. (Engl. Transl.)* **1978**, *47*, 334. (i) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (j) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: Weinheim, West Germany, 1988; p 26.

(2) Darensbourg, D. J.; Kudaroski, R.; Bauch, C. G.; Pala, M.; Simmons, D. J.; White, J. N. *J. Am. Chem. Soc.* **1985**, *107*, 7463.

(3) Darensbourg, D. J.; Darensbourg, M. Y.; Goh, L. Y.; Ludvig, M.; Wiegreffe, P. *J. Am. Chem. Soc.* **1987**, *109*, 7539.

(4) Cooper, J. C.; Johnston, R. F. *Organometallics* **1987**, *6*, 2448.

(5) Kolomnikov, I. S.; Lobeeva, T. S.; Vol'pin, M. E. *Zh. Obshch. Khim.* **1972**, *42*, 2232.

(6) Sullivan, P. B.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1984**, *106*, 1244.