Reactions of the Schiff Base Rhodium Hydride Complex RhH(Bu$_4$salophen) with Olefins. Observations and Mechanistic Studies

D. Joe Anderson and Richard Eisenberg*

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

Received July 31, 1995[⊗]

The tetradentate dianionic Schiff base ligand Bu$_4$salophenH$_2$ reacts with [RhCl(C$_2$H$_4$)$_2$]$_2$ and NR$_4$OH (R = *n*-Bu, Et) to produce the complexes RhR(Bu$_4$salophen) (**1**, R = *n*-Bu; **2**, R = Et), which undergo photolysis (λ > 475 nm) under a hydrogen atmosphere to generate RhH(Bu$_4$salophen) (**3**) and the corresponding alkanes. In benzene at room temperature, olefins insert into the metal−hydride bond of **3** to produce Rh(CH$_2$CH$_2$R)(Bu$_4$salophen) (**2**, R = Et; **4**, R = Ph; **5**, R = CN). In a competition experiment, insertion of styrene is only slightly favored over that of ethylene. For olefinic substrates capable of radical rearrangement (CH$_2$=CHR where R = CH$_2$OCH$_2$CH=CH$_2$ and *c*-C$_3$H$_5$), insertion products are formed that do not correspond to radical rearrangements. Specifically, Rh(CH$_2$CH$_2$OCH$_2$CH=CH$_2$)(Bu$_4$salophen) (**6**) is observed as the only product of the reaction of **3** with bis(allyl) ether while Rh(CH$_2$CH$_2$-*c*-C$_3$H$_5$)(Bu$_4$salophen) (**7**) is seen as the major product in the reaction with vinylcyclopropane. For the vinylcyclopropane reaction, additional products are also identified by 2D NMR methods as Rh(CH$_2$CH$_2$CH=CHCH$_3$)(Bu$_4$salophen) (**8**) and (Bu$_4$salophen)Rh-(μ-CH$_2$CH$_2$CH=CHCH$_2$)Rh(Bu$_4$salophen) (**9**). Both the poor selectivity for styrene versus ethylene insertion and the absence of radical rearranged product with bis(allyl) ether and vinylcyclopropane indicate that, in the reaction of **3** with olefins, an intermediate containing a pure carbon-based radical is not involved.

Introduction

Olefin insertion into a metal−hydride bond plays a fundamental role in many organometallic reactions. This insertion is thought to play a key role in metal-catalyzed olefin hydrogenation, hydroformylation, and possibly hydrosilylation and hydrocyanation. The principal mechanism proposed for olefin insertion involves olefin binding to a coordinatively unsaturated metal hydride to generate an intermediate in which the olefin and hydride ligands occupy mutually *cis* positions about the metal center; the insertion reaction then proceeds through a four-center transition state.[1] Evidence exists, however, for olefin insertion by metal hydride complexes in which no such open site is available or in which an open site appears to be of lesser importance—*i.e.*, trans to the hydride ligand.[1] Specifically, the bis(dimethylglyoximato)cobalt and -rhodium systems first investigated by Schrauzer and co-workers were found to exhibit reversible olefin insertion,[2,3] while styrene insertion into the rhodium hydride bond of RhH(OEP) (OEP = octaethylporphyrin) was observed by Halpern and co-workers.[4] In these systems, the coordination sites *cis* to the hydride ligand were occupied by the chelating dimethylglyoxime or macrocyclic OEP ligands. The Halpern study invoked a radical mechanism to achieve the observed reaction chemistry.

Similar radical and radical chain mechanisms have been proposed by Wayland to explain the versatile reactivity of related rhodium(II) porphyrin systems. In 1981, Wayland and co-workers reported the synthesis and isolation of an unusually stable formyl complex Rh(CHO)(OEP) produced by the carbonylation of [Rh(OEP)]$_2$ in the presence of H$_2$.[5−11] Halpern and co-workers performed a kinetic study of this CO insertion, as well as of the styrene insertion, and a radical chain mechanism was implicated for both.[4] In subsequent studies of the metalloradical character of rhodium(II) porphyrin complexes, Wayland reported the extraordinary activation of the CH bond in methane by Rh(TMP) (TMP = tetramesitylporphyrin) under extremely mild conditions in hydrocarbon solvent.[12] The same Rh(porphyrin) complexes were found to attack benzylic CH bonds in alkylarenes as well.[13−15] The observed chemistry was explained by cooperative attack of two Rh(II)

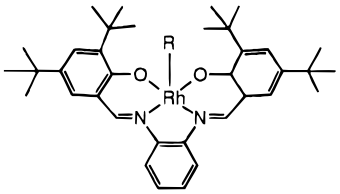
[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

(1) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals,* 2nd ed.; John Wiley & Sons, Inc.: New York, 1994.
(2) Schrauzer, G. N.; Holland, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 1505−1506.
(3) Weber, J. H.; Schrauzer, G. N. *J. Am. Chem. Soc.* **1970**, *92*, 726−727.
(4) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333.
(5) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 700−701.
(6) Wayland, B. B.; Duttaahmed, A.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1983**, 142−143.
(7) Wayland, B. B.; Sherry, A. E.; Coffin, V. L. In *Homogeneous Transition Metal Catalyzed Reactions*; W. R. Moser, W. R., Slocum, D. W., Eds.; American Chemical Society: Washington, DC, 1992; Vol. 230; pp 249−259.
(8) Wayland, B. B.; Coffin, V. L.; Sherry, A. E.; Brennen, W. R. *ACS Symp. Ser.* **1990**, *No. 428*, 148−158.
(9) Wayland, B. B.; Van Voorhees, S. L.; Wilker, C. *Inorg. Chem.* **1986**, *25*, 4039−4042.
(10) Farnos, M. D.; Woods, B. A.; Wayland, B. B. *J. Am. Chem. Soc.* **1986**, *108*, 3659−3663.
(11) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302−303.
(12) Sherry, A. E.; Wayland, B. B. *J. Am. Chem. Soc.* **1990**, *112*, 1259−1261.
(13) Wayland, B. B.; Del Rossi, K. J. *J. Organomet. Chem.* **1984**, *276*, C27C30.
(14) Del Rossi, K. J.; Wayland, B. B. *J. Am. Chem. Soc.* **1985**, *107*, 7941−7944.

0276-7333/96/2315-1697$12.00/0

centers on the alkyl C−H bond to split it homolytically under ambient temperature conditions.[15] Further studies of this reaction system utilized two rhodium porphyrins linked by an alkoxy chain in order to modify the interaction of the rhodium centers with methane from a termolecular process to a bimolecular one, and in keeping with the proposed mechanism, this decrease in molecularity boosted the rate of homolytic methane CH activation.[16] Similar radical and radical chain mechanisms have been used to explain other reactions of rhodium porphyrins with hydrogen, olefins, carbon monoxide, alkyl isocyanides, trialkylsilanes, and trialkylstannanes.[11,17,18]

We have recently sought to extend the diverse reaction chemistry observed for these porphyrin systems to rhodium complexes containing derivatives of the dianionic tetradentate Schiff base ligand salophen. Schiff base ligands lend themselves readily to structural modifications that offer considerable control over complex solubility and reactivity. Such control, for example, has been demonstrated over the last few years with great success in the use of manganese Schiff base complexes to catalyze olefin epoxidation—a reaction previously observed for the analogous manganese porphyrin complex.[19,20] Prior to our initial communication on the RhR(Bu_4salophen) complex **I** and a related report

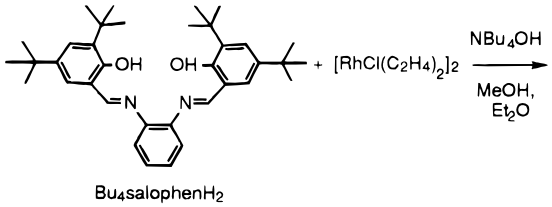


I

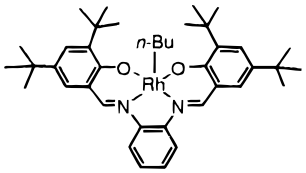
by Wayland,[21,22] most tetradentate Schiff base complexes of rhodium were reported as soluble only in donor solvents.[23−31] In this article, we describe in full the synthesis and characterization of **I** for R = *n*-Bu and Et, photolysis of **I** under hydrogen to produce the corresponding rhodium hydride species, and a study of olefin addition to this hydride species.

Results and Discussion

Synthesis of RhR(Bu_4salophen). Reaction of the chloro-bridged Rh(I) dimer $[Rh(\mu\text{-}Cl)(C_2H_4)_2]_2$ with the free $Bu_4salophenH_2$ Schiff base ligand and excess tetrabutylammonium hydroxide affords a dark purple solution that yields a like colored precipitate upon solvent removal (eq 1). The resultant compound (**1**) is



$Bu_4salophenH_2$



(1)

1

air stable and light sensitive in the solid state, and forms bright red-purple solutions in acetone, ether, THF, methylene chloride, ethanol, methanol, and hydrocarbon solvents. It is insoluble in, but stable to, deoxygenated water.

