

and chemistry of *cis*-(η^5 -C₅R₅)W(CO)₂(H)(CH₂SiMe₂) and related species are in progress.

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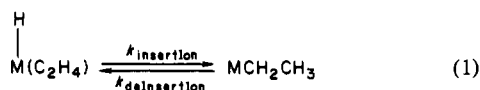
Mechanistic Investigation of Olefin Insertion into the Rhodium-Hydrogen Bond

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Olefin insertion into a metal-hydrogen bond is a key component of many catalytic cycles (e.g., hydroformylation, hydrogenation, and olefin isomerization)¹ and is of fundamental interest with respect to product distribution. In rhodium-catalyzed hydroformylation, for example, it is generally considered that the greater steric bulk of phosphine ligands compared to CO influences the ratio of linear:branched product by favoring insertion to linear alkylrhodium species. Despite the importance of olefin hydrides in catalytic cycles, such species have rarely been amenable to mechanistic study. In fact, the equilibrium between a transition-metal olefin hydride and the corresponding alkyl species (eq 1) has been observed only rarely²⁻⁵ and experimental determination



of the reaction coordinate for insertion is virtually unknown (cf. ref 5). This communication reports the detailed characterization of a hydridorhodium(I) olefin complex that permits evaluation of rate constants for insertion.

Hydrido(ethylene)bis(triisopropylphosphine)rhodium (1) forms readily in solution by displacement of N₂ when the known complex HRh(P-*i*-Pr₃)₂(N₂)⁶ is treated with either a stoichiometric amount or a large excess of ethylene. The ethylene hydride has been characterized spectroscopically⁷ but has not been isolated.

The significant ¹H NMR spectral features of 1 are invariant from -90 to 0 °C. A trans olefin hydride is suggested since the phosphines appear to be equivalent (cf. hydride coupling ²J_{PH}). The coordinated ethylene and hydride resonances broaden above

(1) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980; pp 29-41.

(2) (a) Werner, H.; Feser, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 157-158. (b) Werner, H.; Feser, R. *J. Organomet. Chem.* **1982**, *232*, 351-370.

(3) (a) Byrne, J. W.; Blaser, H. U.; Osborn, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3871-3873. (b) Chaudret, B. N.; Cole-Hamilton, D. J.; Wilkinson, G. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 763-769. (c) Seiwel, L. P. *Inorg. Chem.* **1976**, *15*, 2560-2563.

(4) Klein, H. F.; Hammer, R.; Gross, J.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 809-810.

(5) McGrady, N. D.; McDade, C.; Bercau, J. E. "Organometallic Compounds: Synthesis, Structure and Theory"; Texas A&M University Press: College Station, TX, 1983; pp 46-85.

(6) Yoshida, T.; Okano, T.; Thorn, D. L.; Tulip, T. H.; Otsuka, S.; Ibers, J. A. *J. Organomet. Chem.* **1979**, *181*, 183-201.

(7) ¹H NMR (0.011 M in C₇D₈ at -50 °C) δ -9.21 (dt, 1 H, ¹J_{RhH} = 5.3, ²J_{PH} = 21.4 Hz), 1.11 (q, 36 H, ³J_{HH} = 6.6, ³J_{PH} + ⁵J_{PH} = 13.3 Hz), 1.93 (m, 6 H), 2.66 (s, 4 H); ³¹P NMR (0.022 M in C₇D₈ at 23 °C) δ 67.99 (¹J_{RhP} = 152.3 Hz); ¹³C NMR (0.022 M in C₇D₈ at 23 °C) δ 20.92 (s, CH₃), 28.13 (dt, CH, ²J_{RhC} = 1.5, ¹J_{PC} + ³J_{PC} = 19.6 Hz), 45.36 (d, C₂H₄, ¹J_{RhC} = 6.4 Hz). Gated decoupling ¹³C experiments reveal ¹J_{HC} = 157.5 Hz for coordinated ethylene. IR in toluene solution shows ν(RhH) = 2005, 2042 cm⁻¹.

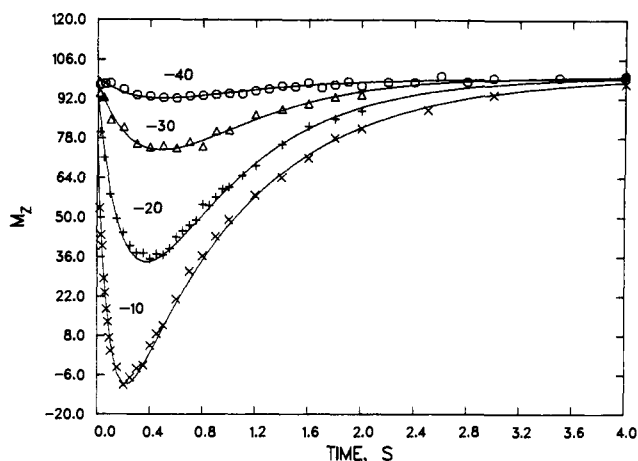


Figure 1. Response of hydride (M_z) to selective inversion of coordinated ethylene at indicated temperatures (°C). Data were acquired out to 8 s in each case. Data obtained at 0 °C are omitted for clarity.

