$\Delta M(t) = M(t) - M^{eq}$, and **K** is a combined exchange and relaxation matrix. The ethylene and hydride data sets are then fit to solutions of eq 2 by standard iterative procedures to obtain the exchange rate k and relaxation times (T_1).[13]

The response of the hydride at several different temperatures to selective inversion of coordinated ethylene is depicted in Figure 1 along with theoretical curves obtained from the above analysis. The associated rate parameters are listed in Table I. No magnetization transfer is observed to free ethylene (if present), and the observed exchange rates are independent of ethylene up to 50 psig. Similarly, there is no dependence of the measured rate on added phosphine (P-*i*-Pr$_3$, 25-fold excess) or concentration of rhodium complex **1** (0.10 M to 0.005 M). These results suggest that the insertion is entirely intramolecular and provide a contrast to the associative mechanisms proposed for insertion in the isoelectronic *trans*-HPt(C$_2$H$_4$)(PEt$_3$)$_2^+$.[14]

Further insight into the mechanism of insertion is derived from IR solution studies which reveal two peaks assigned as Rh–H stretching frequencies at 2005 (major, trans) and 2042 cm^{-1} (ca. 3:1). This observation is consistent with a rapid equilibrium between cis and trans species ($\Delta G°$(25 °C) $\approx$ 0.5 kcal/mol) since ethylene is expected to have a greater "trans effect" than phosphine.[15] The assignment is substantiated by variable-temperature ^{31}P NMR below −40 °C. The initially sharp doublet reaches coalescence at −100 °C, and the slow exchange limit near −130 °C consists of A$_2$X and ABX patterns assigned to trans and cis complexes, respecitvely.[16] Isomerization is sufficiently rapid that ^{1}H, ^{13}C, and ^{31}P NMR spectra above −40 °C represent a fast exchange average.

The mechanism that has been determined (eq 3) leads to a rate

$$\textit{trans}\text{-HRh}(\text{C}_2\text{H}_4)(\text{P-}i\text{-Pr}_3)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \textit{cis}\text{-HRh}(\text{C}_2\text{H}_4)(\text{P-}i\text{-Pr}_3)_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{EtRh}(\text{P-}i\text{-Pr}_3)_2 \quad (3)$$

expression that relates the observed exchange rate k to the insertion rate k_2 (eq 4; $K = k_1/k_{-1}$). The activation parameters for insertion

$$k_2 = \frac{3k}{2(K - k/k_{-1})} \quad (4)$$

from the cis olefin hydride are therefore calculated[17] and constitute the first elements of the reaction coordinate for insertion in this system: $\Delta G^{\ddagger}$ = 12.3 kcal/mol, $\Delta H^{\ddagger}$ = 13.0 kcal/mol, and $\Delta S^{\ddagger}$ = −2 eu.

In summary, we have presented evidence for intramolecular olefin insertion in a *trans*-rhodium(I) olefin hydride by way of a cis intermediate. While the ease of isomerization is surprising, the insertion barrier in four-coorindate d^8 complexes is expected to be relatively small if the phosphine ligands bend together during the insertion process.[18] The propylene hydride analogous to **1** is being investigated currently.

Acknowledgment. I am indebted to D. L. Thorn for assistance in the preparation of the dinitrogen-containing starting material. The excellent technical assistance of G. W. Watunya is gratefully acknowledged.

---

[13] Details of the analysis will be presented elsewhere.

[14] Clark, H. C.; Jablonski, C.; Halpern, J.; Mantonvani, A.; Weil, T. A. *Inorg. Chem.* **1974**, *13*, 1541–1543.

[15] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley: New York, 1980; p 1200.

[16] ^{31}P NMR (0.02 M in pentane–(C$_2$D$_5$)$_2$O at −130 °C) δ 69.01 (d, $^1J_{RhP}$ = 151 Hz), 70.18 and 58.62 (dd, $^1J_{RhP}$ = 150, 153, $^2J_{PP}$ = 193 Hz).

[17] Rates derived from ^{1}H NMR line shape (0–20 °C) are included in the estimate. A factor of $^2/_3$ arises since insertion brings about exchange only $^2/_3$ of the time. While a complete description[13] will include ^{31}P-exchange analysis, the temperature dependence of K appears to be small given the agreement between room-temperature IR and low-temperature NMR results: $K \approx 0.4$ and $k_{-1} >> k$.