The coordinated Schiff base ligand of **1** exhibits a number of characteristic signals by ^1H and ^{13}C NMR spectroscopy, the most prominent of which are two singlets in the ^1H NMR spectrum for each of two sets of *tert*-butyl groups at δ 1.99 (18 H) and 1.45 (18 H) ppm. All other ligand resonances fall much further downfield. The resonance furthest downfield, at δ 8.40 ppm (2 H), is assignable to the imine protons and shows a small splitting (2 Hz) not seen in the free ligand due to $^3J_{Rh-H}$ coupling. Two signals at δ 7.86 (2 H) and 7.33 (2 H) show a through-ring H−H coupling of 2 Hz and are assigned to the aromatic protons adjacent to the *tert*-butyl groups. The remaining two ^1H NMR signals belonging to the Schiff base ligand appear as doublets of doublets, one at δ 7.13 (2 H) and the other at 6.86 ppm (2 H; $^3J_{HH} = 6$ Hz, $^4J_{HH} = 3$ Hz), corresponding to the four aromatic protons of the phenylenediimine moiety. Three sets of ^1H NMR resonances that belong to the complex but are not assignable to the Schiff base ligand appear at δ 2.38 (complex multiplet, 2 H), 0.84−0.95 (broad multiplet, 4 H), and 0.44 ppm (triplet, 3 H). These resonances correspond to the butyl ligand and exhibit a pattern similar to that of the butyl group in *n*-Bu_4N^+. The α-methylene protons of the coordinated butyl group are shown in Figure 1a. Their unique pattern serves as an important guide to the identification and characterization of other Rh(III) alkyl complexes generated in subsequent reactions between RhH(Bu_4salophen) and olefins.

All of the ^{13}C NMR spectra reported herein were recorded using the *J*-modulated spin-echo pulse sequence, also known as the attached proton test (APT), in which signals for carbons with an even number of

(15) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305−5311.
(16) Zhang, X.-X.; Wayland, B. B. *J. Am. Chem. Soc.* **1994**, *116*, 7897−7898.
(17) Poszmik, G.; Carroll, P. J.; Wayland, B. B. *Organometallics* **1993**, *12*, 3410−3417.
(18) Mizutani, T.; Uesaka, T.; Ogoshi, H. *Organometallics* **1995**, *14*, 341−346.
(19) Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. *J. Am. Chem. Soc.* **1991**, *113*, 7063−7064.
(20) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801−2803.
(21) Bunn, A. G.; Wei, M.; Wayland, B. B. *Organometallics* **1994**, *13*, 3390−3392.
(22) Anderson, D. J.; Eisenberg, R. *Inorg. Chem.* **1994**, *33*, 5378−5379.
(23) Levitin, I.; Sigan, A. L.; Vol'Pin, M. E. *J. Chem. Soc., Chem. Commun.* **1975**, 469−470.
(24) Nikitaev, A. T.; Sigan, A. L.; Levitin, Y.; Belyi, A. A.; Vol'Pin, M. E. *Inorg. Chim. Acta* **1982**, *64*, L29−L31.
(25) Aleinikova, V. N.; Vasil'ev, V. V.; Shagisultanova, G. A. *Russ. J. Phys. Chem.* **1986**, *60*, 935−937.
(26) Aleinokova, V. N.; Vasil'ev, V. V.; Timonon, A. M.; Shagisultanova, G. A. *Russian J. Phys. Chem.* **1987**, *61*, 580−582.
(27) Calmotti, S.; Pasini, A. *Inorg. Chim.* **1984**, *85*, L55−L56.
(28) Cozens, R. J.; Murray, K. S.; West, B. O. *J. Chem. Soc., Chem. Commun.* **1970**, 1262−1263.
(29) Cozens, R. J.; Murray, K. S.; West, B. O. *J. Organomet. Chem.* **1972**, *38*, 391−402.
(30) Rogers, C. A.; West, B. O. *J. Organomet. Chem.* **1974**, *70*, 445−453.
(31) Van Den Bergen, A. M.; Elliott, R. L.; Lyons, C. J.; MacKinnon, K. P.; West, B. O. *J. Organomet. Chem.* **1985**, *297*, 361−370.

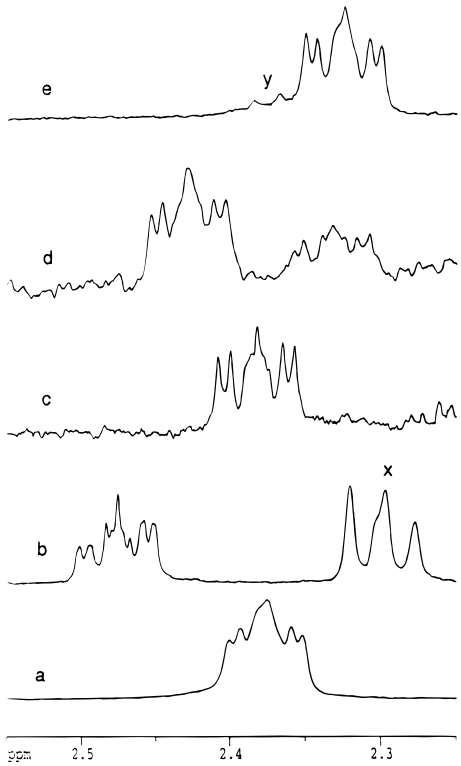


Figure 1. ^{1}H NMR (400 MHz) resonances for rhodium bound methylene units: (a) [Rh]*n*Bu (**1**); (b) [Rh]CH_2-$CH_2C_6H_5$ (**4**); (c) product from allyl ether addition to **3**, [Rh]$CH_2CH_2CH_2OCH_2CH{=}CH_2$ (**6**); (d) products from vinylcyclopropane addition to **3**, [Rh]CH_2CH_2(*c*-C_3H_5) (**7**) (left multiplet) and [Rh]$CH_2CH_2CH{=}CHCH_3$ (**8**) (right multiplet); (e) product from *trans*-1,3-pentadiene addition, [Rh]-$CH_2CH_2CH{=}CHCH_3$ (**8**). Peak "x" is from the β-protons of **4**, while "y" is from unreacted starting material **1**.

attached protons have a phase opposite to signals for carbons with an odd number of attached protons. The ^{13}C NMR spectrum of the complex shows resonances assignable to all of the carbon atoms of the Schiff base ligand as well as to the four distinct butyl carbons at δ 34.36, 25.14 ($^1J_{RhC}$ = 31 Hz), 22.14 ($^2J_{RhC}$ = 2 Hz) and 13.65 ppm. The phase of the first three carbon signals indicates that each carbon has an even number of attached protons, whereas the last has an odd number of attached protons. It is thus possible from the NMR spectroscopic data to identify unequivocally the product of eq 1 as Rh(*n*-Bu)(Bu$_4$salophen) (**1**). A crystal structure analysis, obtained using crystals grown from a benzene/methylene chloride solution and described in detail elsewhere,[22] confirms our assignment of **1** and shows that it possesses a square pyramidal geometry, with the *n*-butyl group occupying the apical position and the four Schiff base donor atoms comprising the base of the pyramid about Rh(III).

Complex **1** exhibits a weak luminescence in fluid solution that intensifies upon freezing the solution to 77 K. The low-temperature emission maximum at 671 nm is accompanied by a shoulder at 745 nm. Features in the low-temperature excitation spectrum of this compound closely parallel features in the room-temperature absorbance spectrum. Figure 2 shows the low-temperature emission and excitation spectra for **1** in toluene glass (77 K) as well as the room-temperature absorption spectrum in benzene. Luminescence from Rh(III) alkyl Schiff base complexes has been reported

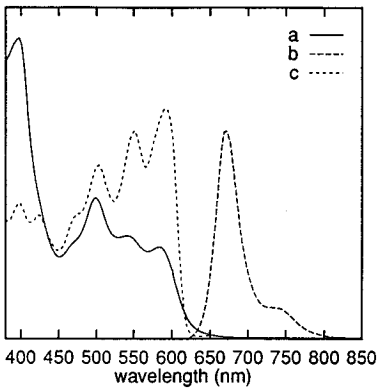


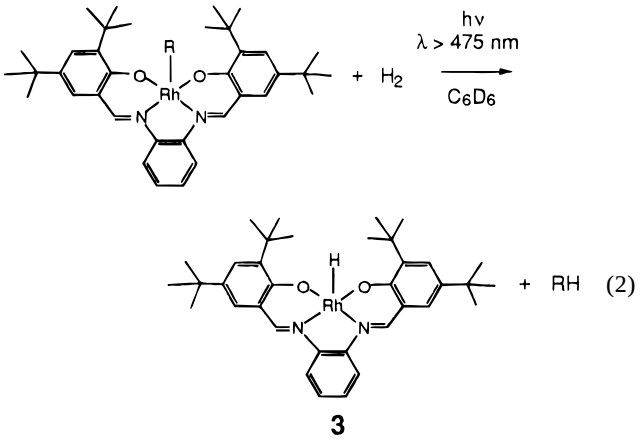
Figure 2. Electronic spectra of Rh(*n*-Bu)(Bu$_4$salophen) (**1**): (a) absorption spectrum at 298 K in benzene; (b) emission spectrum in toluene glass at 77 K, 510 nm excitation wavelength; (c) excitation spectrum in toluene glass at 77 K, emission monitored at 670 nm.

previously by Aleinikova *et al.*,[25] and an analysis of the emitting state in **1** will be presented elsewhere in conjunction with a discussion about related luminescent compounds.[32]