Table I. Exchange Rate and Relaxation Parameters for HRh(C₂H₄)(P-*i*-Pr₃)₂

T, °C	k, s ⁻¹ ^a	T ₁ , s		k ₂ , s ⁻¹ ^b
		C ₂ H ₄	H	
-40	0.29 (0.04)	0.44	0.63	1.1
-30	0.78 (0.06)	0.60	0.70	2.9
-20	2.62 (0.09)	0.67	1.01	9.8
-10	8.01 (0.24)	0.92	1.04	30.0
0	18.6 (0.8)	1.54	1.02	70.0

^a Standard deviations in parentheses. T₁ values are considered to be accurate to no better than ±10%.¹³ ^b See text (eq 4).

0 °C, but above 30 °C irreversible sample decomposition occurs. The observed exchange broadening arises from insertion to alkyl followed by M-C-C single-bond rotation and rapid β-hydride elimination. Further evidence for this insertion process is provided by deuterium-labeling experiments.⁸ Treatment of HRh(P-*i*-Pr₃)₂(N₂) with C₂D₄ brings about loss of the ¹H NMR hydride resonance, while subsequent introduction of C₂H₄ into the same sample results in recovery of hydride intensity.

Attempts to quantify the insertion rate by trapping the alkyl complex once it is formed were not successful, although direct evidence for an ethylrhodium species was obtained.⁹ Furthermore, the narrow temperature range in which line-shape changes were observable precluded complete band-shape analysis as the principal tool for quantification of the insertion rate.

Magnetization-transfer techniques^{10,11} for the study of slow NMR exchange processes are particularly suitable in the case of olefin hydrides.¹² An advantage is derived by selective inversion of the coordinated ethylene resonance (rather than the hydride) since the larger inverted population magnifies the perturbation experienced by the hydride. Application of this technique to 1 extends the temperature range in which exchange is observed to -40 °C. A compact description of the exchange is provided by eq 2 in which M represents a vector of magnetization intensities,

$$\dot{\mathbf{M}}(t) = \mathbf{K} \cdot \Delta \mathbf{M}(t) \quad (2)$$

(8) Olefin exchange between free and coordinated ethylene occurs but is too slow to be observed on the NMR time scale.

(9) Addition of CD₃CN to a toluene-d₈ solution of 1 results in a complex mixture in which 1 still predominates. The other major species appear to be free phosphine and CH₃CH₂Rh(P-*i*-Pr₃)(C₂H₄)_x(CD₃CN)_y (x, y = 1 or 2); the features of interest are ¹H NMR (ca. 0.01 M in C₇D₈/CD₃CN (3:2)) at -40 °C δ -0.40 (d quintet, CH₂, ²J_{RhH} + ³J_{HH} = 7.7, ³J_{PH} = 2.0 Hz), 0.20 (t, CH₃, ³J_{PH} = 7.6 Hz).

(10) Forsen, S.; Hoffman, R. A. *J. Chem. Phys.* **1963**, *39*, 2892-2901; **1964**, *40*, 1189-1196.

(11) Alger, J. R.; Prestegard, J. H. *J. Magn. Reson.* **1977**, *27*, 137-141.

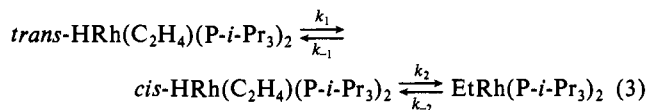
(12) All spectra were acquired on a Nicolet NT-360WB spectrometer. Suitable attenuation of the low-power transmitter resulted in selective inversion pulses that were typically 10-15 ms.

$\Delta M(t) = M(t) - M^{eq}$, 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 iso-electronic *trans*-HPt(C₂H₄)(PEt₃)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 ($\Delta G^\ddagger(25^\circ\text{C}) \approx 0.5$ kcal/mol) since ethylene is expected to have a greater "trans effect" than phosphine.¹⁵ The assignment is substantiated by variable-temperature ³¹P NMR below -40 °C. The initially sharp doublet reaches coalescence at -100 °C, and the slow exchange limit near -130 °C consists of A₂X and ABX patterns assigned to *trans* and *cis* complexes, respectively.¹⁶ Isomerization is sufficiently rapid that ¹H, ¹³C, and ³¹P NMR spectra above -40 °C represent a fast exchange average.

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



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 calculated¹⁷ 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-coordinate d⁸ 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.; Mantovani, 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) ³¹P NMR (0.02 M in pentane-(C₂D₅)₂O 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 ¹H 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 description¹³ will include ³¹P-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 $k_{-1} \gg k$.

(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

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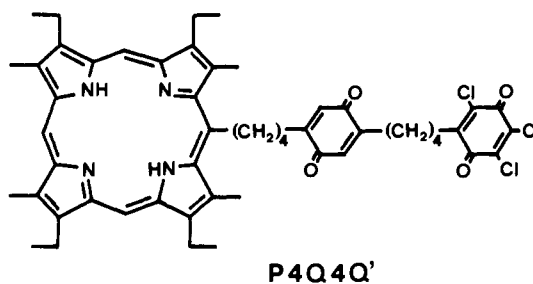
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Various acceptor-linked porphyrins have so far been prepared¹ in order to understand the mechanism of the first critical electron-transfer reaction in photosynthesis. However, no model compound has been known to mimic the in vivo photoinduced multistep 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.

The Wittig reaction of 2,5-dimethoxycinnamaldehyde³ and phosphonium bromide **1**, prepared via two steps from 3,4,6-trichloro-2,5-dimethoxytoluene,⁴ gave quantitatively butadiene **2**,⁵ which was converted to **3** by hydrogenation over Pd-C. The Rieche reaction of **3** was carried out with dichloromethyl methyl ether and titanium tetrachloride in CH₂Cl₂ 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-carboxylate⁷ 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. Soc.* **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-bromobutanol.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.