[18] Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079–2090.

A New Model for the Study of Multistep Electron Transfer in Photosynthesis

Shinji Nishitani, Nobuyuki Kurata, Yoshiteru Sakata,* and Soichi Misumi

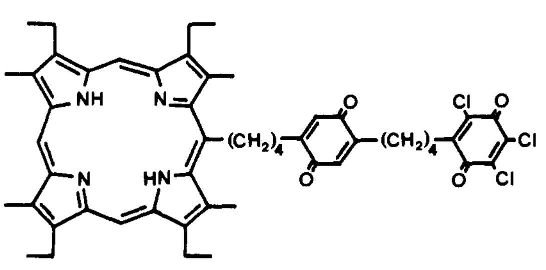
The Institute of Scientific and Industrial Research
Osaka University, Mihogaoka
Ibaraki, Osaka 567, Japan

Akiya Karen, Tadashi Okada, and Noboru Mataga*

Department of Chemistry
Faculty of Engineering Science, Osaka University
Toyonaka, Osaka 560, Japan

Received May 17, 1983

Various acceptor-linked porphyrins have so far been prepared[1] in order to understand the mechanism of the first critical electron-transfer reaction in photosynthesis. However, no model compound has been known to mimic the in vivo photoinduced multistep electron transfer, which is believed, on the basis of recent picosecond spectroscopic studies,[2] to be responsible for the stable, highly efficient charge separation. We now report on the first model for the multistep electron transfer, P4Q4Q′, where two types of quinone rings are connected in series to etioporphyrin, so as to produce an engineered gradient of redox potential in the molecule.



P4Q4Q′

The Wittig reaction of 2,5-dimethoxycinnamaldehyde[3] and phosphonium bromide **1**, prepared via two steps from 3,4,6-trichloro-2,5-dimethoxytoluene,[4] gave quantitatively butadiene **2**,[5] which was convereted to **3** by hydrogenation over Pd–C. The Rieche reaction of **3** was carried out with dichloromethyl methyl ether and titanium tetrachloride in CH$_2$Cl$_2$ at room temperature to give aldehyde **4** in 74% yield. Condensation of **4** with phosphonium salt **5**[6] followed by hydrogenation over Pd–C and by deprotection with acid gave **6** in 71% yield. Aldehyde **6** was condensed with benzyl 3-ethyl-4-methylpyrrole-2-carboxylate[7] in the presence of *p*-TsOH to give **7** in 85% yield. Catalytic hydrogenation of **7** over 10% Pd–C gave quantitatively 8, which was coupled with 4,4′-diethyl-5,5′-diformyl-3,3′-dimethyl-2,2′-

---

[1] (a) Tabushi, I.; Koga, N.; Yanagita, M. *Tetrahedron Lett.* **1979**, *20*, 257. (b) Dalton, J.; Milgrom, L. R. *J. Chem. Soc., Chem. Commun.* **1979**, 609. (c) Boxer, S. G.; Bucks, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 1883. (d) Kong, J. L. Y.; Loach, P. A. *J. Heterocycl. Chem.* **1980**, *17*, 737. (e) Ganesh, K. N.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1980**, 1129. (f) Ho, T.-F.; McIntosh, A. R.; Bolton, J. R. *Nature (London)* **1980**, *286*, 254. (g) Nishitani, S.; Kurata, N.; Sakata, Y.; Misumi, S.; Migita, M.; Okada, T.; Mataga, N. *Tetrahedron Lett.* **1981**, *22*, 2099. (h) Migita, M.; Okada, T.; Mataga, N.; Nishitani, S.; Kurata, N.; Sakata, Y.; Misumi, S. *Chem. Phys. Lett.* **1981**, *84*, 263. (i) Bergkamp, M. A.; Dalton, J.; Netzel, T. L. *J. Am. Chem. Sooc.* **1982**, *104*, 253. (j) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A. *Tetrahedron Lett.* **1982**, *23*, 3215. (k) Lindsey, J. S.; Mauzerall, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 4498.

[2] Jortner, J. *J. Am. Chem. Soc.* **1980**, *102*, 6676 and references cited therein.