Use of tetraethylammonium hydroxide in place of tetrabutylammonium hydroxide in the above reaction gives a similar dark purple product which is distinct by ^{1}H NMR spectroscopy from **1** only in the appearance of NMR signals at δ 2.37 (qd, J_{RhH} = 3.2 Hz, J_{HH} = 7.4 Hz) and 0.23 (td, J_{RhH} = 1.1 Hz, J_{HH} = 7.4 Hz) and the absence of the *n*-butyl group signals. The two resonances unique to this product are assigned to a rhodium-bound ethyl group in RhEt(Bu$_4$saloph) (**2**) (eq 1, R = Et). Formation of the ethyl complex in this reaction indicates that the tetralkylammonium ion serves as the source of the alkyl groups in compounds **1** and **2**.[18,33]

Reactivity of 1 and 2. Benzene solutions of **1** are stable at room temperature for several days in the dark, even in the presence of hydrogen or carbon monoxide. However, *in situ* photolysis of a benzene-d_6 solution of **1** under hydrogen with long-wavelength visible light (λ > 475 nm) generates a red solution which exhibits a broad featureless ^{1}H NMR signal at δ −25.8 ppm (1 H) in addition to resonances assignable to the coordinated Bu$_4$salophen ligand and to free *n*-butane in solution (multiplets at δ 1.23 ppm and 0.86 ppm). Production of *n*-butane is confirmed by GC/MS analysis of the volatiles from this solution. Photolysis of **2** under a hydrogen atmosphere also produces the characteristic ^{1}H NMR signal at δ −25.8 ppm (1 H) and a sharp singlet at 0.80 ppm assignable to ethane. In the presence of trace amounts of donor solvents in benzene-d_6, the upfield ^{1}H NMR resonance resolves into a broad doublet with 51 Hz coupling, while photolysis of **1** in THF-d_8 leads to a sharp doublet at δ −22.52 ppm with 37 Hz coupling. The presence in these ^{1}H NMR spectra of a signal in the metal−hydride region along with production of the alkane derived from **1** and **2** is consistent with homolytic metal−alkyl bond hydrogenolysis and formation of the hydride product RhH(Bu$_4$salophen) (**3**), eq 2. When a solution of **3** is placed under an atmosphere of D_2, immediate formation of HD (δ 2.42 ppm, J_{HD} = 43 Hz) accompanies the disappearance of the

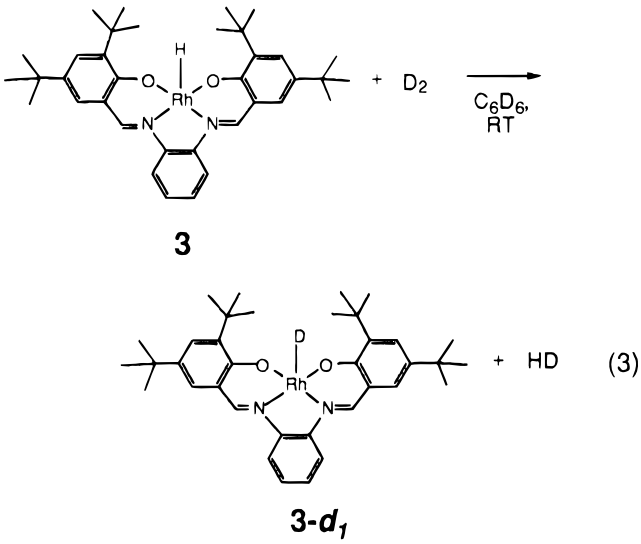
(32) Anderson, D. J.; Eisenberg, R. To be submitted for publication.
(33) Collman, J. P.; Brauman, J. I.; Madonik, A. M. *Organometallics* **1986**, *5*, 215−218.



(2)

3

upfield resonance at δ −25.8 ppm within minutes. The production of HD and the disappearance of the hydride resonance is consistent with the formation of RhD(Bu_4salophen) (**3**-d_1) through rapid, thermally promoted exchange between D_2 and RhH(Bu_4salophen), eq 3.

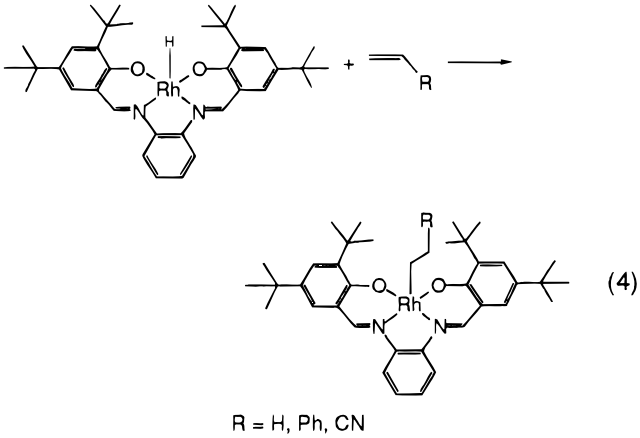


(3)

3

3-d_1

Reaction of RhH(Bu_4salophen) (3) with Olefins. Benzene solutions of **3** generated *in situ* react readily at room temperature with a number of olefins to form the corresponding alkyl product as shown in eq 4 for R



(4)

R = H, Ph, CN

= H, C_6H_5, and CN. Inspection of the ^{1}H NMR signals for the Schiff base ligand in each of these reactions indicates that in every case a single diamagnetic product with approximate C_s or mirror symmetry predominates.

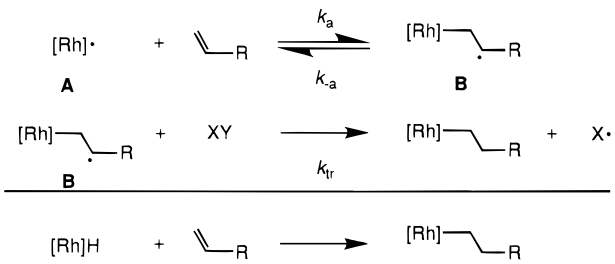
For the reaction of **3** with ethylene, the dark purple product is identified as **2** by the characteristic splitting pattern (*vide supra*) of the ethyl group seen in the product's ^{1}H NMR spectrum along with the Schiff base resonances. However, for olefins other than ethylene, unambiguous identification of the reaction product necessitated further spectroscopic characterization. In each case, a ^{13}C spectrum was acquired which revealed all Bu_4salophen resonances (*i.e.*, nine aromatic carbons at δ ∼168−120 ppm, the imine carbon at δ ∼115 ppm, two *tert*-butyl quaternary carbons at δ ∼37 and ∼34 ppm, and two *tert*-butyl methyl carbons at δ ∼32 and ∼30 ppm) as well as those of the alkyl ligand generated upon olefin insertion.

The reaction of **3** with styrene leads to the observation of two complex ^{1}H NMR multiplets in addition to those of the Bu_4salophen ligand. The coupling pattern of the multiplet at δ 2.47 ppm (2 H, Figure 1b) resembles that of the rhodium-bound methylene unit in **1** and is therefore assigned to the protons of an analogous rhodium-bound methylene carbon. The remaining complex multiplet appears as a distorted triplet at δ 2.29 ppm (2 H). Homonuclear decoupling of either of these resonances collapses the other into a broad singlet. By ^{13}C NMR spectroscopy, two signals are found at δ 25.22 (J_{RhC} = 25.2 Hz) and δ 38.55 (6 Hz) ppm that correspond to the carbon atoms of a β-phenylethyl group in the Rh(CH_2CH_2Ph)(Bu_4salophen) insertion product (**4**). Consistent with this formulation, the ^{13}C NMR spectrum shows six peaks in the aromatic region assignable to the phenyl group. A series of overlapping ^{1}H NMR multiplets from δ 6.67 to 6.79 ppm (5 H) were assigned to the aromatic protons of this phenyl group. These resonances, along with the multiplet at δ 2.47 ppm, are not seen in the ^{1}H NMR spectrum of the product which results from the addition of styrene-d_8 to **3**, although a broad singlet could still be seen at δ 2.29 ppm (1 H) corresponding to the former hydride ligand after insertion.

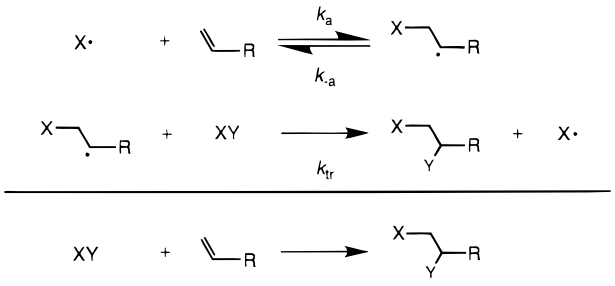
Although solutions of the hydride complex **3** are air-sensitive and labile in the absence of a dihydrogen atmosphere, the alkyl complexes are not. The thermal insertion of styrene was therefore used to trap photolytically-generated hydride **3** and to monitor the progress of preparative-scale photolysis. During the course of the photolysis, the photolysis vessel was temporarily removed from the photon flux of the lamp while samples were withdrawn under H_2 into an NMR tube containing excess styrene. NMR spectra of these samples showed unreacted *n*-Bu complex **1** and the β-phenylethyl complex **4** from the thermal reaction of hydride **3** and styrene. The relative amounts of these complexes in the NMR sample were taken as indication of the progress of the photolysis in the bulk solution. If the NMR spectra indicated that starting material remained, photolysis of the bulk solution was continued. When NMR analysis of samples taken from the bulk solution showed that all of the starting *n*-Bu complex **1** was gone, photolysis was halted and excess styrene was added to the bulk solution to produce Rh(CH_2CH_2Ph)(Bu_4salophen) (**4**) in ∼100 mg quantities.

In the reaction of hydride **3** with acrylonitrile, chemical shifts within the ^{1}H NMR spectrum of the product were highly dependent on the constitution of the solu-

Scheme 1



Scheme 2



tion. Complex multiplets assignable to the methylene units of a β-cyanoethyl ligand in Rh(CH_2CH_2CN)(Bu$_4$salophen) (**5**) were identified at δ 1.94 and 2.12 ppm in the presence of excess acrylonitrile. However, removal of all solvent and acrylonitrile from this solution under vacuum and introduction of fresh solvent shifted these resonances to positions where they were obscured by large signals from the *tert*-butyl groups of the Schiff base ligand. In neither case was accurate integration possible. Even so, a cross-peak in the ^{1}H$-^1$H COSY spectrum of this product at (δ 1.81 ppm, 1.66 ppm) confirmed the adjacency of the two groups giving rise to these signals, while two resonances at δ 12.73 (J_{RhC} = 32.6 Hz) and 17.61 ppm in the ^{13}C NMR spectrum of **5** had phases and chemical shifts consistent with two methylene groups, one of which was directly bound to rhodium.

Mechanistic Probes of Olefin Insertion: Competitive Ethylene and Styrene Addition. The regioselectivity observed in the addition of styrene and acrylonitrile to the hydride complex **3** is consistent with the radical chain mechanism proposed by Halpern for the addition of styrene to RhH(OEP).[4] In the propagation steps of this mechanism, shown with the overall reaction in Scheme 1, olefin addition is catalyzed by a Rh(II) radical species **A** that binds olefin to yield a metal alkyl radical **B** having significant unpaired spin on the carbon atom β to the rhodium center. The observed kinetics of the addition are consistent with a facile equilibrium yielding radical **B** that in turn abstracts a H atom irreversibly from the starting Rh(III) hydride to form the olefin insertion product while regenerating the chain-propagating Rh(II) species **A**.

Addition of styrene to the Rh−H bond of RhH(OEP) as formulated by Halpern and co-workers belongs to the more general class of XY addition to olefins by the radical chain pathway shown in Scheme 2. The literature provides numerous examples of such additions in which X = halide, N, P, RS, R$_3$Si, R$_3$Ge, and R$_3$Sn and Y = H.[33] Typically for these reactions, addition of XY to styrene contrasts markedly with that to olefins lacking aromatic substituents.

For example, in tin hydride additions to the selectively deuterated olefins styrene, 1-hexene, and *cis*- and *trans*-2-butene, Kuivila and Sommer found that initial attack of Bu$_3$Sn$^\bullet$ on hexene and butene was reversible whereas attack of the tin radical on styrene was irreversible.[34] For radically-promoted hydrothiolation of olefins, Sivertz and co-workers observed that, for RS$^\bullet$ addition, k_a(styrene) is much greater than k_a(1-pentene) but, for the hydrogen transfer step, k_{tr}(1-pentene) exceeds k_{tr}(styrene).[35] In each of these cases, benzylic stabilization of either the transition state for X$^\bullet$ addition to the olefin or the carbon-based radical intermediate accounted for the differences in olefin reactivity. For example, benzylic stabilization of Bu$_3$SnCH$_2$CHPh hindered dissociation to styrene and Bu$_3$Sn$^\bullet$ leading to the observed irreversibility, while, for thiol addition, benzylic stabilization of the RS$^\bullet$ addition product led to a slower H-atom transfer step.

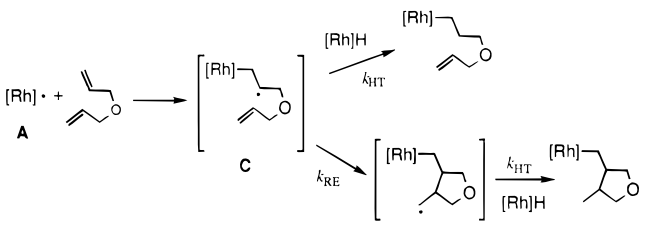
In this context, we sought evidence for participation of metal alkyl radical intermediates in the addition of olefins to RhH(Bu$_4$salophen) (**3**). To that end, a competition reaction between styrene and ethylene with **3** was conducted. When a 4:1 ratio of ethylene to styrene was introduced to a benzene solution of hydride **3**, the styrene addition product **4** was favored over the ethylene product **2** by *only* a 2:1 ratio, yielding an overall preference of 8:1 for styrene over ethylene.

For the mechanism of Rh−H addition to olefins via Scheme 2, two limiting cases can be considered. In the first, the Rh$^\bullet$ addition step is fast with subsequent H-atom transfer slow, whereas, in the second, the relative rates of the two steps are reversed. For the first of these limiting cases, ethylene addition would be expected to be more favorable whereas for the second styrene addition should predominate. The relatively meager 8:1 preference that is observed for styrene addition to **3** (a $\Delta\Delta G^\ddagger$ of $<$0.9 kcal) suggests that if Scheme 2 is operative, the competition is not determined solely by one or the other of the mechanism's steps but rather that both steps influence the observed preference. Alternatively, and in keeping with the observations described below, we think that the 8:1 styrene:ethylene preference indicates that the species resulting from metalloradical addition to the olefin is not adequately described as the C-based radical **B** and instead that stabilization from the metal center affects the reactivity of the Rh$^\bullet$ addition species for both of the olefins.

Reaction of 3 with Bis(allyl) Ether. Further investigation of the possible radical nature of olefin addition to hydride **3** utilized the well-studied rearrangements of certain unsaturated organic radicals. These rearrangements have been used to "clock" competitive reaction pathways for both organic and organometallic systems.[36−39] For olefin addition to **3** by the radical chain pathway of Scheme 1, the species subject to rearrangement is produced by the addition of the metalloradical **A** to the olefin. Subsequent H atom transfer to **B** then competes with the rearrangement so

(34) Kuivila, H. G.; Sommer, R. *J. Am. Chem. Soc.* **1967**, *89*, 5616−5619.
(35) Sivertz, C. *J. Phys. Chem.* **1959**, *63*, 34−38.
(36) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317−323.
(37) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151−1176.
(38) Bullock, R. M.; Samsel, E. G. *J. Am. Chem. Soc.* **1990**, *112*, 6886−6898.
(39) Hembre, R. T.; Ramage, D. L.; Scott, C. P.; Norton, J. R. *Organometallics* **1994**, *13*, 2995−3001.

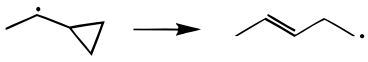
Scheme 3



that the ratio of rearranged to unrearranged product indicates the relative rates of hydrogen atom transfer and radical rearrangement as shown in Scheme 3 for bis(allyl) ether. For bis(allyl) ether, the rearrangement corresponds to ring closure that would yield a (4-methyl-3-tetrahydrofuranyl)methylrhodium derivative. Independent studies have shown that the parent organic radical for **C** rearranges with a unimolecular rate constant of $k = 4 \times 10^6$ s^{-1} at 25 °C.[37]

When excess bis(allyl) ether was added to a benzene-d_6 solution of **3**, however, only a single major product (56%) was identified that corresponded to anti-Markovnikov addition of the rhodium−hydride bond across the substrate double bond *without* rearrangement. The identity of this product, Rh($CH_2CH_2CH_2OCH_2CH$=CH_2)(Bu_4salophen) (**6**), was established by ^{1}H NMR spectroscopy, and, in particular, by Schiff base ligand resonances and a characteristic rhodium-bound methylene signal at δ 2.38 ppm (m, 2 H, Figure 1c). The absence of any rearranged product suggested that on the basis of Scheme 3, the hydride atom abstraction reaction proceeded much faster than the rearrangement. On the basis of the first-order rate constant for the parent radical cyclization of 4×10^6 s^{-1}, the H atom abstraction reaction would have to proceed near the diffusion controlled limit to avoid forming observable amounts of rearranged product. With a concentration of *ca.* 1×10^{-3} M for hydride **3**, the second-order rate constant would have to be *ca.* 1×10^{10} M^{-1} s^{-1} to explain the observed result using Scheme 3.

Reaction of 3 with Vinylcyclopropane. In order to test the proposed radical insertion mechanism of Scheme 1 more definitively, attention next focused on the cyclopropylcarbinyl radical and the use of vinylcyclopropane as a substrate in reaction with **3**. Since the rate of ring opening for the cyclopropylcarbinyl radical, eq 5, is one of the fastest of the standard radical "clocks"



(5)

with $k = 4 \times 10^7$ s^{-1}, reaction of **3** with vinylcyclopropane should yield significant ring opened product—*i.e.*, Rh(CH_2CH=$CHCH_2CH_3$)(Bu_4salophen)—if the radical mechanism of Scheme 1 was followed. Surprisingly, this turned out *not* to be the case.