[3] Billman, J. H.; Tonnis, J. A. *J. Pharm. Sci.* **1971**, *60*, 1188.

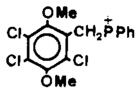
[4] Wallenfels, K.; Hofmann, D.; Kern, R. *Tetrahedron* **1965**, *21*, 2231.

[5] All new compounds showed satisfactory spectral properties. Satisfactory elemental analyses were obtained on all new compounds except for **1**, **3**, **7**, and **8**. Details are recorded in the supplementary material.

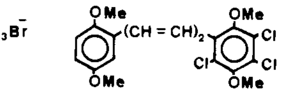
[6] Compound **5** was prepared from 4-bromobutanal.[12]

[7] Collman, J. P.; Chong, A. O.; Jameson, G. B.; Oakley, R. T.; Rose, E.; Schmittou, E. R.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 516.

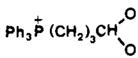
0002-7863/83/1505-7771$01.50/0



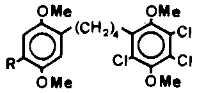
1



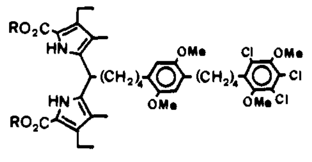
2



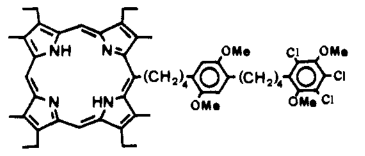
5



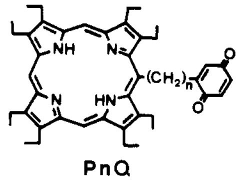
3 R = H
4 R = CHO
6 R = $(CH_2)_4CHO$



7 R = $CH_2C_6H_5$
8 R = H



9



PnQ

methylenebis(pyrrole)[8] in a similar manner to Collman et al.[7] to give **9** in 24% yield. Demethylation of **9** with 30 equiv of BBr_3 at −20 °C for 2 h and then at room temperature for 5 h followed by oxidation with DDQ gave the desired compound P4Q4Q′ in 24% yield.

In ^1H NMR spectra the quinone protons of P4Q4Q′ (δ 6.42) show small upfield shift relative to 2,5-dimethyl-*p*-benzoquinone (δ 6.59). Since this shift results from the ring current of the adjacent macrocycle, the quinone rings seem to be located above the porphyrin ring. However, the electronic spectrum of P4Q4Q′ in the region of 350–650 nm is very similar to that of 5-ethyletioporphyrin (EEP),[9] indicating no significant electronic interaction among the chromophores in the ground state. A quite similar result has been obtained also in the case of P4Q.[1g] Moreover, the redox potentials (in CH_3CN vs. SCE) of the two quinones incorporated in P4Q4Q′ (−0.75, −0.22 V) are almost the same as those of the reference quinones (2,5-dimethyl-*p*-benzoquinone, −0.73 V; trichlorotoluquinone, −0.24 V). This fact also suggests negligible interaction among the three chromophores and hence the existence of the gradient redox potential in the molecule.

Detailed picosecond laser photolysis studied upon P4Q4Q′ as well as related compounds are now going on[10] and results of measurements in benzene solution are discussed briefly in this report. Picosecond transient absorption spectra were measured by means of a microcomputer-controlled double-beam picosecond spectrometer with a repetitive mode-locked Nd^{3+}/YAG laser as the excitation source.[11]

It has been confirmed that, in benzene solution, immediately after excitation (at 33-ps delay time) we can observe clearly the characteristic porphyrin cation-like band in the wavelength region of 600–800 nm in the case of both P4Q4Q′ and P4Q systems. This absorption band, which can be ascribed to the porphyrin → quinone charge-transfer state, shows approximately exponential decay in both of P4Q4Q′ and P4Q systems. However, the decay time of P4Q4Q′ (τ_{CT} ~300 ps) is much more longer than that of P4Q (τ_{CT} ~130 ps). This result demonstrates clearly the importance of the more extensive charge separation due to the multistep electron transfer for preventing the radiationless deactivation due to the back charge transfer. Of course, if the intervening methylene chain of PnQ is too long, the photoinduced charge separation becomes quite inefficient because of the very slow electron transfer. Actually, we have confirmed that it takes more than 500 ps for the photoinduced charge transfer in P6Q,[10] in contrast to the fact that we have observed clearly the porphyrin cation-like absorption band immediately after excitation in the case of P4Q4Q′.