When vinylcyclopropane was reacted with hydride **3**, two major sets of product resonances were observed in the ^{1}H NMR spectrum, but neither corresponded to the 2-pentenylrhodium complex expected from radical ring opening. Associated with two sets of Schiff base ligand resonances were two complex multiplets at δ 2.42 and 2.31 ppm (Figure 1d), which, through comparison with similar signals in the spectra of compounds **1, 4**, and **6** (Figure 1a−c), were assigned to rhodium-bound methylene units of two separate square pyramidal addition

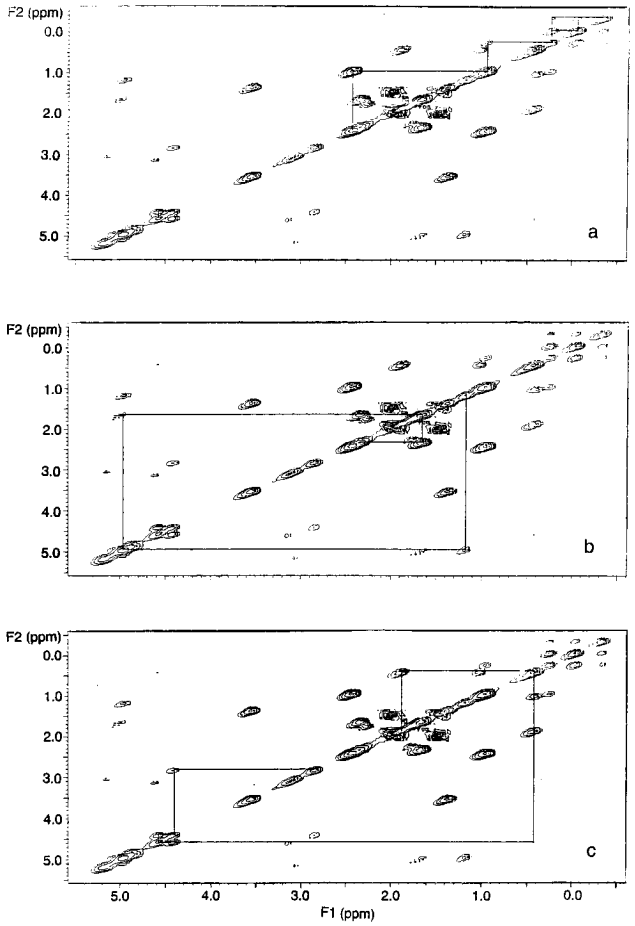
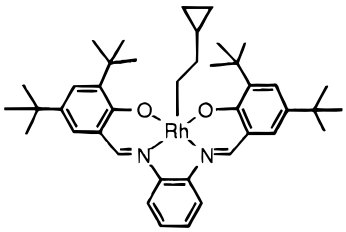


Figure 3. ^{1}H−^{1}H COSY (500 MHz) spectrum of products from vinylcyclopropane addition to rhodium hydride **3**. Correlations are for (a) Rh(CH_2CH_2(*c*-C_3H_5))(Bu_4salophen) (**7**), (b) Rh(CH_2CH_2CH=$CHCH_3$)(Bu_4salophen) (**8**), and (c) (Bu_4saloph)Rh(CH_2CH=$CHCH_2CH_2$)Rh(Bu_4saloph) (**9**).

products. A ^{1}H−^{1}H COSY spectrum of this reaction mixture, acquired using a double-quantum filter to reduce near-diagonal effects of the large *tert*-butyl singlets, led to assignment of the two major products. As shown in Figure 3a, a COSY walk originating at the rhodium-bound methylene signal at δ 2.42 ppm proceeds through several cross peaks located at (2.42, 0.95 ppm), (0.95, 0.23 ppm), (0.23, −0.058 ppm), (0.23, −0.35 ppm), and (−0.058, −0.35 ppm). The two multiplets at δ −0.058 and −0.35 ppm have coupling patterns which are very similar to those seen for the cyclopropyl methylene groups in vinylcyclopropane, although shifted significantly upfield. On the basis of this similarity, together with the rhodium-bound methylene ^{1}H NMR signal and the connectivity information provided by the COSY spectrum, these resonances are assigned to the product Rh(2-cylopropylethyl)(Bu_4salophen) (**7**). Inte-

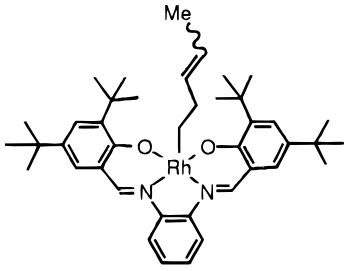


7

gration of the two high-field resonances at δ −0.058 and

−0.35 ppm and of the methylene resonance at δ 2.42 ppm versus the imine region in the ^{1}H NMR spectrum indicated that **7** was the *major* observable product formed and accounted for 32% of the total Schiff base species in the product mixture.

A COSY walk (Figure 3b) originating at the other rhodium-bound methylene peak, at δ 2.32 ppm, passes through cross peaks at (2.32, 1.65 ppm), (1.65, 4.90 ppm), and (4.90, 1.16 ppm). These resonances (4.90, 2.32, 1.65, and 1.16 ppm) are assigned to the 3-pentenyl group of the ring-opened addition product Rh(CH_2CH_2-CH═$CHCH_3$)(Bu$_4$salophen) (**8**), in which the two olefinic



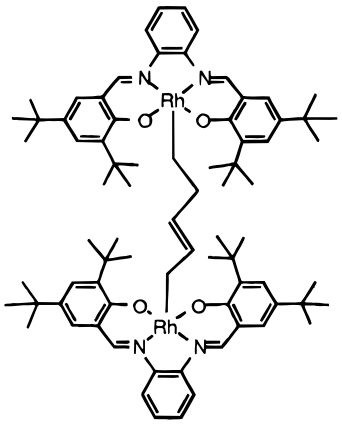
8

proton signals overlap at δ 4.90 ppm. Integration of the δ 2.32 ppm signal indicated that **8** accounts for 17−24% of the total Schiff base containing product. Compound **8** is the product expected for addition of hydride **3** across the terminal double bond of 1,3-pentadiene. Support for the assignment of **8** was obtained by reacting excess *trans*-1,3-pentadiene with hydride **3** in a benzene-d_6 solution and confirming that the resonances of **8** are the same as those of the terminal olefin insertion product. In the original reactions of vinylcyclopropane with **3**, no 1,3-pentadiene was observed in the initial reaction system, although afterwards small quantities (trace to no more than 15% of total olefin) of 1,3-pentadiene could be seen. Its formation may result from rhodium-catalyzed isomerization of vinylcyclopropane to pentadiene,[40] or via β-elimination from **8**, but in neither case does it arise from radical-promoted cyclopropylcarbinyl ring opening.

In addition to the two major products, a minor product was seen which could not be identified reliably due to the proximity of its ^{1}H NMR signals to residual ridges of F1 noise in the COSY spectrum. Integration of the α-methylene ^{1}H resonance of this product at δ 2.24 ppm showed that it constituted 1−8% of the observed products containing the Bu$_4$salophen ligand.

An essential point of the reaction of vinylcyclopropane with hydride **3** is that despite the mixture of products, no *major* component corresponded to the 2-pentenylrhodium complex expected from the radical promoted ring-opening of the substrate. While the alkyl (∼0−2 ppm) and aryl (∼6−8 ppm) regions of the ^{1}H NMR spectrum were quite crowded and dominated by Schiff base resonances, the spectrum between these regions (∼2−6 ppm) was by comparison quite clean. Protons of the rhodium-bound $-CH_2-$ group (*i.e.*, RhCH_2-CH═$CHCH_2CH_3$) predicted for the ring-opened product were not observed in this region downfield of the rhodium-bound methylene protons described above, and no allylic group assignable to Rh(2-pentenyl)(Bu$_4$-salophen) was seen in either 1D or 2D spectra acquired with this reaction mixture.

However, an additional product was sometimes seen in this reaction that did possess an allyl group but was not Rh(2-pentenyl)(Bu$_4$salophen). In reactions where this product was present, the yield of the unrearranged insertion product **7** was reduced by a proportionate amount. The identity of this compound was established by careful NMR analysis as the binuclear alkenyl bridged species (Bu$_4$salophen)Rh(CH_2CH═$CHCH_2CH_2$)-Rh(Bu$_4$salophen) (**9**). This compound exhibited two



9

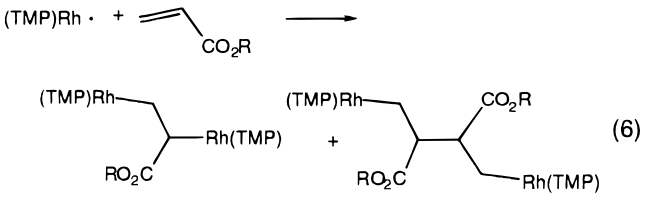
distinct sets of Schiff base resonances in equal intensity and shifted slightly upfield from those of other Bu$_4$-salophen products. The alkenyl bridge of **9** was determined by a rhodium-bound methylene signal at δ 2.84 (2 H, dd 3.5, 8.2 Hz) that according to ^{1}H−^{1}H COSY data (Figure 3c) was coupled to two complex olefinic multiplets at δ 4.56 (1 H) and 4.39 (1 H), which in turn were coupled to each other and to a signal at δ 0.4 ppm that was further coupled to another resonance at δ 1.9 ppm. Formation of **9** is a matter of speculation that is best done on the basis of the mechanistic conclusions drawn from the reactions of RhH(Bu$_4$salophen) with various olefins. We address this matter below.

Mechanistic Conclusions Regarding the Olefin Insertion Reactions of RhH(Bu$_4$salophen). Reactions of hydride **3** with substrates capable of radical rearrangement produce insertion products which exhibit no radical rearrangement. The lack of such rearrangement strongly suggests that Scheme 1 must be modified as an accurate description of the insertion mechanism. Specifically, it appears that while Rh(II) species undoubtedly play a role in the reaction chemistry, the generation of a simple carbon-based radical by olefin addition to Rh(II) seems problematic. If such a radical were generated, radical-promoted rearrangement should have occurred, but experimental evidence indicates otherwise. This is particularly compelling in the reaction of vinylcyclopropane with **3** that gave major products devoid of radical-based rearrangements.

Support for the view that olefin addition to a Rh(II) metalloradical does not generate the simple carbon radical shown as **B** in Scheme 1 is eloquently provided by Wayland through both experiment and analysis. In the low-temperature EPR spectrum of the $^{13}C_2H_4$ adduct of Rh(TTiPP) (TTiPP = tetrakis(2,4,6-triisopropylphenyl)porphyrin), Wayland observed a doublet of triplets assignable to hyperfine coupling to rhodium and to *both*

(40) Khusnutdinov, R. I.; Dzhemilev, U. M. *J. Organomet. Chem.* **1994**, *47*, 1−18.

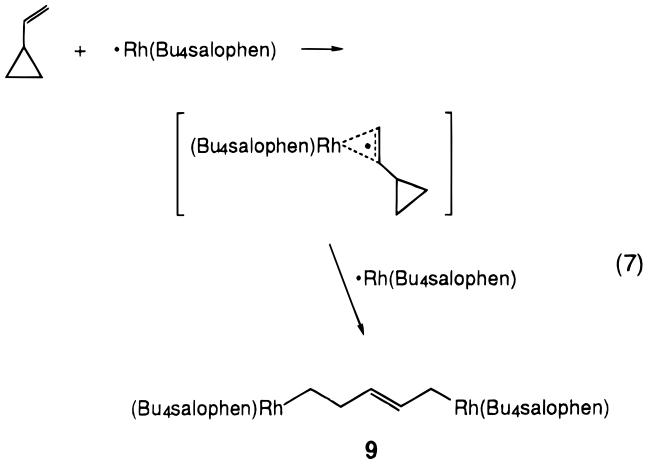
olefinic carbons, thus providing clear evidence that unpaired spin density in this adduct is distributed across *both* the metal and the olefinic carbon atoms.[41,42] Furthermore, in reactions of Rh(II) porphyrins with olefinic substrates capable of radical polymerization, such as acrylic acid and methyl acrylate (eq 6 for R=H,



(6)

Me), no such polymerization was found although coupling products were generated that were consistent with initial olefin addition to a metalloradical species.[43] An analysis of radical stability indicated that the addition of Rh(II) porphyrin to a simple olefin to generate a C-based radical would be thermodynamically unfavorable—formation of a Rh−C bond (∼50 kcal mol^{-1}) does not provide the necessary driving force for breaking an alkene π bond (∼64 kcal mol^{-1}) which is necessary to form a C-based radical.[43,44] The driving force for olefin activation by these compounds derives from the formation of additional bonds. In eq 6, additional Rh−C and C−C σ bonds contribute to that driving force. It thus appears that the species generated upon Rh$^{\bullet}$ addition to olefin in the present study must be a significantly stabilized radical that is not best described by that shown in Scheme 1.

With this background, we can now address the one reaction that shows evidence of radical rearrangement, namely the formation of **9** from the reaction of hydride **3** with vinylcyclopropane. We view the formation of **9** as a coupling reaction that leads to ring opening *only* when two Rh(II) centers are involved in the reaction system. Similar coupling reactions were described by Wayland leading to C_2- and C_4-bridged products in the reactions of olefins with Rh(porphyrins), but again no polymerization products resulting from pure C-based radicals were seen.[41−43,45] In the formation of **9**, the initial vinylcyclopropane addition does not result in ring opening, but in the presence of a second Rh(II), ring opening occurs concomitant with formation of the second Rh−C bond, eq 7. The intermediate shown in eq 7 is a metal-stabilized radical having a delocalized structure that is not expected to undergo the traditional radical rearrangements prior to bimolecular H-atom transfer or radical coupling reactions.



(7)

9

Experimental Section

General Considerations. All manipulations were performed under a nitrogen atmosphere, either in a Vacuum Atmospheres glovebox or using Schlenck techniques, unless otherwise noted. Solvents were dried and distilled prior to use. Diethyl ether and benzene were distilled under nitrogen from dark blue or purple solutions of sodium benzophenone ketyl. Benzene-d_6 was vacuum distilled from a potassium mirror or from sodium benzophenone ketyl. Methanol and ethanol were refluxed over magnesium and distilled under nitrogen. All NMR spectra were recorded in benzene-d_6 solution, unless otherwise noted. ^{1}H NMR spectra were recorded on a Bruker WP200, a GE QE-300, a Bruker AMX-400, or a Varian VXR 500 at 200, 300, 400.13, and 500 MHz, respectively. ^{13}C NMR spectra were recorded on a Bruker AMX-400 at 100.62 MHz, using a *J*-modulated spin echo pulse sequence, in which quaternary carbons are detected and appear with the same phase as methylene carbons. Chemical shifts for ^{1}H NMR spectra are reported relative to TMS but were referenced from the residual proton impurity peak in benzene-d_6 at δ 7.15 ppm. Chemical shifts for ^{13}C NMR spectra are also reported relative to TMS and were referenced to the solvent triplet for benzene-d_6 at δ 128.0 ppm (J_{CD} = 24.2 Hz). Infrared spectra were recorded on a Mattson Galaxy 6020 spectrometer. Electronic absorption data were recorded in benzene on a Hitachi U-2000 spectrophotometer in benzene solution. Luminescence spectra were recorded in toluene at room temperature and at 77 K in 5 mm glass NMR tubes on a SPEX Fluorolog-2 fluorimeter equipped with a 450 W Xenon lamp and a Hamamatsu R929 phtomultiplier tube. Elemental analyses were performed by Desert Analytics of Tucson, AZ.

Hydrogen (UHP grade) and ethylene (CP grade) were used as purchased from Air Products. Vinylcyclopropane,[46] 3,5 di-*tert*-butylsalicylaldehyde,[47] Bu$_4$salophenH_2[48] and [Rh(μ-Cl)-(C_2H_4)$_2$]$_2$[49] were prepared according to literature methods. Other olefins were purchased from Aldrich. Styrene was dried over calcium hydride and vacuum distilled prior to use. All other olefins were vacuum transferred prior to use.

Rh(*n*-Bu)(Bu$_4$salophen) (1). A three neck round bottom flask containing Bu$_4$salophenH_2 (1.8675 g, 3.453 mmol) was fitted with a reflux condenser and a side arm containing 0.6450 g (1.658 mmol) of [Rh(μ-Cl)(C_2H_4)$_2$]$_2$. This system was flushed with nitrogen, after which *ca.* 30 mL of diethyl ether was added under nitrogen to give a transparent yellow solution of Bu$_4$salophenH_2. This solution turned transparent red-orange upon addition of 1 M TBA(OH) (Aldrich) in methanol (16.8 mL, 16.8 mmol). Solid [Rh(μ-Cl)(C_2H_4)$_2$]$_2$ was added slowly over the course of several minutes to give an opaquely dark, yet clear, deep green solution. Upon gentle reflux over the course of 4 h, this solution turned brown, and then deep red-purple. This purple solution was cooled, reduced in volume under a stream of nitrogen, filtered, and washed with metha-

(41) Bunn, A. G.; Wayland, B. B. *J. Am. Chem. Soc.* **1992**, *114*, 6917−6919.
(42) Wayland, B. B.; Sherry, A. E.; Bunn, A. G. *J. Am. Chem. Soc.* **1993**, *115*, 7675−7684.
(43) Wayland, B. B.; Poszmik, G.; Fryd, M. *Organometallics* **1992**, *11*, 3534−3542.
(44) Wayland, B. B. *Polyhedron* **1988**, *7*, 1545−1555.
(45) Wayland, B. B.; Feng, Y.; Ba, S. *Organometallics* **1989**, *8*, 1438−1441.
(46) Tsunoda, T.; Hudlicky, T. *Syn. Lett.* **1990**, 322.
(47) Casiraghi, G.; Casnati, G.; Puplia, G.; Sartori, G.; Terenghi, G. *J. Chem. Soc., Perkin 1* **1980**, 1862−1865.
(48) Kawato, T.; Kanatomi, H.; Koyama, H.; Igarashi, T. *J. Photochem.* **1986**, *33*, 199−208.
(49) Parshall, G. W. In *Inorganic Syntheses*; Parshall, G. W., Ed.; McGraw-Hill Book Co.: New York, 1974; Vol. XV, p 14.

nol to give 1.6715 g (72% yield) of dark purple powder upon vacuum drying. This powder was generally used without further purification, though analytically pure, diffraction quality crystals were grown by slow evaporation of solvent from a benzene:methylene chloride solution at room temperature. Anal. Calcd for $C_{40}H_{55}N_2O_2Rh$: C, 68.75; H, 7.93; N, 4.01. Found: C, 68.28; H, 7.80; N 3.80. Electronic absorption: λ_{max} = 583 nm, log ϵ 3.90; 548 nm, log ϵ 3.85; 497 nm, log ϵ 3.97; 394 nm, log ϵ 4.53. Emission ($\lambda_{excitation}$ = 510 nm): λ_{max} = 671 nm, 745 nm (sh). Exitation ($\lambda_{observed}$ = 670 nm): 475 nm (sh), 503 nm, 551 nm, 592 nm. ^{1}H NMR**:** δ 8.40 (d, 2 H, J_{Rh-H} = 1.9 Hz, −N=C*H*−); 7.86, 7.33 (d, 4 H, J_{H-H} = 2.4 Hz, −C$_6H_2$(C(CH$_3$)$_3$)$_2$); 7.13, 6.86 (dd, 4 H, $^3J_{H-H}$ = 6.2 Hz, $^4J_{H-H}$ = 3.2 Hz, −NC$_6H_4$N−); 2.36 (m, 2 H, RhC*H*$_2$CH$_2$CH$_2$-CH$_3$); 1.99, 1.45 (s, 36 H, −C(C*H*$_3$)$_3$); 0.90 (m, 2 H, RhCH$_2$-C*H*$_2$C*H*$_2$CH$_3$); 0.44 (t, 3 H, J_{H-H} = 7.0 Hz, RhCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR**:** δ 167.52, 151.95, 144.38, 143.26, 136.03, 130.31, 129.1, 125.47, 120.36 (2 Hz), 114.85, 36.7, 34.25, 31.62, 30.38, 34.36, 25.14 (30.5 Hz), 22.53 (2.4 Hz), 13.65.