In view of the result of P6Q, a possibility of direct electron transfer from the porphyrin to the trichloroquinone moiety owing to the coiling back of the chain seems to be small. Moreover, if such a direct electron transfer due to the coiling back occurs, the radiationless deactivation of the charge transfer state to the ground state may be easier due to the smaller energy gap than in the P4Q system, which contradicts the observed result. Therefore, the photoinduced electron transfer P4Q4Q′ seems to take place most probably by two steps along the gradient redox potential of quinone groups.

Acknowledgment. The present work was supported in part by Grants-in-Aid for Science Research (No. 56470018 and 57045075) from the Ministry of Education, Science and Culture, Japan.

Registry No. 1, 87883-35-0; **2**, 87883-36-1; **3**, 87883-37-2; **4**, 87883-38-3; **5**, 76235-79-5; **6**, 87883-39-4; **7**, 87883-40-7; **8**, 87883-41-8; **9**, 87883-42-9; P4Q4Q′, 87901-19-7; EEP, 87883-43-0; benzyl 3-ethyl-4-methylpyrrole-2-carboxylate, 5866-56-8; 4,4′-diethyl-5,5′-diformyl-3,3′-dimethyl-2,2′-methylenebis(pyrrole), 4758-81-0; 2,5-dimethoxycinnamaldehyde, 33538-93-1.

Supplementary Material Available: Spectral data for P4Q4Q′, **2–4**, **6–9**, and EEP and electronic spectra of EEP and P4Q4Q′ (4 pages). Ordering information is given on any current masthead page.

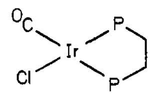
Stereoselectivity and Kinetic Control of Hydrogen Oxidative Addition to Iridium(I) Complexes

Curtis E. Johnson, Barbara J. Fisher, and
Richard Eisenberg*

Department of Chemistry, University of Rochester
Rochester, New York 14627

Received September 12, 1983

The oxidative addition of H_2 to d^8 square-planar complexes plays a central role in homogeneous hydrogenation and hydroformylation catalysis.[1] The reaction has been extensively studied for systems such as Vaska's complex, *trans*-IrCl(CO)$(PPh_3)_2$, and is generally thought to proceed via concerted H_2 addition leading to cis dihydride products.[2] We describe herein studies of H_2 oxidative addition with new Ir(I) complexes that indicate that subtle and previously unrecognized electronic factors are at work



1a–e, X = Cl, Br, I, CN, H; P⌒P = $Ph_2PCH_2CH_2PPh_2$ = dppe

---

[8] Markovac, A.; MacDonald, S. F. *Can. J. Chem.* **1965**, *43*, 3364.

[9] EEP was prepared in a manner similar to the synthesis of **9**.

[10] Karen, A.; Okada, T.; Mataga, N., unpublished results.

[11] (a) Masuhara, H.; Ikeda, N.; Miyasaka, H.; Mataga, N. *J. Spectrosc. Soc. Jpn.* 1982, *31*, 19. (b) Martin, M. M.; Ikeda, N.; Okada, T.; Mataga, N. *J. Phys. Chem.* **1982**, *86*, 4148. (c) Miyasaka, H.; Masuhara, H.; Mataga, N. *Laser Chem.*, in press.

[12] Vedejs, E.; Arnost, M. J.; Hagen, J. P. *J. Org. Chem.* **1979**, *44*, 3230.

(1) (a) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980. (b) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980. (c) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; Chapter 30.

(2) (a) James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973, and references therein. (b) Vaska, L.; Werneke, M. F. *Ann. N. Y. Acad. Sci.* **1971**, *172*, 546–562. (c) Halpern, J. *Acc. Chem. Res.* **1970**, *3*, 386–392. (d) Drouin, M.; Harrod, J. F. *Inorg. Chem.* **1983**, *22*, 999–1001. (e) Longato, B.; Morandini, F.; Bresadola, S. *Ibid.* **1976**, *15*, 650–656.

0002-7863/83/1505-7772$01.50/0