Synthesis of RhEt(Bu$_4$salophen) (2). The same procedure as for **1** was used. A 0.0775 g (0.143 mmol) amount of Bu$_4$salophenH$_2$, 0.034 g (0.087 mmol) of [Rh(μ-Cl)(C$_2$H$_4$)$_2$]$_2$, and 0.86 mL (0.69 mmol) of 0.8 M TEA(OH) in methanol were used to give 30 mg (31%) of product. ^{1}H NMR: δ 8.35 (d, 2 H, J_{Rh-H} = 1.9, −N=C*H*−); 7.87, 7.32 (d, 4 H, J_{H-H} = 2.6, −C$_6H_2$-(C(CH$_3$)$_3$)$_2$−); 7.10, 6.85 (dd, 4 H, $^3J_{H-H}$ = 6.3 Hz, $^4J_{H-H}$ = 3.3 Hz, −NC$_6H_4$N−); 2.37 (qd, 2 H, RhC*H*$_2$CH$_3$, $^2J_{Rh-H}$ = 3.2 Hz,$^3J_{H-H}$ = 7.4 Hz); 1.98, 1.46 (s, 36 H, −C(C*H*$_3$)$_3$); 0.23 (td, 3 H, RhCH$_2$C*H*$_3$, $^3J_{Rh-H}$ = 1.1 Hz, $^3J_{Rh-H}$ = 7.4 Hz).

***In Situ* preparation of RhH(Bu$_4$salophen). (A) NMR Scale.** In a glovebox, 5 mg (7 μmol) of **1** in 0.5 mL (14 mM) of benzene-d_6 was loaded into a 5 mm diameter NMR tube fitted with a concentric J. Young vacuum-line-adapted Teflon valve. The tube was closed, removed from the glovebox, attached to a high-vacuum manifold, immersed to the valve in liquid nitrogen, and opened to vacuum to evacuate the headspace, which was subsequently filled with ∼700 Torr of hydrogen. The valve was closed and the tube brought to room temperature. (*Safety note*: A simple ideal gas law calculation shows that the headspace of a tube so prepared holds in excess of 3 atm. Any sample so prepared should be handled with care.) The sample was irradiated using light from an Oriel lamp fitted with a 475 nm cutoff filter. Progress of the photolysis was monitored spectroscopically via ^{1}H NMR. Typically, photolysis was complete within 1 h. No reaction was observed in a sample prepared as detailed above when it was kept rigorously in the dark, though solutions so prepared would photolyze slowly over the course of several days if kept in ambient room light. Yields (NMR) typically range 50−75%. ^{1}H NMR: δ 8.26 (bs, 2 H, −N=C*H*−); 7.85, 7.20 (bs, 4 H, −C$_6H_2$(C(C H$_3$)$_3$)$_2$−); 7.02, 6.81 (dd, 4H, −NC$_6H_4$N−); 1.98, 1.48 (s, 36 H, −C(C*H*$_3$)$_3$); −25.77 (bd, 1 H, Rh*H*, $^1J_{Rh-H}$ = 51 Hz). ^{13}C NMR: δ 168.32, 152.72, 144.64, 142.97, 136.19, 130.3, 129.07, 125.3, 120.61, 114.56, 36.73, 34.25, 31.65, 30.24.

(B) Preparative Scale. A cylindrical Schlenk tube of approximate dimension 15 cm long and 2.5 cm in diameter was loaded with a magnetic stir bar and with 155 mg of Rh(*n*-Bu)(Bu$_4$salophen) (**1**) in approximately 50 mL of solvent (0.4 mM). The tube was closed with a rubber septum and removed from the glovebox. On a standard Schlenk line, the headspace of the vessel was purged under a steady stream of hydrogen for several minutes. It was then again closed and with stirring was photolyzed as above. Progress of the photolysis was monitored by periodic removal, under hydrogen pressure via cannula, of small (<1 mL) reaction mixture samples. These samples were cannulated through the rubber septum of a septum-closed NMR tube containing benzene-d_6 (>0.25 mL) and a drop of styrene. Proton NMR spectra of these samples were inspected for loss of Rh(*n*-Bu)(Bu$_4$salophen) (**1**) butyl-group signals and for growth of the methylene signals of Rh(CH$_2$CH$_2$Ph)(Bu$_4$salophen) (**4**). Photolysis times of about 2 h were needed for complete loss of the Rh(*n*-Bu)(Bu$_4$salophen), at which time the solution was used for subsequent reactions.

Reaction of D$_2$ with 3. A solution of **3** (method A) in a J. Young vacuum-line-adapted NMR tube was attached to a vacuum line and frozen in liquid N_2. The headspace of the tube was evacuated then filled with *ca*. 700 Torr of D_2. The tube was thawed and removed from the line, and a ^{1}H NMR spectrum was immediately acquired. HD was observed in this first spectrum as a 1:1:1 triplet at δ 4.43 ppm with J_{HD} = 43 Hz. Within 10 min, the hydride resonance at δ −25.77 ppm had completely vanished while the HD triplet continued to grow in.

Addition of Olefins to RhH(Bu$_4$salophen). Olefin addition products were prepared from solutions of **3** generated by either method A or B as detailed above and, in some cases, both. For olefins liquid at room temperature, a drop of the olefin was added under the nitrogen atmosphere of a glovebox to an NMR tube containing **3** prepared via method A. The tube was then shaken and removed immediately from the glovebox, and progress of the reaction was monitored by ^{1}H NMR. Once the reaction was complete, solvent and excess olefin were removed under vacuum, fresh solvent was vacuum transferred into the tube, and the NMR data listed below were acquired. Alternatively, solutions of liquid olefins in benzene were prepared in a glovebox and subsequently transferred under hydrogen into a Schlenk tube containing **4** prepared by method B. The reaction solution was allowed to stir for ∼8 h, at which point solvent was removed under vacuum and the residue collected.

Addition of C$_2$H$_4$. Ethylene was reacted only with **3** prepared by method A. An NMR sample of **4** was attached to a high-vacuum line and frozen in liquid nitrogen to the top of the solution. The headspace of the tube was then evacuated and filled with 700 Torr of ethylene. Progress of the reaction was monitored by ^{1}H NMR spectroscopy.

Addition of Styrene. Rh(CH$_2$CH$_2$Ph)(Bu$_4$salophen) (4). Styrene was added to samples of **3** prepared by both methods. For the preparative-scale reaction (B) 155 mg of **2** was used. The product residue was collected on sintered glass, washed with several <2 mL portions of methanol, and dried under vacuum to afford 94 mg of product (57% yield). ^{1}H NMR: δ 8.35 (d, 2 H, J_{Rh-H} = 1.8 Hz, −N=C*H*−); 7.88, 7.3 (d, 4H, J_{H-H} = 2.6 Hz, −C$_6H_2$(C(CH$_3$)$_3$)$_2$); 7.1, 6.86 (dd, 4 H, $^3J_{H-H}$ = 6.3 Hz, $^4J_{H-H}$ = 3.4 Hz, −NC$_6H_4$N−); 6.67−6.79 (m, 5 H, −CH$_2$-CH$_2$C$_6H_5$); 2.48 (m, 2 H, RhC*H*$_2$CH$_2$C$_6$H$_5$); 2.29 (“t”, 2 H, RhCH$_2$C*H*$_2$C$_6$H$_5$); 2.00, 1.46 (s, 36 H, −C$_6$H$_2$(C(C*H*$_3$)$_3$)$_2$). ^{13}C NMR: δ 167.48, 152.15, 144.27, 143.24, 136.1, 130.44, 129.21, 128.73, 128.32, 128.46, 126.55, 125.55, 125.41, 120.32, 114.91, 36.71, 34.26, 31.63, 30.64, 38.55 (d, 0.8 Hz), 25.22 (d, $^1J_{RhC}$ = 31.4 Hz). Anal. Calcd for $C_{44}H_{55}N_2O_2Rh$: C, 70.76; H, 7.42; N, 3.75. Found: C, 70.73; H, 7.60; N, 3.74.

Addition of Styrene-d_8. A drop of styrene-d_8 was added to a solution of **4** (method A). ^{1}H NMR: δ 8.34 (d, 2 H, J_{RhH} = 2.1 Hz, −N=C*H*−); 7.88, 7.30 (d, 4 H, J_{HH} = 2.6 Hz, −C$_6H_2$-(C(CH$_3$)$_3$)$_2$); 7.10, 6.86 (dd, 4 H, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 3.3 Hz, −NC$_6H_4$N−); 2.27 (“t”, 1 H, RhCD$_2$C*H*D$_2$C$_6$D$_5$); 2.00, 1.46 (s, 36 H, −C$_6$H$_2$(C(C*H*$_3$)$_3$)$_2$).

Competitive Addition: Ethylene vs Styrene. A solution of **4** (method A) was taken into a glovebox and frozen. The tube was opened, and a drop of styrene was placed on the top wall of the tube. The tube was closed, removed from the box, and placed on the high vacuum line. It was immediately immersed in liquid nitrogen before it thawed. Ethylene was then placed over the sample as above. The sample was thawed and immediately placed in the NMR probe, in which the reaction was followed by ^{1}H NMR spectroscopy. Large excesses of both styrene and ethylene were seen in solution by integration of the respective ^{1}H NMR signals for the olefins and the metal complexes.

Addition of Acrylonitrile. Rh(CH$_2$CH$_2$CN)(Bu$_4$salophen) (5). **5** was prepared from **3** (method A) by addition of excess (988 equiv) acrylonitrile. Yield (^{1}H NMR): 73%. ^{1}H

NMR (with excess acrylonitrile): δ 8.46 (d, 2 H, J_{RhH} = 1.7 Hz, −N=C*H*−); 7.69, 7.24 (d, 4 H, J_{HH} = 2.4 Hz, −C_6H_2-($C(CH_3)_3)_2$); 7.38, 6.95 (dd, 4 H, $^3J_{HH}$ = 6.2 Hz, $^4J_{HH}$ = 3.4 Hz, −NC_6H_4N−); 2.12 (m); 1.94 (m); 1.75, 1.39 (s, 36 H, −C_6H_2-($C(CH_3)_3)_2$). ^{13}C NMR: δ 167.17, 152.64, 143.83, 142.8, 135.79, 130.52, 129.47, 125.77, 119.7, 115.19, 36.38, 34.16, 31.59, 30.14, 17.61, 12.73 (d, $^1J_{RhC}$ = 32.6 Hz).

Addition of Bis(allyl) Ether. $RhCH_2CH_2CH_2OCH_2CH$=CH_2(Bu$_4$salophen) (6). Approximately 285 equiv of bis(allyl) ether was vacuum transferred into a previously prepared solution of **3** (method A). The amount of excess allyl ether and yields were determined spectroscopically, and then the solvent and excess allyl ether were removed under vacuum. NMR data listed are for product in the absence of excess allyl ether. Yield (^{1}H NMR): 56%. ^{1}H NMR: δ 8.32 (d, 2 H, J_{RhH} = 2.2 Hz, −N=C*H*−); 7.86, 7.30 (d, 4 H, J_{HH} = 2.5 Hz, −C_6H_2-($C(CH_3)_3)_2$); 7.07, 6.83 (dd, 4 H, $^3J_{HH}$ = 6.1 Hz, $^4J_{HH}$ = 3.2 Hz, −NC_6H_4N−); 5.47 (m, 1 H, −$CH_2CH_2CH_2OCH_2CH$=CH_2), 4.86 (dm, $^3J_{HH}$ = 17.2, −$CH_2CH_2CH_2OCH_2CH$=CH_2 (*trans*)), 4.74 (dm, $^3J_{HH}$ = 10.4, −$CH_2CH_2CH_2OCH_2CH$=CH_2 (*cis*)), 2.38 (m, 2 H, −C$H_2CH_2CH_2OCH_2CH$=CH_2); 1.98, 1.45 (s, 36 H, −C_6H_2-($C(CH_3)_3)_2$), 1.22 (m, 2 H, −$CH_2CH_2CH_2OCH_2CH$=CH_2), 2.82 (t, 2 H, $^3J_{HH}$ = 7 Hz, −$CH_2CH_2CH_2OCH_2CH$=CH_2), 3.37 (d, 2 H, $^3J_{HH}$ = 5.3, −$CH_2CH_2CH_2OCH_2CH$=CH_2).

Addition of Vinylcyclopropane. Addition of a slight excess (1.8 equiv) of vinylcyclopropane to a solution of **3** (method A) gave a mixture of products. Due to the position of the cyclopropyl resonances in the ^{1}H NMR spectrum, typical nonreactive alkane or alkyl silane internal standards were not used. In the presence of THF as a standard, the overall yield of Schiff-base-containing product was 94% (^{1}H NMR) as shown by integration of the spectral regions in which the imine protons of the Schiff base resonate (8.5−8.1 ppm), though selectivity for the identified products was lower (34%) in this reaction than in those carried out in the absence of THF (typically 57%). Percentage composition ranges for the products listed below were based on integration of resonances unique for each product versus integration of the imine region.

Rh(CH_2CH_2(*c*-C_3H_5))(Bu$_4$salophen) (7). (26−32%). ^{1}H NMR: δ 8.38 (bs, −N=C*H*−); 7.86, 7.31 (obscured, −C_6H_2-($C(CH_3)_3)_2$); 7.1, 6.86 (obscured, −NC_6H_4N−); 2.42 (cm, 2 H, RhCH_2CH_2(*c*-C_3H_5)), 1.97, 1.44 (s, −$C_6H_2(C(CH_3)_3)_2$), 0.941 (cm, 2 H, RhCH_2CH_2(*c*-C_3H_5)), 0.214, −0.054, −0.35 (cm, 5 H, RhCH_2CH_2(*c*-C_3H_5)).

Rh(CH_2CH_2CH=$CHCH_3$)(Bu$_4$salophen) (8) (17−24%). ^{1}H NMR: δ 8.36 (d, J_{Rh-H} = 1.7 Hz, 2 H, −N=C*H*−); 7.87, 7.32 (d, J_{H-H} = 2.2 Hz, 4 H, −$C_6H_2(C(CH_3)_3)_2$); 7.10 (dd, 2 H, $^3J_{H-H}$ = 6.1 Hz, $^4J_{H-H}$ = 3.4 Hz, −NC_6H_4N−); 6.85 (obscured dd, −NC_6H_4N−); 4.94 (cm, $RhCH_2CH_2CH$=C*H*CH_3); 2.32 (cm, RhCH_2CH_2CH=$CHCH_3$); 1.98, 1.46 (s, −$C_6H_2(C(CH_3)_3)_2$), 1.65 ($RhCH_2CH_2CH$=$CHCH_3$), 1.16 (bm, $RhCH_2CH_2CH$=$CHCH_3$).

Unidentified $RhCH_2$-Containing Product. (1−8%). ^{1}H NMR: δ 2.24 (cm).

(Bu$_4$saloph)$RhCH_2CH$=$CHCH_2CH_2$Rh(Bu$_4$saloph) (9) (0−6%). ^{1}H NMR: δ 8.28 (d, 2 H, J_{RhH} = 2.1 Hz, −N=C*H*−); 8.18 (d, 2 H, J_{RhH} = 1.3 Hz, −N=C*H*−); 7.85 (d, 2 H, J_{HH} = 2.7 Hz, −$C_6H_2(C(CH_3)_3)_2$); 7.76 (d, 2 H, J_{HH} = 2.4 Hz, −C_6H_2-($C(CH_3)_3)_2$); 7.29 (d, 4 H, J_{HH} = 2.4 Hz, −$C_6H_2(C(CH_3)_3)_2$); 7.19 (d, partially obscured by solvent, −$C_6H_2(C(CH_3)_3)_2$), 7.05 (dd, 2 H, $^3J_{HH}$ = 6.1 Hz, $^4J_{HH}$ = 3.4 Hz, −NC_6H_4N−), 7.01 (dd, 4 H, $^3J_{HH}$ = 6.1 Hz, $^4J_{HH}$ = 3.7 Hz, −NC_6H_4N−); 6.83 (dd, partially obscured by other products), 6.71 (dd, 4 H, $^3J_{HH}$ = 6.1 Hz, $^4J_{HH}$ = 3.4 Hz, −NC_6H_4N−); 4.56 (m, 1 H, $RhCH_2CH$=$CHCH_2CH_2Rh$), 4.39 (m, 1 H, $RhCH_2CH$=C*H*CH_2CH_2Rh), 2.84 (dd, 2 H, J_{RhH} = 3.5 Hz, J_{HH} = 8.2 Hz, RhCH_2CH=$CHCH_2$-CH_2Rh), 1.9 ($RhCH_2CH$=$CHCH_2CH_2Rh$), 0.4 ($RhCH_2CH$=C-HCH_2CH_2Rh).

Addition of *trans*-1,3-Pentadiene. $RhCH_2CH_2CH$=$CHCH_3$(Bu$_4$salophen) (8). Approximately 2 equiv of 1,3-pentadiene were dropped into a previously prepared solution of **3** (method A). The amount of excess 1,3-pentadiene and yields were determined spectroscopically, and then the solvent and excess 1,3-pentadiene were removed under vacuum. NMR data listed are for the product in absence of excess pentadiene. Yield (^{1}H NMR): 59%.

Acknowledgment. We wish to thank the Department of Energy, Division of Chemical Sciences, for support of this research. A generous loan of rhodium salts from Alfa/AESAR Johnson Matthey Co. is also gratefully acknowledged.

OM950595K